Applications of Redox Processes to Molybdenum and Tungsten Dearomatization Agents

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Acknowledgments:

As many of you who are about to read this know, I am not good with words. As such, I will try to keep my semi-coherent rambling to a minimum and try to be as succinct as possible. While I will not be able to thank everyone that has had an impact on my life in the past 5 years, know that if your name is not listed here that I am gravely sorry and I thank you still. It has been both the best and worst five years of my life and everyone that I have met here has had a great impact on me. Thank you for the time, help, and reading (at least) my acknowledgments.

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Mom and Dad so that you could beat the hard parts. When you went away for the first time for the Meyerhoff bridge program, I was a wreck. I missed my big bother but I managed. This was the first time we were apart before you went to college and it was miserable. I still miss the times before you went to college. The one year together at UMBC before you went to dental school and became a real person was the first time in three years that I was able to spend more than a week being near you. Eating lunch with you every day was a great joy. While I am the taller sibling now, you will always be my big brother. I hope that you and Amanda (and of course Garrus too) are happy and have a good life together, wherever you end up. I love and miss you big brother. And Amanda and Garrus too!! Again, I want to give you a hug while writing this.

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Benjamin Liebov was the second oldest graduate student when I arrived in lab. I inherited his lab jobs and became our stockroom liaison as well as our GCMS person. I kept the stockroom job almost the entire time I worked in lab, until about a month before my defense. It was an excellent fit for me and he knew it would be. I also inherited his distaste for the GCMS and I gave that up far sooner. Which makes sense, because my projects didn't use it at all.

I remember one day when I was going through candidacy and was having a difficult time. Bri and Ben both pulled me aside, helped me pull myself together, and got me through the ordeal of candidacy. Their 30-minute meeting allowed me to center myself and push the last bit to pass the big exam. I thank both of you for your help.

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Steven Dakermanji

Abstract

Chapter 1 is a brief introduction to the electron rich, π basic metal fragments {MoTp(NO)(DMAP)} and {WTp(NO)(PMe_3)} used in dihapto-coordination of aromatic molecules. The resulting dearomatization caused by the metal's electron donation increases the reactivity of the arene. Initial reductions and ligand exchanges that lead to the metal binding the aromatic molecules are described. In addition, mechanisms for ligand isomerizations are introduced.

Chapter 2 looks at the accelerated rates of exchange reactions with the molybdenum system. Using small amounts of a redox catalyst, a purported electron chain transfer process assists in the net exchange of alkene and aromatic ligands for carbonyl ligands. Kinetic studies and mechanism investigations for this process are reported. In addition, the application of the process is reported for exchanges of ketone bound ligands.

In Chapter 3, a variation of redox catalysis mechanism is used to convert complex mixtures of coordination diastereomers of alkene complexes to a single, most stable isomer. Multiple examples were tested and are reported here using both the molybdenum and tungsten systems. The application of this isomerization method to the synthesis of novel small molecules is also discussed here.

The final chapter reports initial observations of reductions for the molybdenum and tungsten metal fragments with magnesium. In addition to the pyrophoric sodium that is typically used for this process, shelf stable magnesium powder was found to also accomplish this reaction. Large scale application of magnesium reductions to the molybdenum fragment were investigated and are reported. Initial experiments of magnesium reductions for the tungsten system were also investigated.

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List of Abbreviations

BArF	Tetrakis(3,5-bis(trifluoromethyl)phenyl)borate Anion
$CoCp_2$	Cobaltocene (Cobaltocenium Cation)
Cp	Cyclopentadienyl (Cyclopentadienide Anion)
Cp*	Pentamethylcyclopentadienyl (Pentamethylcyclopentadienide Anion)
DMA	N,N-dimethylacetamide
DMAP	4-N,N-Dimethylaminopyridine
DME	1,2-Dimethoxyethane
DMF	N,N-Dimethylformamide
EA	Elemental analysis
$FeCp_2$	Ferrocene (Ferrocenium Cation)
$FeCp^*_2$	Per- or Decamethylferrocene (Per- or Decamethylferrocenium Cation)
HATR	Horizontal attenuated total reflectance
IR	Infrared
MeIm	1-Methylimidazole
MS	Mass spectrometry
NHE	Normal hydrogen electrode
NMR	Nuclear magnetic resonance
NOE	Nuclear Overhauser effect
$N(Tf)_2$ or $(Tf)_2N$	Bis(trifluoromethane)sulfonimide (Bistriflimide) Anion
ORTEP	Oak Ridge Thermal Ellipsoid Program
OTf	Trifluoromethanesulfonate (Triflate) anion
Pz	A pyrazole group in hydridotris(pyrazolyl)borate
TBAH	Tetrabutylammonium hexafluorophosphate
TFT	α,α,α-Trifluorotoluene

THF	Tetrahydrofuran
TLC	Thin layer chromatography
Tp	Hydridotris(pyrazolyl)borate anion

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Chapter 1:

Introduction

1.1: Introduction

In contrast to the large number of unsaturated flat rings in molecular libraries, medicinal chemists are looking to saturate carbon scaffolds to produce stereospecific three dimensional structures.[1] In order to more efficiently produce more varied saturated carbon ring structures, work to dearomatize the large feedstock of aromatic molecules is on-going.[2-4] From classical Birch reductions,[5] metal catalysis,[6-9] and transition metal scaffolds,[10-16] there are plenty of methods to dearomatize aromatics in order to create diverse structures.

The niche of dearomatization that we seek to explore is dihapto-coordination of aromatic molecules to π basic, d^6 metal scaffolds.[2, 17-19] The dπ orbitals of the metal system are able to overlap with the anti-bonding orbitals of an alkene bond and donate electron density into the unfilled orbitals (Figure 1.1).[2] Net effects of this interaction produce a metallacyclopropane structure between the metal and two of the carbons of the ring. In contrast to electron poor metal centers that bind a six membered ring in a hexahapto fashion,[20] the unequal distribution of electrons into the bound ring breaks the symmetry afforded by aromaticity.[2] The remainder of the dihapto bound ring becomes more diene like in character (Figure 1.1).[21]

The dihapto-coordinated ring has reactivity similar to that of a conjugated diene system rather than the stability of the parent aromatic.[2] Tandem electrophilic-nucleophilic additions[10-12, 22] and Diels–Alder reactions[23-25] can then be performed regio- and stereoselectively to functionalize the aromatic ring as desired. Once modified, the metal can be oxidized to release the final organic molecule.

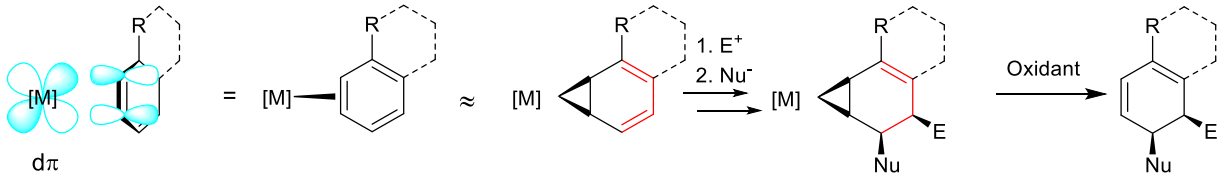
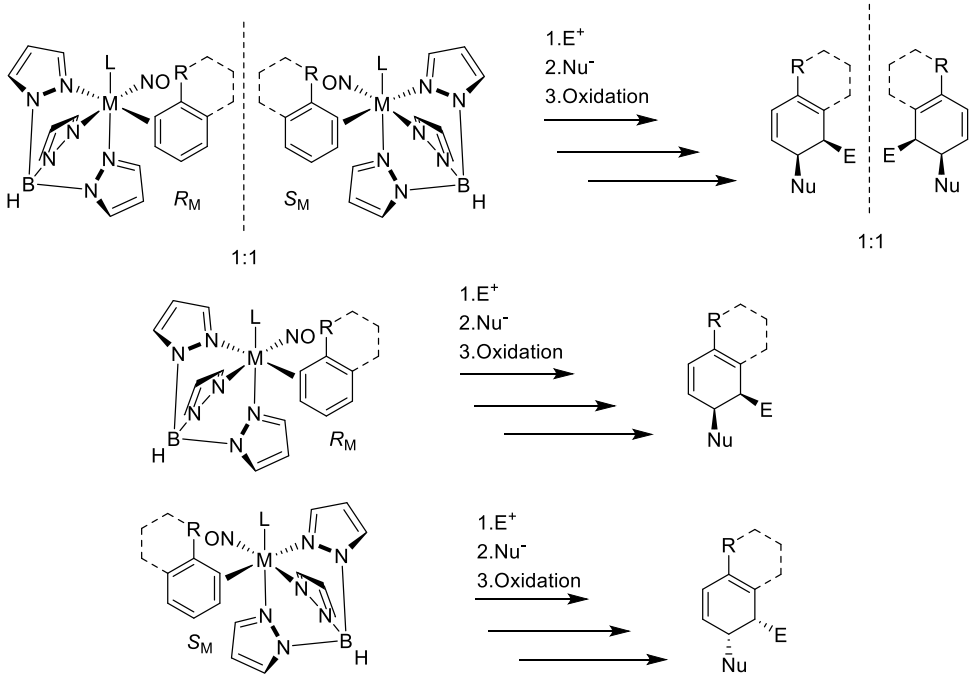


Figure 1.1: Interaction of the HOMO dπ orbital of the metal into the antibonding LUMO of the alkene/aromatic molecule.

To afford the diahpto-coordination, the {MoTp(NO)(DMAP)} (where Tp = hydridotris(pyrazolyl)borate and DMAP = 4-(dimethylamino)pyridine) and {WTp(NO)(PMe_3)} metal fragments are used. Both of these d^6 metal centers have been shown to be effective at binding a wide variety of aromatic molecules and alkene ligands.[11-12, 14-16, 22] The resulting complexes can then undergo the modifications listed above. If an enantiopure sample of the chiral metal complex is used, the regio- and stereoselective nature of the organic modifications allows for production of single enantiomers of the product organic (Scheme 1.1).[11, 16]



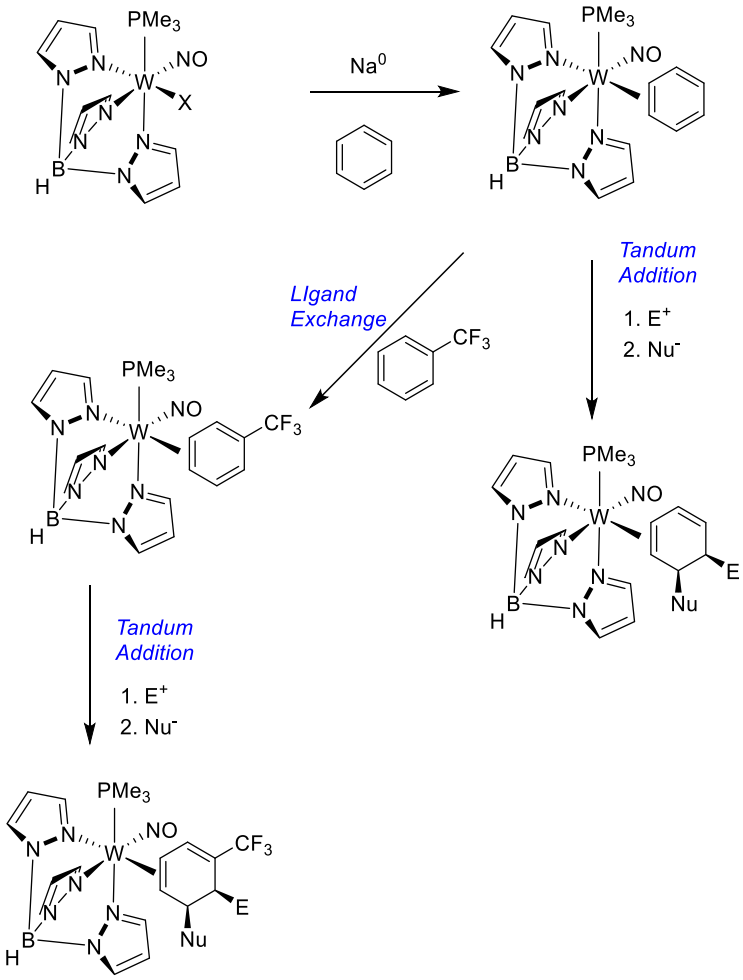
Scheme 1.1: Synthesis of enantiopure organic products from enantiopure metal compounds.

While a significant portion of the work that is currently done in the Harman group is oriented to the organic modification of the dearomatized ring, there is a constant desire to improve the dearomatization process. For this purpose, there are three topics unrelated to organic modification that have been investigated and will be discussed in detail. The first study involved modifications of the intermolecular exchanges of the dihapto-coordinated ligand. (Chapter 2). The second field of this investigation focused on intramolecular isomerization (Chapter 3). The third topic is the initial synthesis of the dihapto-coordinated molybdenum and tungsten complexes using more mild reducing agents (Chapter 4).

1.2: Sodium Reductions

Production of the M(I) halide precursors to the dihapto coordinated complex are done on large scale (>150 g scale for Mo[12] and 100 g for W[21]). The isolated WTp(NO)(PMe_3)(Br) and MoTp(NO)(DMAP)(I) are subjected to one electron reductions with sodium metal to form the dihapto-coordinated complexes (Schemes 1.2 and 1.3).[11-12, 14, 26] While the sodium allows for reductions to the proper metal electronic state, the pyrophoric nature of alkali metals brings in safety concerns and ligand incompatibility for these reactions. Large scale reductions (37 g product from 50 g MoTp(NO)(DMAP)(I)) can use almost 10 g of sodium metal.[14] Once the reaction is completed and the solid product is isolated, the sodium metal that is left needs to be quenched prior to disposal. The addition of methanol produces sodium methoxide and hydrogen gas in an exothermic reaction. Unquenched sodium has the ability to react violently and be a safety hazard. [27-28] While furans,[12, 29] naphthalene,[12, 30] benzenes,[14, 26] terpenes,[11] and fluorinated ligands[12, 26] can survive the interaction with sodium, there are many classes of organic ligands that cannot be bound with by the sodium reduction. Amines,[15] pyridines,[31-32] and those containing ketones[14] have to be bound through exchanges, not sodium reductions.

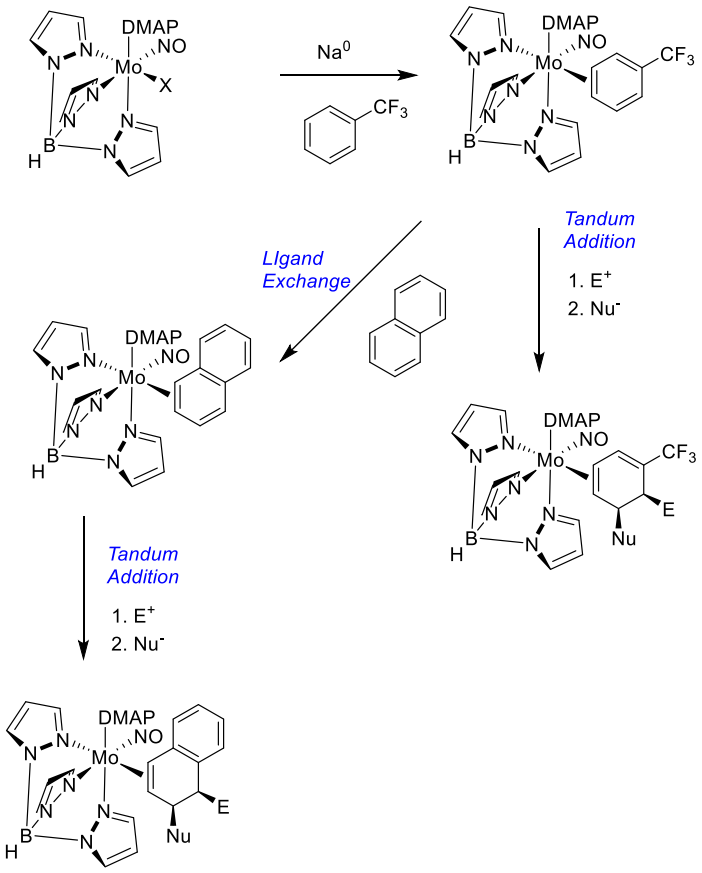
The production of WTp(NO)(PMe_3)(η^2-benzene) from WTp(NO)(PMe_3)(Br) yields an exchange precursor ($t_{1/2}$= 1.1 hours at 22°C)[26] for a multitude of ligands, including phenols,[33] pyridines,[32, 34] alkenes,[35] heterocycles,[36-37] and other benzenes(Scheme 1.3).[26] Once primed, the tungsten system is able to afford transformations to the unbound portion of the dearomatized arene to produce varied organic products (vide supra).



Scheme 1.2: Synthesis of dihapto coordinated W-Benzene and further functionalization of the bound organic.

Reductions to the MoTp(NO)(DMAP)(η^2-trifluorotoluene (TFT)) system afford an exchange precursor similar to the tungsten system.[11, 14] Again, sodium is used for the reduction of the

MoTp(NO)(DMAP)(I) complex in the presence of TFT. Upon dissociation of the TFT ligand from the metal core, pyridines, alkenes,[11] heterocycles, and other aromatics[14] can be bound (Scheme 1.3) and functionalized. Like the tungsten synthon, the parent MoTp(NO)(DMAP)(η²-TFT) complex can be functionalized[14] as well.



Scheme 1.3: Synthesis of dihapto coordinated Mo-TFT and further functionalization of the bound organic.

In contrast to the previously stated metal fragments, the {$[Os(NH_3)_5]^{2+}$} fragment can be reduced by magnesium.[38-40] The predecessor to the tungsten and molybdenum dearomatization agents, the osmium system was originally found over 30 years ago. When an acetone solution of $[Os(NH_3)_5(OTf)](OTf)_2$ and "several pieces of scraped magnesium" generated a dihapto-coordinated acetone complex.[40] Use of magnesium for the tungsten and molybdenum reductions would allow for safer reaction conditions (Chapter 4).

1.3: Ligand Exchanges

Once the WTp(NO)(PMe_3)(η^2-benzene) and MoTp(NO)(DMAP)(η^2-TFT) complexes are isolated from the sodium reductions, the labile nature of these synthons allows for exchange to other ligands.[2, 11, 14] A small variety of ligand types that can be bound is shown in Figure 1.2. The diversity of ligands that can be produced from exchanges allow for a wide variety of functionalized organic products from use of the metal scaffold.[12, 14-15, 22, 36] Examples include complexes of chiral ligands such as the α-pinene compound.

Because of the chiral nature of the metal complex, binding a chiral ligand to the metal will form diastereomers. Binding (*R*)-α-pinene to the racemic mixture of the WTp(NO)(PMe_3)(η^2-benzene) complex allows the formation of a thermally stable, matched W_RTp(NO)(PMe_3)(η^2-R-α-pinene) complex and the thermally unstable mismatched W_STp(NO)(PMe_3)(η^2-R-α-pinene) complex (Scheme 1.4 A).[35] Heating this mixture to 60°C allows for displacement of the α -pinene ligand from the unstable diastereomer to a more stable complex while remaining W_S.[35] The stable matched isomer will remain as the α-pinene complex. Overall, the α -pinene methodology has the ability to isolate one diastereomer of the tungsten system, at up to 50% yield from both enantiomers of the metal. Recent work with the chiral acid dibenzoyl-L-tartaric acid allows for isolation of both enantiomers of the tungsten system in one step, without losing half of the metal center (Scheme 1.4 B).[16] As stated before, isolation of the enantiomers of the tungsten system allows for generation of enantiopure organic products.

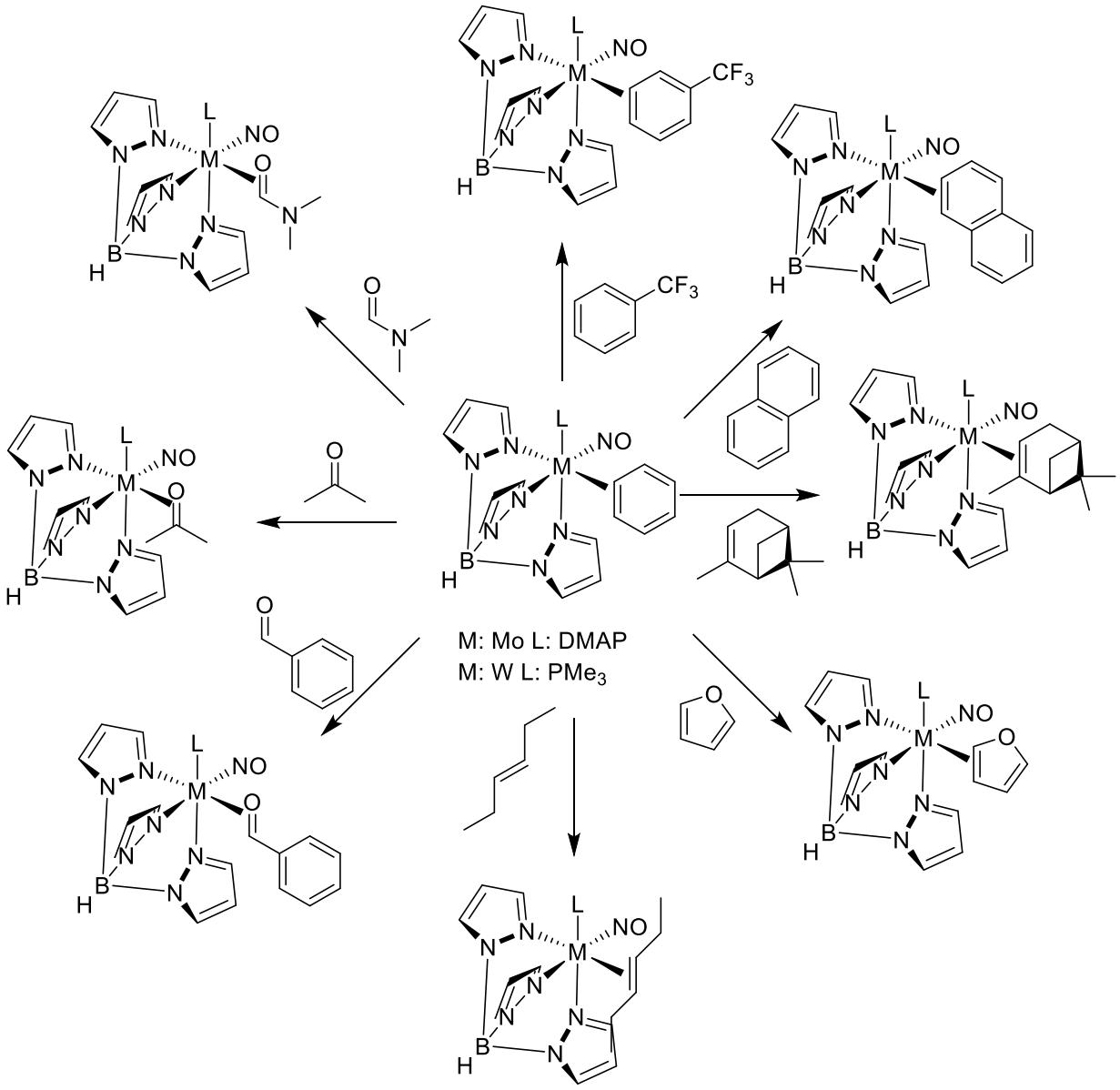
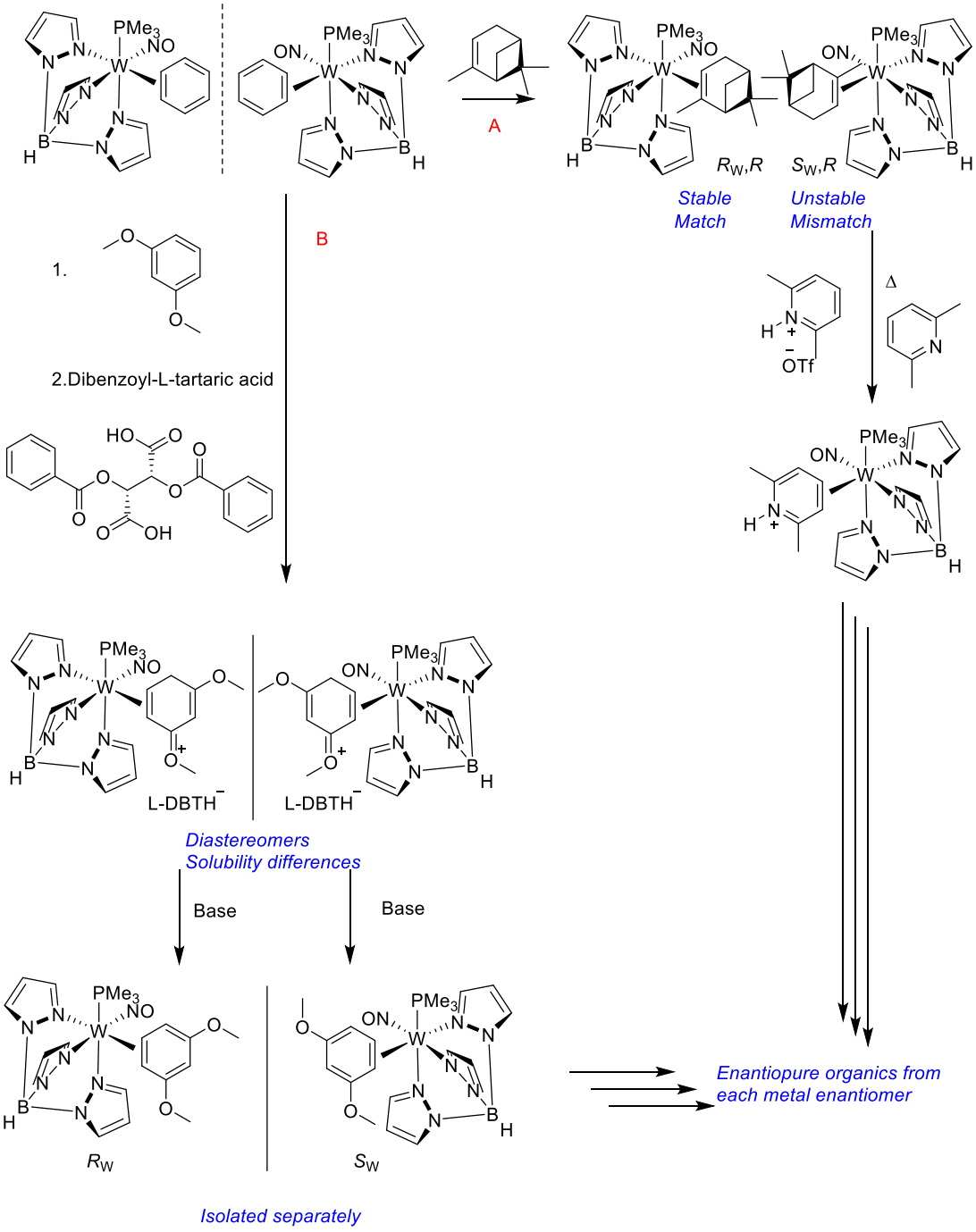


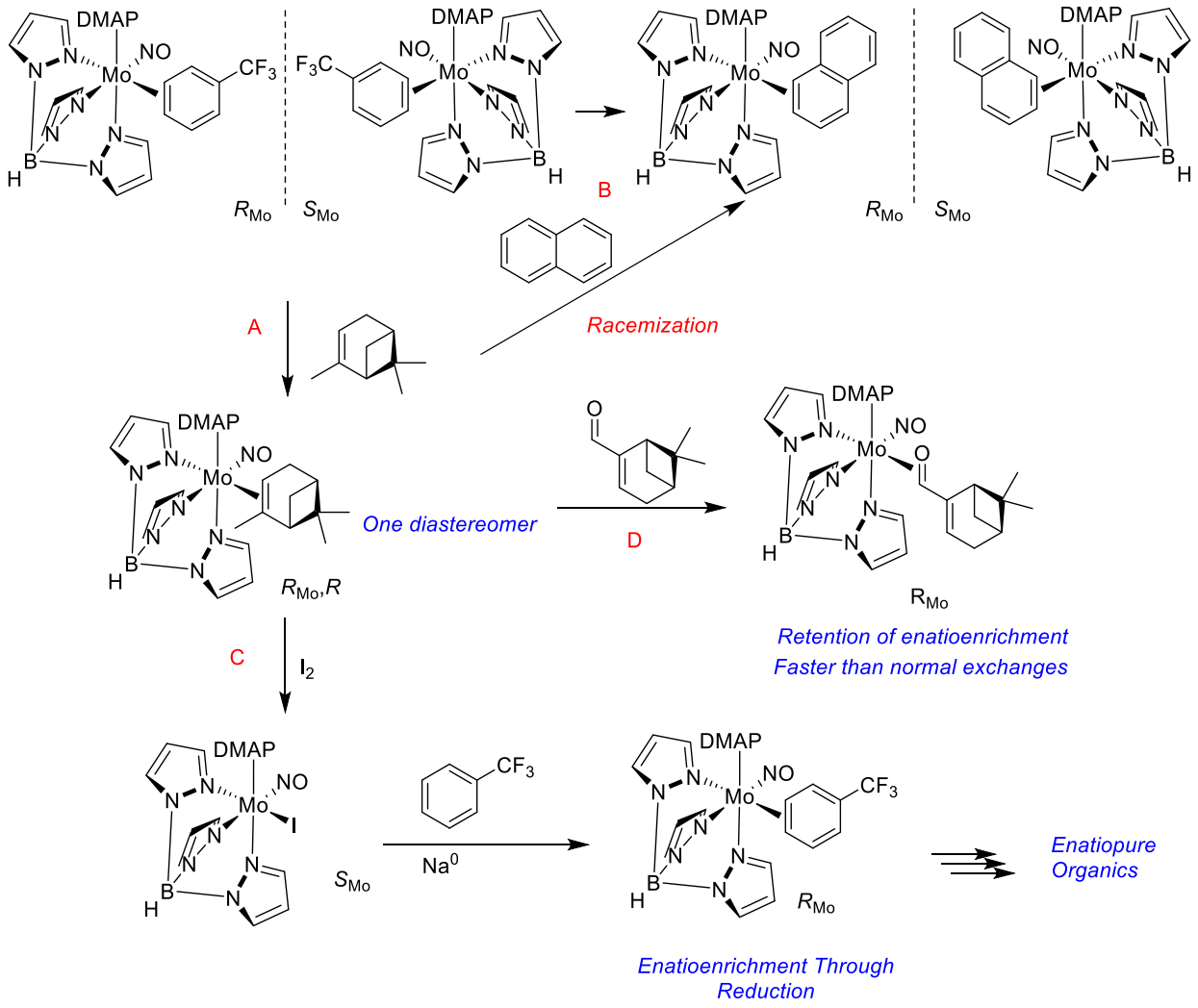
Figure 1.2: Examples of different classes of ligands that are able to be bound η^2 to the Mo and W metal fragments[2] (and this work).



Scheme 1.4: Enantioenrichment methods of the W complexes

When α-pinene is bound to the Molybdenum system, only one stable MoTp(NO)(DMAP)(η²-α-pinene) complex is formed (Scheme 1.5 A).[11] At >90% conversion, the molybdenum fragment is able to

epimerize to match the hand of the α-pinene added. Only the stable matched isomer Mo_R(Tp)(NO)(DMAP)(η^2-*R*-α-pinene) is formed when *R*-α-pinene is used.[11]



Scheme 1.5: Enantioenrichment method for the Mo metal core.

Unfortunately, the epimerization process occurring during synthesis of the α-pinene complex also allows for racemization when exchanging the α-pinene for more synthetically interesting ligands (Scheme 1.5 B).[11] In contrast of the tungsten system, the molybdenum system cannot retain the metal enantiomer during exchanges.[11] The ability to convert all of a racemic starting material to enantiopure product is negated by subsequent exchanges. Different methodologies to retain enantiopure molybdenum

complexes are required. Recent work from our lab shows that exchanges proceeding through a Mo(I) transition state will retain the enantioenrichment of the metal center (Scheme 1.5 C).[11]

During the investigation a chiral reporter ligand for the Mo system,[11] it was noted that the exchange from the Mo-α-pinene complex to the chiral aldehyde *R*-myrtenal was faster than expected (18 hours for reaction vs 3 days,[11] Scheme 1.5 D). The increased reaction rate was accompanied by retention of the metal stereocenter as well. An independent test with benzaldehyde displayed similar reaction speed increase. Investigations found that a small amount of the corresponding carboxylic acid of the aldehydes was present. An oxidation catalyzed pathway granted by the acids was investigated and applied to other ligand types. It was hoped that a catalyzed pathway could universally increase the synthesis rate and yield of dihapto-coordinated aromatics. A two step, oxidation and reduction pathway allowed for successful synthesis of enantioenriched Mo-TFT complex in a separate study (Scheme 1.5 C).[11] It is also noted that use of this redox process can allow for decomplexation of organic products from the metal scaffold under more mild conditions. The development of the catalytic process for is reported in chapter 2.

1.4: Ligand Isomerization

Orientation of the dihapto bound ligand on the molybdenum and tungsten systems is based on several factors. With the nitrosyl ligand lowering two d orbitals of the metal, the remaining higher energy d orbital interacts with the alkene bond (Figure 1.1).[2, 41] With the single d orbital to donate, the orientation of the dihapto bond is in line with the metal ancillary ligand bond, orthogonal to the NO ligand. With this one orientation, the metal can coordinate a single alkene bond with four different orientations.[42-43] An example of the four propene coordination diastereomers are shown in Figure 1.3. To determine which of the four different possible orientations will be present when bound, the steric profile of the face of the metal helps to bias the ligand orientations.[41, 44] Two of the pyrazole rings of the Tp ligand, especially the

one trans to the nitrosyl ligand, protrude into the face of the metal that coordinates the ligand. These help to bias the steric bulk of the ligand away from the Tp ligand. A more in-depth description of the general binding profile is in chapter 3. For aromatic complexes, control of the diastereomer ratio is based on thermodynamic factors.[45]

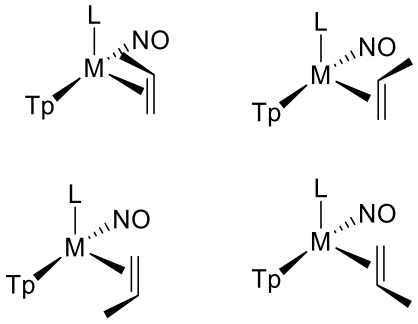
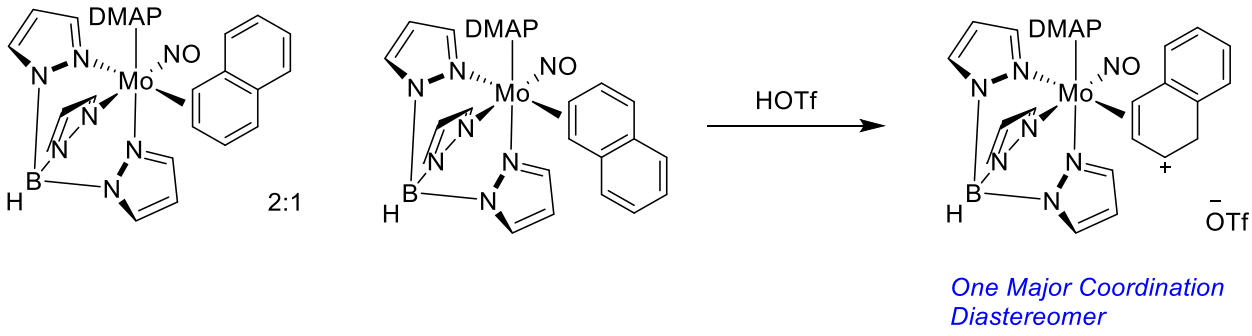


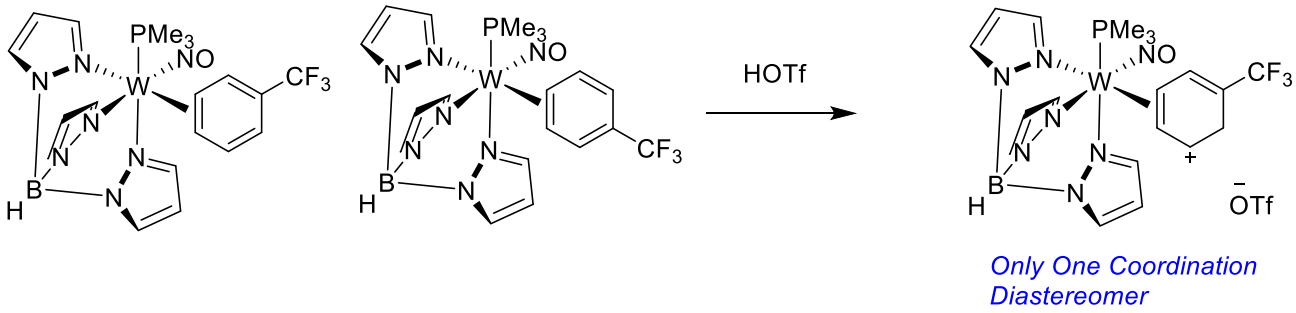
Figure 1.3: Four possible coordination diastereomers of propene to the metal complexes

With aromatic molecules bound to these metal centers, the ligand can isomerize very quickly. The MoTp(NO)(DMAP)(η^2-napthalene) complex is one such case. While dissolved in solution, the complex quickly isomerizes between diastereomers.[46] Upon protonation of the naphthalene, a single diastereomer forms in excess.[12] Further modifications of the ring then occur primarily to the one diastereomer (Scheme 1.6).



Scheme 1.6: Coordination diastereomers of MoTp(NO)(DMAP)(η^2-napthalene) and resolution by protonation

For the WTp(NO)(PMe_3)(η^2-TFT) complex, the molecule quickly converts between two diastereomers in solution.[22] Upon addition of an acidic proton, the complex converts to one isomer (Scheme 1.7).[10] From the single diastereomer, a myriad of different modifications can be done to the ring to synthesize single diastereomers of the organic product.



Scheme 1.7: Coordination diastereomers of the WTp(NO)(PMe_3)(η^2-TFT) complex and resolution by protonation

For complexes where the dihapto ligand is an alkene, a kinetic mixture of isomers forms initially.[44] In contrast to the fluxional movement of the aromatic complexes (vide supra), the alkene ligands are more static. While rotation of the alkene around the metal system is able to occur, there is significant barrier to a face-flip isomerization pathway. Figure 1.4 shows the model propene system with ligand isomerization pathways shown.[44] Without control of the coordination diastereomers, organic modifications to the bound ligand will yield a mixture of product isomers. If one of the coordination diastereomers can be selected over the others, the final organic products can be controlled.

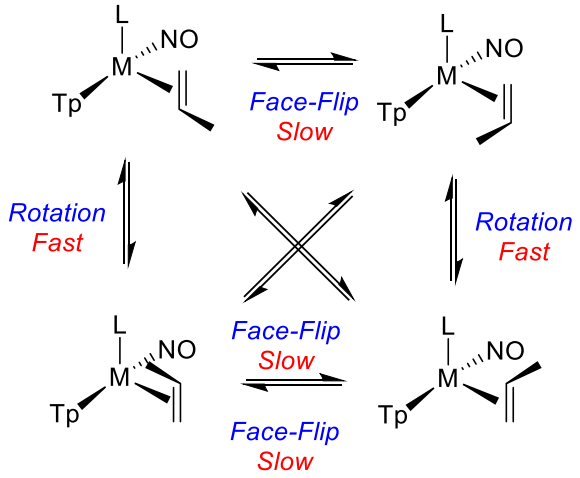


Figure 1.4: Movement of propene on the metal scaffold with relative speed.

For systems where the face flip of an alkene or intramolecular movement between alkenes is desired, methodology to induce the molecular movement has been developed. Use of a mild oxidant to transiently oxidize the metal has shown isomerization on the same alkene and between alkenes (chapter 3).

1.5: Goals of this Work

This work primary focuses on the manipulation of ligands based on modulating the electronics of the metal system. Elucidation of a redox-promoted catalytic cycle has allowed for accelerated exchange reactions with the molybdenum system. These were found to maintain enantioenrichment of the metal (Chapter 2). Method development for isomerizations have allowed for simplification of coordination diastereomers mixtures of alkene complexes (Chapter 3). And at the basic level, discovery of new reduction pathways that use magnesium instead of sodium will hopefully make this research safer and more appealing to other researchers. By using molecular movements seen in the catalytic exchanges, reductions with the weaker reducing agent magnesium have been shown for both the molybdenum and tungsten systems. In the case of the former system, some magnesium reductions outperform the reported reaction conditions on large reaction scales[12] (Chapter 4).

1.6: References

1. Lovering, F.; Bikker, J.; Humblet, C., Escape from Flatland: Increasing Saturation as an Approach to Improving Clinical Success. *Journal of Medicinal Chemistry* **2009,** *52* (21), 6752-6756.

2. Liebov, B. K.; Harman, W. D., Group 6 Dihapto-Coordinate Dearomatization Agents for Organic Synthesis. *Chemical Reviews* **2017,** *117* (22), 13721-13755.

3. Wertjes, W. C.; Southgate, E. H.; Sarlah, D., Recent advances in chemical dearomatization of nonactivated arenes. *Chemical Society Reviews* **2018,** *47* (21), 7996-8017.

4. Zheng, C.; You, S.-L., Catalytic Asymmetric Dearomatization by Transition-Metal Catalysis: A Method for Transformations of Aromatic Compounds. *Chem* **2016,** *1* (6), 830-857.

5. Lei, P.; Ding, Y.; Zhang, X.; Adijiang, A.; Li, H.; Ling, Y.; An, J., A Practical and Chemoselective Ammonia-Free Birch Reduction. *Organic Letters* **2018,** *20* (12), 3439-3442.

6. Weetman, C.; Hill, M. S.; Mahon, M. F., Magnesium-catalysed hydroboration of pyridines: Kinetic analysis and poly-pyridine dearomatisation. *Polyhedron* **2016,** *103*, 115-120.

7. Yang, D.; Wang, L.; Han, F.; Li, D.; Zhao, D.; Wang, R., Intermolecular Enantioselective Dearomatization Reaction of β-Naphthol Using meso-Aziridine: A Bifunctional In Situ Generated Magnesium Catalyst. *Angewandte Chemie International Edition* **2015,** *54* (7), 2185-2189.

8. Yang, D.; Wang, L.; Kai, M.; Li, D.; Yao, X.; Wang, R., Application of a C□C Bond-Forming Conjugate Addition Reaction in Asymmetric Dearomatization of β-Naphthols. *Angewandte Chemie International Edition* **2015,** *54* (33), 9523-9527.

9. Arrowsmith, M.; Hill, M. S.; Hadlington, T.; Kociok-Köhn, G.; Weetman, C., Magnesium-Catalyzed Hydroboration of Pyridines. *Organometallics* **2011,** *30* (21), 5556-5559.

10. Wilson, K. B.; Smith, J. A.; Nedzbala, H. S.; Pert, E. K.; Dakermanji, S. J.; Dickie, D. A.; Harman, W. D., Highly Functionalized Cyclohexenes Derived from Benzene: Sequential Tandem Addition Reactions Promoted by Tungsten. *The Journal of Organic Chemistry* **2019**.

11. Shivokevich, P. J.; Myers, J. T.; Smith, J. A.; Pienkos, J. A.; Dakermanji, S. J.; Pert, E. K.; Welch, K. D.; Trindle, C. O.; Harman, W. D., Enantioenriched Molybdenum Dearomatization: Dissociative Substitution with Configurational Stability. *Organometallics* **2018,** *37* (23), 4446-4456.

12. Myers, J. T.; Dakermanji, S. J.; Chastanet, T. R.; Shivokevich, P. J.; Strausberg, L. J.; Sabat, M.; Harman, W. D., 4-(Dimethylamino)pyridine (DMAP) as an Acid-Modulated Donor Ligand for PAH Dearomatization

Organometallics **2017,** *36* (3), 543-555.

13. Welch, K. D.; Harrison, D. P.; Sabat, M.; Hejazi, E. Z.; Parr, B. T.; Fanelli, M. G.; Gianfrancesco, N. A.; Nagra, D. S.; Myers, W. H.; Harman, W. D., Michael-Aldol Ring Closures with Dihapto-Coordinated Pyrrole Complexes and the Synthesis of Tetrahydroindole Cores. *Organometallics* **2009,** *28* (20), 5960-5967.

14. Myers, J. T.; Smith, J. A.; Dakermanji, S. J.; Wilde, J. H.; Wilson, K. B.; Shivokevich, P. J.; Harman, W. D., Molybdenum(0) Dihapto-Coordination of Benzene and Trifluorotoluene: The Stabilizing and Chemo-Directing Influence of a CF3 Group. *Journal of the American Chemical Society* **2017,** *139* (33), 11392-11400.

15. MacLeod, B. L.; Pienkos, J. A.; Wilson, K. B.; Sabat, M.; Myers, W. H.; Harman, W. D., Synthesis of Novel Hexahydroindoles from the Dearomatization of Indoline. *Organometallics* **2016,** *35* (3), 370-387.

16. Lankenau, A. W.; Iovan, D. A.; Pienkos, J. A.; Salomon, R. J.; Wang, S.; Harrison, D. P.; Myers, W. H.; Harman, W. D., Enantioenrichment of a Tungsten Dearomatization Agent Utilizing Chiral Acids. *Journal of the American Chemical Society* **2015,** *137* (10), 3649-3655.

17. Harman, W. D., Conformational and linkage isomerizations for dihapto-coordinated arenes and aromatic heterocycles: controlling the stereochemistry of ligand transformations. *Coordination Chemistry Reviews* **2004,** *248* (9), 853-866.

18. Brooks, B. C.; Gunnoe, T. B.; Harman, W. D., Dihapto binding of aromatic molecules by p-basic transition metal complexes: development of alternatives to the $\{Os(NH_3)_5\}^{2+}$ fragment. *Coord. Chem. Rev.* **2000,** (206-207), 3-61.

19. Harman, W. D., The Activation of Aromatic Molecules with Pentaammineosmium(II). *Chem. Rev.* **1997,** *97*, 1953-1978.

20. Kundig, E. P., *Transition Metal Arene Complexes in Organic Synthesis and Catalysis*. Springer: Berlin, 2004; Vol. 7.

21. Graham, P.; Meiere, S. H.; Sabat, M.; Harman, W. D., Dearomatization of Benzene, Deamidization of N,N-Dimethylformamide, and a Versatile New Tungsten Base. *Organometallics* **2003,** *22*, 4364-4366.

22. Wilson, K. B.; Myers, J. T.; Nedzbala, H. S.; Combee, L. A.; Sabat, M.; Harman, W. D., Sequential Tandem Addition to a Tungsten–Trifluorotoluene Complex: A Versatile Method for the Preparation of Highly Functionalized Trifluoromethylated Cyclohexenes. *Journal of the American Chemical Society* **2017,** *139* (33), 11401-11412.

23. Salomon, R. J.; Lis, E. C.; Kasbekar, M. U.; Bassett, K. C.; Myers, W. H.; Trindle, C. O.; Sabat, M.; Harman, W. D., Stereoelectronic Effects in Dihapto-Coordinated Complexes of TpW(NO)(PMe3) and Their Manifestation in Diels,àíAlder Cycloaddition of Arenes. *Organometallics* **2009,** *28* (16), 4724-4734.

24. Kosturko, G. W.; Graham, P. M.; Myers, W. H.; Smith, T. M.; Sabat, M.; Harman, W. D., Tungsten-Promoted Diels−Alder Cycloaddition of Pyridines: Dearomatization of 2,6-Dimethoxypyridine Generates a Potent 2-Azadiene Synthon. *Organometallics* **2008,** *27* (17), 4513-4522.

25. Liu, W.; You, F.; Mocella, C. J.; Harman, W. D., A New Approach to Promoting Sluggish Diels-Alder Reactions: Dihapto-Coordination of the Diene. *J. Am. Chem. Soc.* **2006,** *128* (5), 1426-1427.

26. Welch, K. D.; Harrison, D. P.; Lis, E. C.; Liu, W.; Salomon, R. J.; Harman, W. D.; Myers, W. H., Large-Scale Syntheses of Several Synthons to the Dearomatization Agent {TpW(NO)(PMe3)} and Convenient Spectroscopic Tools for Product Analysis. *Organometallics* **2007,** *26* (10), 2791-2794.

27. Malet, J. C. *Ignition and combustion of sodium, fire consequences, extinguishment and prevention*; International Atomic Energy Agency (IAEA), 1996; pp 13-37.

28. Luster, V. P.; Freudenstein, K. F. *Feedback from practical experience with large sodium fire accidents*; International Atomic Energy Agency (IAEA), 1996; pp 233-254.

29. Bassett, K. C.; You, F.; Graham, P. M.; Myers, W. H.; Sabat, M.; Harman, W. D., Furan [3 + 2] Dipolar Cycloadditions Promoted by a -Basic Tungsten Metal Fragment. *Organometallics* **2006,** *25*, 435-439.

30. Strausberg, L.; Li, M.; Harrison, D. P.; Myers, W. H.; Sabat, M.; Harman, W. D., Exploiting the o-Quinodimethane Nature of Naphthalene: Cycloaddition Reactions with η2-Coordinated Tungsten–Naphthalene Complexes. *Organometallics* **2013,** *32* (3), 915-925.

31. Harrison, D. P.; Iovan, D. A.; Myers, W. H.; Sabat, M.; Wang, S.; Zottig, V. E.; Harman, W. D., [4 + 2] Cyclocondensation Reactions of Tungsten–Dihydropyridine Complexes and the Generation of Tri- and Tetrasubstituted Piperidines. *Journal of the American Chemical Society* **2011,** *133* (45), 18378-18387.

32. Harrison, D. P.; Sabat, M.; Myers, W. H.; Harman, W. D., Polarization of the Pyridine Ring: Highly Functionalized Piperidines from Tungsten−Pyridine Complex. *Journal of the American Chemical Society* **2010,** *132* (48), 17282-17295.

33. Zottig, V. E.; Todd, M. A.; Nichols-Nielander, A. C.; Harrison, D. P.; Sabat, M.; Myers, W. H.; Harman, W. D., Epoxidation, Cyclopropanation, and Electrophilic Addition Reactions at the meta Position of Phenol and meta-Cresol. *Organometallics* **2010,** *29* (21), 4793-4803.

34. Harrison, D. P.; Iovan, D. A.; Myers, W. H.; Sabat, M.; Wang, S.; Zottig, V. E.; Harman, W. D., [4 + 2] Cyclocondensation Reactions of Tungsten,ÄìDihydropyridine Complexes and the Generation of Tri-

and Tetrasubstituted Piperidines. *Journal of the American Chemical Society* **2011,** *133* (45), 18378-18387.

35. Graham, P. M.; Delafuente, D. A.; Liu, W.; Myers, W. H.; Sabat, M.; Harman, W. D., Facile Diels-Alder Reactions with Pyridines Promoted by Tungsten. *Journal of the American Chemical Society* **2005,** *127* (30), 10568-10572.

36. Bassett, K. C. The Reactivity of Furan Promoted by a Tungsten(0) π-Basic Transition Metal Fragment. Universty of VIrginia, 2007.

37. Myers, W. H.; Welch, K. D.; Graham, P. M.; Keller, A.; Sabat, M.; Trindle, C. O.; Harman, W. D., Tungsten(0) and Rhenium(I) η2-Pyrrole Complexes: Dearomatization of Pyrroles and Their Facile Isomerizations, Protonations, and Reductions. *Organometallics* **2005,** *24* (22), 5267-5279.

38. Harman, W. D.; Taube, H., Synthesis of $[Os(NH_3)_5(\eta^2\text{-TMB})]^{2+}$: A Valuable Precursor for Pentaammineosmium(II) Chemistry. *Inorg. Chem.* **1987,** *26*, 2917.

39. Harman, W. D.; Taube, H., Reactivity of pentaammineosmium(II) with benzene. *Journal of the American Chemical Society* **1987,** *109* (6), 1883-1885.

40. Harman, W. D.; Fairlie, D. P.; Taube, H., Synthesis, characterization, and reactivity of the (.eta.2-acetone)pentaammineosmium(II) complex. *Journal of the American Chemical Society* **1986,** *108* (26), 8223-8227.

41. Mocella, C. J.; Delafuente, D. A.; Keane, J. M.; Warner, G. R.; Friedman, L. A.; Sabat, M.; Harman, W. D., Coordination Chemistry and Properties of Unusually π-Basic Molybdenum Fragments. *Organometallics* **2004,** *23* (16), 3772-3779.

42. Bodner, G. S.; Fernández, J. M.; Arif, A. M.; Gladysz, J. A., Selective Binding of One Enantioface of Monosubstituted Alkenes to the Chiral Transition Metal Lewis Acid $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$. *J. Am. Chem. Soc.* **1988,** *110*, 4082.

43. Bodner, G. S.; Peng, T.-S.; Arif, A. M.; Gladysz, J. A., Synthesis, Structure, and Reactivity of Chiral Rhenium Alkene Complexes of the Formula $[(h^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C = CHR)]^+X^-$. *Organometallics* **1990,** *9*, 1191.

44. Meiere, S. H.; Harman, W. D., Binding Selectivity of Dihapto-Coordinated Olefins, Ketones, and Aldehydes Utilizing the Asymmetric π-Basic Metal Fragment {TpRe(CO)(1-methylimidazole)} (Tp = Hydridotris(pyrazolyl)borate). *Organometallics* **2001,** *20* (18), 3876-3883.

45. Keane, J. M.; Harman, W. D., A New Generation of Pi-Basic Dearomatization Agents. *Organomet.* **2005,** *24*, 1786-1798.

46. Keane, J. M.; Ding, F.; Sabat, M.; Harman, W. D., Solid-State Induced Control of Kinetically Unstable Stereoisomers. *J. Am. Chem. Soc.* **2004,** *126*, 785-789.

Chapter 2:
Exchange of Dihapto-Coordinated Ligands on Molybdenum: Electron-Transfer Catalysis through a Radical Chain Mechanism

Adapted from a manuscript (in preparation):
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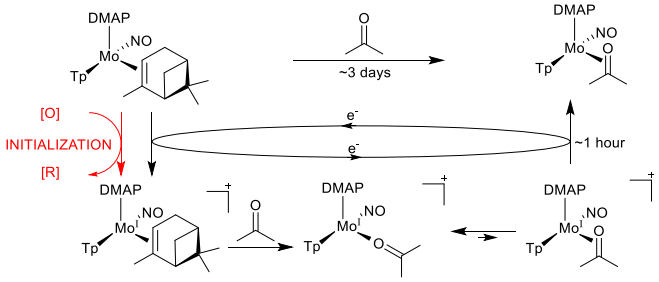
Abstract.



Development and description of a redox initiated, electron transfer process for exchange of a dihapto-coordinated ligand are presented. The complex MoTp(NO)(DMAP)(η^2-α-pinene) (where Tp = hydridotris(pyrazolyl)borate and DMAP = 4-(dimethylamino)pyridine) was found to have an accelerated exchange of the dihapto-coordinated ligand when trace Lewis acid impurities were present in solution. Treatment of the Mo complex with metallocene oxidants (ferrocenium, cobaltocenium) mimicked this observation and allowed for broader application to other aldehydes and ketones. Subsequent tests with MoTp(NO)(DMAP)(η^2-α, α, α-trifluorotoluene), MoTp(NO)(DMAP)(η^2-naphthalene), and even MoTp(NO)(DMAP)(η^2-acetone) showed the ubiquity of the initiation step. From experimental observations, a mechanism for the transfer process is proposed and supported. In addition, initial experiments for reductions to the MoTp(NO)(DMAP)(η^2-naphthalene), MoTp(NO)(DMAP)(η^2-α-pinene), and MoTp(NO)(DMAP)(η^2- α, α, α-trifluorotoluene) complexes using magnesium have been found.

2.1: Introduction

Ligand substitution reactions play a fundamental role in organotransition metal chemistry. Like their organic counterparts, they can proceed by either two-electron or one-electron mechanisms, and can be associative, dissociative, or concerted in nature.[1-2] Which mechanism applies to a given reaction depends on the metal geometry, oxidation state, electron configuration, and nature of the ligand. In general, octahedral d^6 complexes of second- and third-row transition metals tend to undergo substitution through a dissociative mechanism (Figure 2.1).[1] For these reactions, the specific rate of dissociation (*k*) tends to strongly correlate with the metal-ligand bond strength (ΔG), which approximates the free energy of activation ($\Delta G^{\ddagger}$).[3] Such has been our experience with octahedral complexes of Os(II),[4] Ru(II),[5-6] Re(I),[7-8] W(0),[8-9] and Mo(0),[8, 10] where the outgoing ligand is a dihapto-coordinated alkene, arene, or carbonyl.

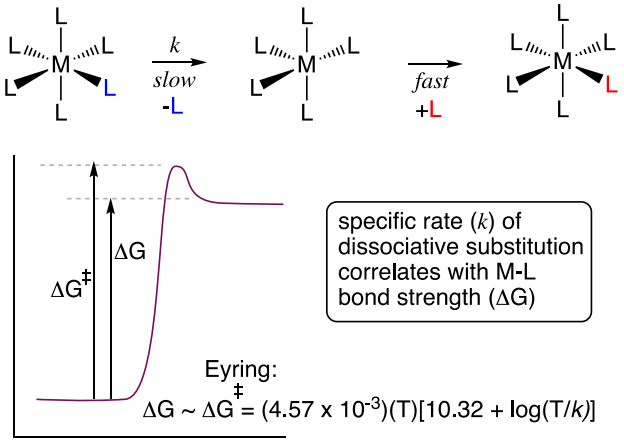


Figure 2.1: General mechanism for dissociative substitution.

It is in this context that we set out to measure rates of substitution for various alkene complexes of the molybdenum π-base {MoTp(NO)(DMAP)}. The α-pinene complex MoTp(NO)(DMAP)(η^2-α-pinene) (**1**) is calculated to have a bond strength of 24 kcal/mol, which leads to a predicted half-life in acetone of 16 hours at 25°C. This complex undergoes clean ligand substitution with a variety of different ligands (L = acetone, naphthalene, ethyl acetate, acetonitrile) to form MoTp(NO)(DMAP)(η^2-L), with similar rates

(expressed as free energies) (Table 2.1).[11] In most cases half-lives ranged from 10-15 h at 25 °C, independent of the chemical nature of ligand, solvent (i.e., neat or as a benzene solution), or concentration. Treating these reactions as pseudo first order in **1**, this range of half-lives would correspond to a free energy of activation of 24.0 ±0.1 kcal/mol.

However, an outlier was revealed when we examined the substitution of the α-pinene ligand of **1** with benzaldehyde. Instead of a half-life of >10 h to form MoTp(NO)(DMAP)(η^2-*CO*-benzaydehyde) (**2**), substitution occurred with a half-life of 1.5 hours at 25°C. This unusual feature was reminiscent of behavior exhibited by $[Os(NH_3)_5(acetone)]^{2+}$, which was reported to undergo facile ketone exchange, but was otherwise substitution-inert.[12] In the case of this osmium complex, a catalytic process was identified that involved an adventitious *one-electron oxidant*,[12] and we suspected a similar electron transfer catalysis (ETC) mechanism[13] was in play with the reaction of benzaldehyde and the α-pinene complex **1**.

2.2: Results and Discussion

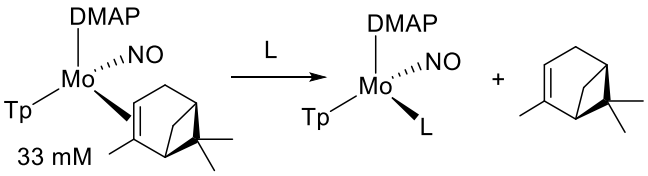
2.2.1: Initial Observations

To test the theory that ligand substitution on {MoTp(NO)(DMAP)} could be catalyzed by redox-active species, we repeated the reaction of α-pinene complex (**1**, 33 mM) and benzaldehyde, along with 0.5 eq (1.6 mM) of the oxidant [Fe(Cp)$_2$]bis(trifluoromethanesulfonyl)imide (Tf_2N^+). Ferrocenium salts are commonly used as redox catalysts in organometallic chemistry[13] and organic synthesis.[14] In the presence of this ferrocenium additive, the exchange was >95% complete in 15 minutes, and the yield improved to >90% (Table 2.1). Further, when the reaction was repeated with 0.5 eq of the *reductant* $FeCp_2$ added in place of the oxidant, the rate of substitution with benzaldehyde was suppressed to the point that the exchange half-life approximated those of other ligands (Table 2.1). Complexes of the form MoTp(NO)(DMAP)(η^2-L) are known to be susceptible to oxidation by Brønsted acids.[15-16] The erratic behavior of the benzaldehyde reaction with pinene complex **1** was ultimately attributed to the

contamination of benzaldehyde with benzoic acid. Supporting this notion, when the aldehyde was first passed through basic alumina, the half-life for the conversion of **1** to **2** was ~10 h, in agreement with that seen for exchanges with other ligands.

Similar to the exchange with benzaldehyde, the substitution of α-pinene (**1**, 30 mM) by acetone to form MoTp(NO)(DMAP)(η^2-acetone) (**3**), was also found to be catalyzed by 0.1 eq of $FeCp_2^+$ (5.0mM), reducing the half-life from 10.3 to 0.6 h. Ferrocenium salts can also act as Lewis acids.[14] In order to rule out a mechanism involving this pathway, 1.5 eq of Et_3N was added to a solution of the pinene complex in acetone, prior to the addition of permethylferrocenium (+40 mV vs NHE, $FeCp_2^{*+}$). The amine additive did not appear to inhibit the ligand exchange catalysis. Since water is a common impurity in acetone,[17] we also investigated its role in the substitution reaction. When the pinene complex **1** was dissolved in acetone-d_6 and monitored with 10% D_2O added, the yield was found to drop from 89% to 58%. However, *the rate of the reaction actually increased*. This observation suggested that, like the benzoic acid impurity, the water may be reacting in such a way as to generate an adventitious redox–active species that could catalyze the substitution. Remarkably, when the ferrocenium catalyst was present along with 10% D_2O, displacement of pinene by acetone not only happened at an accelerated rate, the yield was restored from 58% to 86%. A similar effect was even observed using the weaker oxidant $CoCp_2^+$ as the catalyst (-0.78 V *cf.* 0.55 V for $FeCp_2^+$), with the yield approaching 100% (Table 2.1). In addition, use of several different counter-ions (PF_6^-, tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ($BArF^-$), or Tf_2N^-) showed no dependence on anion used.

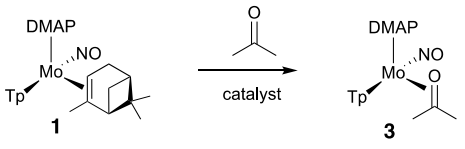
Table 2.1: Kinetic Data for **1** to Various Ligands



L	Product Compound	NMR Yield	Half-life deuterated solvent (h)	$\Delta G^{\ddagger}$ (25 °C) kcal/mol
Benzaldehyde (0.1M benzene-d6)	**2**	70%	1.5	—
Benzaldehyde (0.1M benzene-d6) with 0.5 eq of FeCp2+	**2**	>90%	<0.1	—
Benzaldehyde (0.1M benzene-d6) passed through basic alumina with 0.5 eq of FeCp2	**2**	40%	17.5	23.9
Benzaldehyde (0.1M benzene-d6) passed through basic alumina	**2**	46%	14.8	—
Acetone (neat)	**3**	89%	10.3	23.9
Acetone (neat) with 0.1 eq FeCp2+	**3**	93%	0.6	—
Acetone (0.1M benzene-d6)	**3**	88%	16.3	24.2
Acetone (neat) with 0.1 eq FeCp*2+ and 1.5 eq Et3N	**3**	91%	1.1	—
Acetone-d6 (10% D2O)	**3**	58%	6.8	—
Acetone-d6 (10% D2O) with 0.1 eq CoCp2+	**3**	95%	0.9	—
Naphthalene (0.1M benzene-d6)	**4**	75%	15.6	24.1
Ethyl acetate (0.1M benzene-d6)	**6**	49%	15.5	24.1
Acetonitrile (neat)	**7**	58%	11.5	24
DMF (neat)	**8**	63%	15	24.1

2.2.2: Kinetics studies

To study the mechanism more closely, the exchange of pinene for acetone was explored in depth (Eqn 2.1):



Eqn 2.1.

As an initial test, addition of 0.1 eq of the $FeCp_2^+$ (1.7 mM) to a solution of 1 in acetone (17 mM) enhanced the rate of reaction and was accompanied by an improvement in yield from 90% to >98%. Using NMR data (Figure 2.2) to compare the resolved Tp ligand pyrazole (Pz) protons of the pinene and acetone complexes (Figure 2.2), a plot of ln[**1**] vs. time for the catalyzed reaction was found to be linear, indicative of pseudo first order kinetics (Figure 2.3). As seen in Figure 2.3, the decrease of the Pz4 peak associated with the pinene complex at 6.10 ppm is followed by the concomitant growth of the Pz4 peak at 6.15 ppm associated with the acetone complex. Comparison of kinetic data for the catalyzed and uncatalyzed reactions show stark visual differences (Figure 2.3).

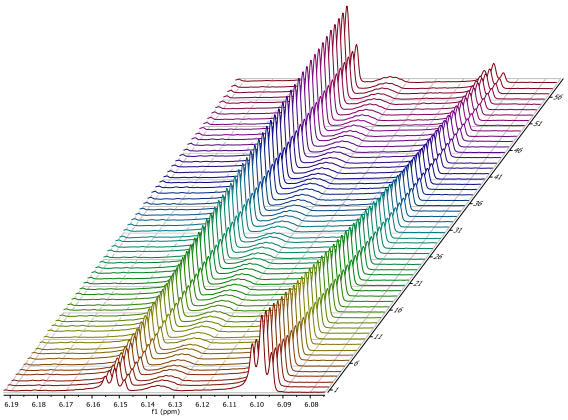


Figure 2.2: ^{1}H NMR data for the conversion of **1** (17 mM) to **3** with $FeCp_2^+$ (0.1 eq, 1.7 mM). Each scan is taken automatically 30 seconds after the previous scan ended.

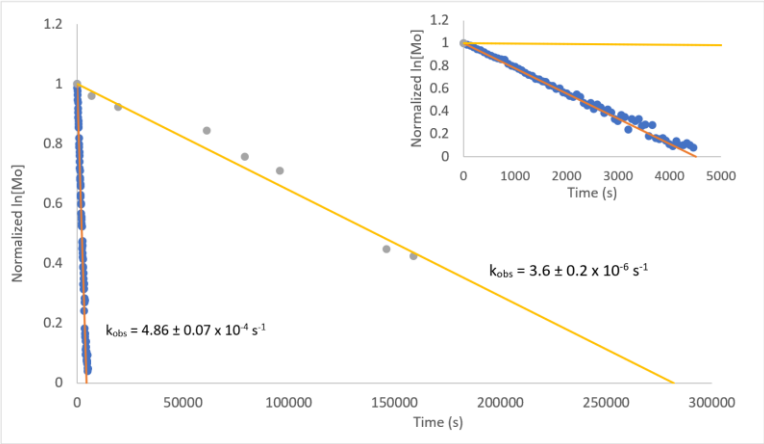


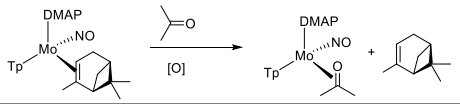
Figure 2.3: Comparison of catalyzed and an uncatalyzed substitution reaction of **1** (50 mM) to **3**. The reaction catalyzed with $FeCp_2^+$ (0.1 eq, 5 mM) is inset.

Standard reaction conditions were designed to be 0.01 g of the pinene complex (**1**, 0.0167 mmol) in 1 mL of a 1:9 mixture of acetone to acetone-d_6 (17 mM **1**). Catalyst loading was changed from 0.05 eq (9 µM) to 25 eq (4 mM) across ferrocenium, permethylferrocenium, and cobaltocenium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (BArF) salts. These were used to determine effect of the strength of the oxidant (**O**) on the catalytic process. All relevant kinetic data is listed in Table 2.2 and the aggregation of the half-life data is shown in Figure 2.4. The inherent rate constant, k_{uncat}, of a normal uncatalyzed exchange (i.e. when [**O**] = 0, k_{uncat} = 0.0008 min^{-1}) is removed from each data point by assuming that the experimentally found k_{obs}, is the sum of k_{uncat} and the catalyzed rate constant, k_{cat} (i.e. $k_{cat} = k_{obs} - k_{uncat}$, vide infra).

One note is the trouble with reproduction of the experiments. Over the course of collecting this data, the pinene complex **1** needed to be synthesized multiple times. With each preparation of **1**, there are slight differences in the amount of oxidized materials that are isolated with the product. While there might not be enough to see the impurity by CV, the oxidized species can have an effect on the reaction rate. Like the trace benzoic acid (vide supra), the oxidized species can increase the reaction rate. As such, trying to compare the reaction rates of different sources of **1** can lead to inconsistent reaction

rates. Looking at the trials listed in Table 2.2 of ~ 1 mM catalyst loading have a range in half-lives from ~15 mins to 45 mins. It is of note that all three catalyst have at least one trial where the reaction half-life is around 15 minutes, despite all three having different reduction potentials

Table 2.2: All kinetic data collected at 25 ± 2 °C.



$[FeCp_2]^+$				$[FeCp^*_2]^+$				$[CoCp_2]^+$			
[O] (mM)	$t_{1/2}$ (min)	k_{obs} (min^{-1})	k_{cat} (min^{-1})	[O] (mM)	$t_{1/2}$ (min)	k_{obs} (min^{-1})	k_{cat} (min^{-1})	[O] (mM)	$t_{1/2}$ (min)	k_{obs} (min^{-1})	k_{cat} (min^{-1})
0	900.00	0.0008	0.0000	0	900.00	0.0008	0.0000	0	900.00	0.0008	0.0000
0.0092	850.00	0.0008	0.00005	0.010	626.65	0.0011	0.0003	0.100	419.08	0.0017	0.0009
0.094	519.00	0.0013	0.0006	0.051	413.79	0.0017	0.0009	0.25	150.64	0.0046	0.0038
0.19	54.92	0.0126	0.0119	0.077	351.49	0.0020	0.0012	0.50	68.08	0.0102	0.0094
0.32	39.94	0.0174	0.0166	0.083	656.00	0.0011	0.0003	0.75	50.25	0.0138	0.0130
0.48	26.85	0.0258	0.0250	0.10	80.82	0.0086	0.0078	1.00	45.83	0.0151	0.0144
0.92	18.98	0.0365	0.0357	0.21	76.06	0.0091	0.0083	1.0	24.96	0.0278	0.0270
0.96	19.25	0.0360	0.0352	0.30	30.30	0.0229	0.0221	1.0	20.22	0.0343	0.0335
0.97	36.23	0.0191	0.0184	0.42	32.10	0.0216	0.0208	1.0	15.43	0.0449	0.0442
0.97	39.93	0.0174	0.0166	0.51	23.05	0.0301	0.0293	1.5	11.14	0.0622	0.0615
0.98	38.70	0.0179	0.0171	0.63	29.91	0.0232	0.0224	1.9	21.72	0.0319	0.0311
1.0	15.50	0.0447	0.0439	0.77	23.69	0.0293	0.0285	2.5	10.33	0.0671	0.0663
1.6	16.90	0.0410	0.0402	0.83	23.01	0.0301	0.0294	2.5	14.66	0.0473	0.0465
1.9	15.55	0.0446	0.0438	0.85	20.54	0.0337	0.0330	2.6	12.81	0.0541	0.0533
2.4	22.16	0.0313	0.0305	1.00	17.00	0.0408	0.0400	2.6	11.31	0.0613	0.0605
2.4	26.74	0.0259	0.0252	1.02	44.02	0.0157	0.0150	3.0	19.17	0.0362	0.0354
2.5	22.27	0.0311	0.0303	1.02	47.71	0.0145	0.0138	3.5	7.88	0.0880	0.0872
2.6	11.13	0.0623	0.0615	1.03	47.69	0.0145	0.0138	3.9	5.83	0.1189	0.1181
2.9	10.73	0.0646	0.0638	1.27	15.61	0.0444	0.0436	4.1	9.16	0.0757	0.0749
3.6	10.15	0.0683	0.0675	1.67	12.75	0.0544	0.0536	4.2	8.58	0.0808	0.0800
3.9	17.13	0.0405	0.0397	1.96	12.75	0.0544	0.0536	4.2	5.90	0.1176	0.1168
3.9	17.06	0.0406	0.0399	2.50	9.93	0.0698	0.0690	4.4	5.73	0.1210	0.1202
3.9	20.31	0.0341	0.0334	2.56	26.17	0.0265	0.0257				
4.2	10.75	0.0645	0.0637	2.56	18.34	0.0378	0.0370				
				2.56	26.89	0.0258	0.0250				
				3.40	8.99	0.0771	0.0763				
				3.83	9.32	0.0744	0.0736				
				4.10	19.30	0.0359	0.0351				
				4.10	16.24	0.0427	0.0419				

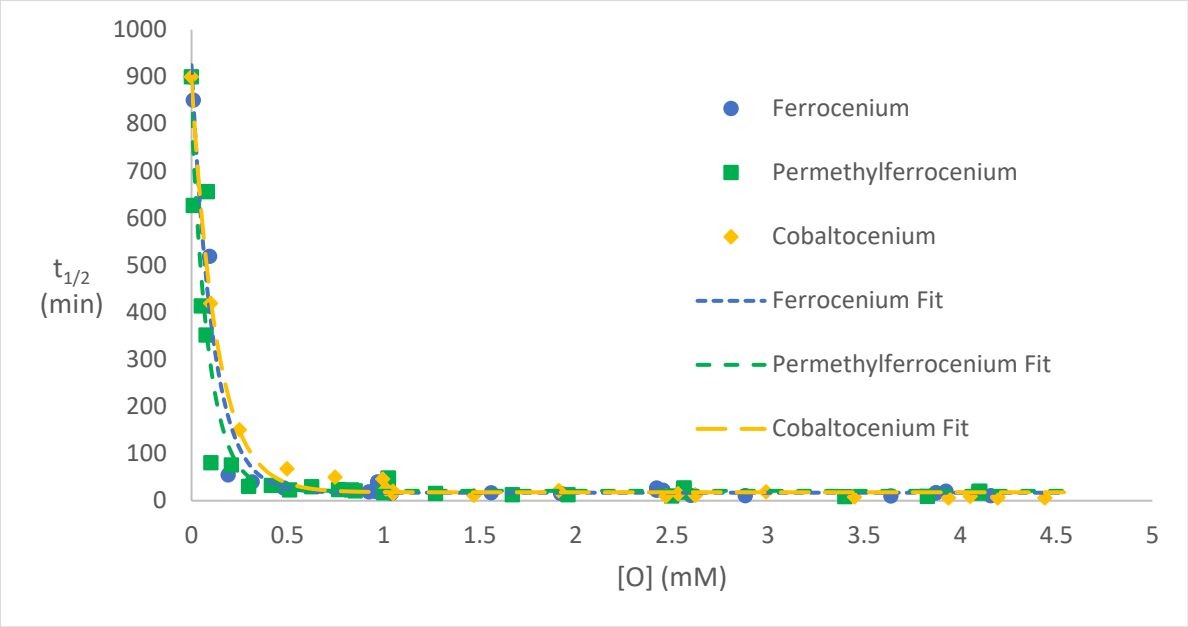


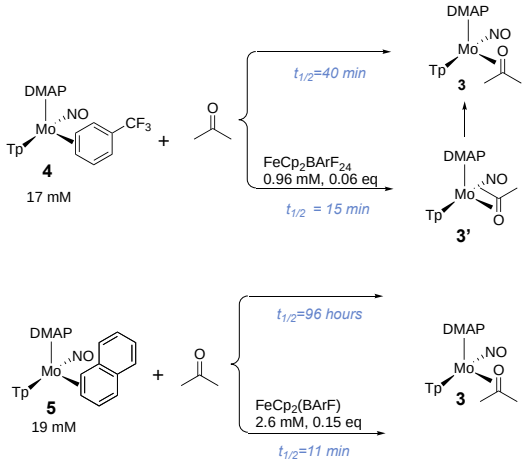
Figure 2.4: Plot of reaction half-life vs [O] using three different metallocene redox catalysts.

The three catalysts show similar abilities to catalyze the reaction. At micromolar concentrations of catalyst (< 0.001 eq), the reaction half-life approaches that of the uncatalyzed reaction as expected. From 1 μM to 4 mM, a plot of k_{cat} vs. [**O**] is roughly linear (vide infra), supporting the general relationship: $k_{cat} = k'[\mathbf{O}]$, where k' is = 0.023 ± 0.003$mM^{-1}\,s^{-1}$ for $CoCp_2^+$, 0.011 ± 0.002 $mM^{-1}\,s^{-1}$ for $FeCp^*_2^+$, and 0.010 ± 0.002 $mM^{-1}\,s^{-1}$ for $FeCp_2^+$, where the rate of the reaction depends on concentration of **O**. Remarkably, the weakest oxidant appears to have the highest rates of reaction.

Similar to the behavior of the pinene-to-acetone exchange, the conversion of arene complexes MoTp(NO)(DMAP)(η^2-trifluorotoluene) (**4**), and MoTp(NO)(DMAP)(η^2-naphthalene) (**5**), to acetone complex **3** was also catalyzed by the one-electron oxidants. The labile trifluorotoluene complex has an uncatalyzed exchange half-life of about 40 minutes at 25 °C in acetone-d_6. At relatively low catalytic loading ($FeCp_2^+$, 0.06 eq 0.96 mM), the reaction half-life is reduced to 15 minutes. From initial exchanges of the more labile TFT complex, it was noted that there was an additional MoTp complex observed in the NMR spectra, thought to be a second isomer of the acetone complex in which the carbonyl was oriented

away from the DMAP ligand (Scheme 2.1). Over time, the second isomer was seen to convert to the major isomer with an approximate half-life of 50 minutes (0.96mM $FeCp_2^+$) (Figure 2.5a).[8]

The naphthalene complex **5** has an uncatalyzed half-life of 118 hours to acetone at 25 °C, allowing convenient observation of the effect of redox catalysts on its ligand exchange. The addition of 0.05 eq of $FeCp_2BArF$ (0.86 mM) decreases the half-life from 118 h to 26 minutes. A plot of ln[**5**] vs time again shows a linear relationship indicating pseudo first order behavior (Figure 2.5b). As a note on this reaction, the raw data shows what could be an increase in reaction rate over time. While an exhaustive study was not carried out for the naphthalene system, it was noted that the initial trend for the half-life dependence on concentration matches that of **1**.



Scheme 2.1: Acceleration of the exchange from **4** and **5** to **3** with addition of ferrocenium.

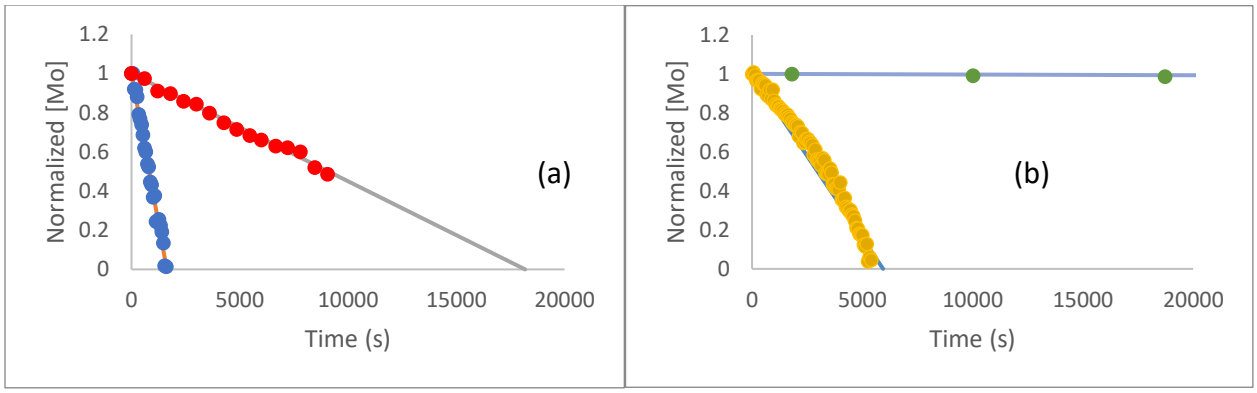


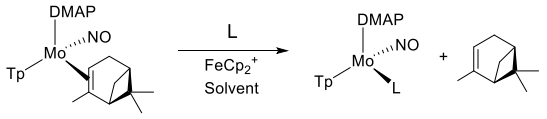
Figure 2.5: Catalyzed and uncatalyzed substitution reactions of: (a) Mo-TFT (**4**, 16 mM) with and without $FeCp_2^+$ (0.96 mM) and (b) Mo-naphthalene (**5,** 17 mM) with and without $FeCp_2^+$ (0.86 mM).

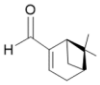
While the previously described experiments of the catalytic substitution reaction on {MoTp(NO)(DMAP)} focused primarily on acetone as the incoming ligand, other molecules with the potential to form π-complexes were also explored. Despite its bulky t-butyl group, pinacolone was also found to be suitable as the incoming ligand. The exchange of α-pinene for this ketone showed significant acceleration in the presence of $FeCp_2(PF_6)$ (0.34 eq, 13 mM). We note however that the relative substitution rates for pinacolone were found to be significantly slower than were observed for acetone. The exchange of pinene for *R*-camphor and *R*-fenchone were also catalyzed by addition of an oxidant, but like pinacolone, the acceleration of the reaction rate was more modest than for acetone at similar concentrations. Further, the exchange reactions with the two terpenoid ketones were accompanied by significant decomposition with little project generation. Other carbonyl-containing compounds that form dihapto-coordinate complexes with {MoTp(NO)(DMAP)} such as ethyl acetate or DMF failed to show any increase in substitution rate upon exposure to $FeCp_2(BArF)$ (0.1 eq, 5 mM). In contrast, aldehydes like benzaldehyde and R-myrtenal show dramatic acceleration, significantly faster than observed for acetone at low catalyst loading $FeCp_2(BArF)$ (0.1 eq, 5 mM). These results are summarized in Table 2.3.

Attempts to exchange the pinene ligand in **1** with acetonitrile in the presence of the metallocene salts resulted in decomposition, with no diamagnetic structures identifiable in ^1H NMR spectra after an

hour. Likewise, attempts to promote the exchange of pinene for cyclopentene and cyclohexene were also largely unsuccessful as no significant acceleration of the substitution reaction was detected in the presence of the metallocene oxidants. Similarly, the displacement of the pinene ligand in **1** by the arenes trifluorotoluene and naphthalene failed to be accelerated by exposure to the metallocene salts.

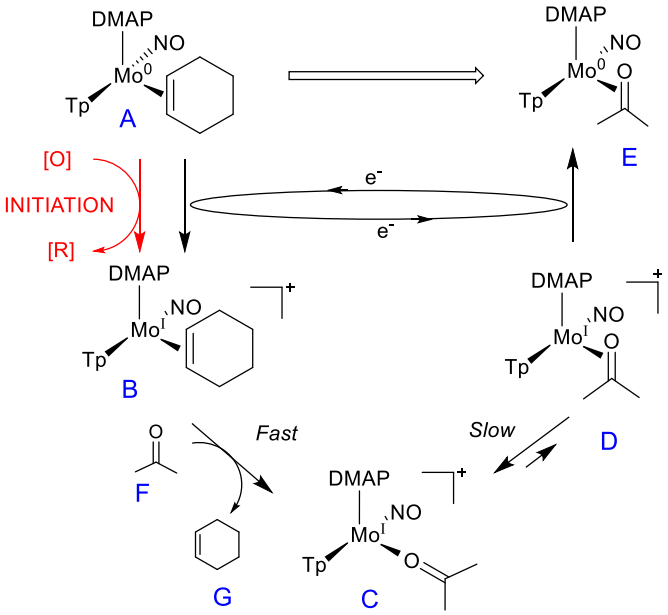
Table 2.3: Half-lives for substitution in the presence and absence of $FeCp_2^+$.



L	Half-life (h)	Half-life (h) with $[FeCp_2^+]$ (~2 mM, 0.1 eq)	Cpd #
	4	>0.1	**10**
	10	>0.1	**2**
	15	0.3	**3**
	19	10	**9**
	15.5	15.5	**6**
	15	15	**8**
 THF cosolvent	15	15	**11**
 THF solvent	15	15	**5**

2.2.3: Mechanism for Exchange

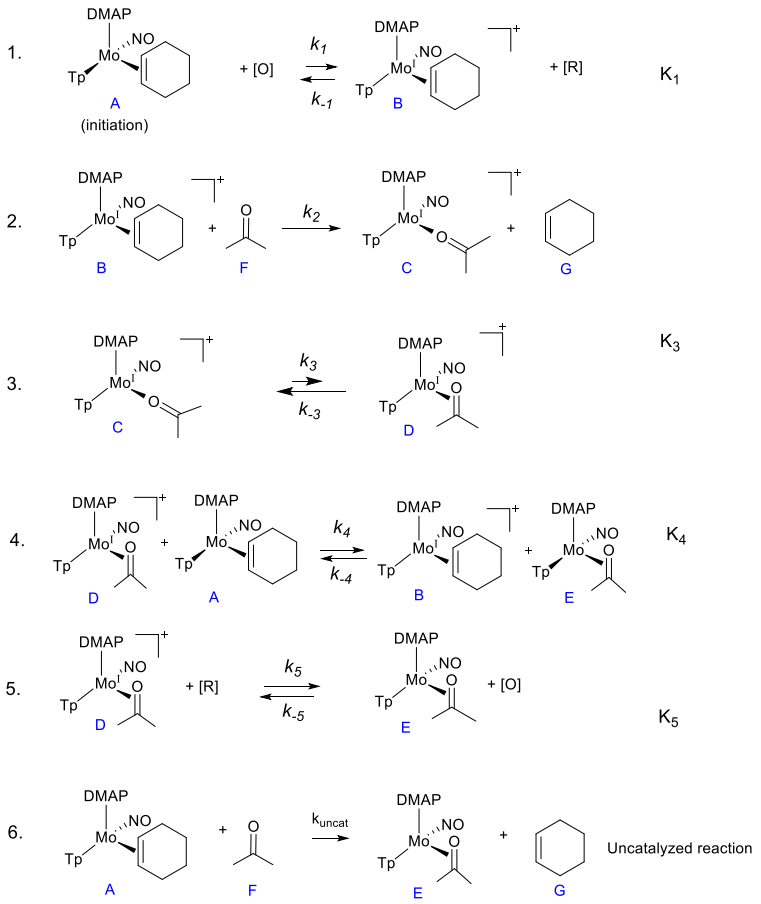
From our observations, a possible electron transfer catalysis cycle is described in Scheme 2.2, using cyclohexene and acetone as representatives of a generic alkene and carbonyl, respectively.



Scheme 2.2: The proposed catalytic cycle for the accelerated exchanges of an alkene or arene for an aldehyde or ketone.

The process is proposed to be initiated by the metallocene salt (**O**) oxidizing the alkene or arene complex (**A**). In its oxidized form, the resulting Mo(I) complex (**B**) undergoes rapid and irreversible ligand displacement to form the ketone complex **C**. This species, while most stable in its κ^1 form, has access to the dihapto-coordinated isomer (**D**). Judging from the osmium analog $[Os(NH_3)_5(\eta^2\text{-acetone})]^{2+}$,[18] the dihapto-coordinated form is a much stronger oxidant than the sigma complex, and is capable of reacting with the starting complex **A** to form the product ketone **E**, along with regeneration of the oxidized alkene complex **B**.

The individual mechanistic steps for the proposed cycle described above are shown in Scheme 2.3 (steps 1-4).



Scheme 2.3: The proposed mechanistic steps for the redox-catalyzed exchange of an alkene for a ketone.

Depending on the nature of the oxidant used, its conjugate **R** may also be capable of electron-transfer with the molybdenum ketone complex **D** to reform **O** and generate the product **E** (step 5). In this scenario, **O** functions as a true catalyst rather than an initiator. Reviewing the relevant experimental observations:

1. Under conditions where the concentration of incoming ligand **F** is constant (~10 M), the half-life of the reaction (pseudo first order) depends on the concentration of **O**.

2. A plot of 1/half-life vs concentration of **O** is roughly linear as well as a derived k_{cat} for the catalyzed reaction process (vide infra, Figure 2.6).

3. The rate of reaction is fastest for aldehydes followed by ketones, with esters and amides showing no acceleration with an added oxidant.

4. While triethylamine does not significantly alter the catalysis, addition of an amide inhibits the reaction.

It is possible that both the chain-propagation (i.e., step 4) and redox catalysis (i.e., step 5) mechanisms are operative. Considering a scenario where reaction 5 is inactive (no redox catalysis) and reaction 4 is rate-limiting after the initiation step:

$$Rate = -d[A]dt = k_4[C]K_3[A] + k_{uncat}[A] \qquad \text{Eqn 2.2}$$

where K_3, the equilibrium of η^2/κ^1 for the carbonyl, is a pre-equilibrium prior to the rate limiting step. Also included is the base uncatalyzed rate. Given that step two is rapid and irreversible, all of $\mathbf{O}^0$ is immediately converted into **C**, which can be assumed to be steady state for much of the reaction: $[O]^0 \sim [C]$~

$$-d[A]dt = K_3k_4[O]^0[A] + k_6[A] \text{ and } k_{obs} = K_3k_4[O]^0 + k_6 = \frac{\ln 2}{t_{1/2}} \qquad \text{Eqn 2.3.}$$

Thus: $$t_{1/2} = \frac{\ln 2}{K_3k_4[O]^0 + k_6} \qquad \text{Eqn 2.4.}$$

To normalize the data to account for the baseline uncatalyzed rate, a k_{cat} term can be defined as the rate of reaction based just on the catalytic process (Eqn 2.5).

$$k_{cat} = K_3k_4[O]^0 = k_{obs} - k_{uncat} \qquad \text{Eqn 2.5}$$

Under these conditions, a plot of k_{cat} vs [**O**] should be linear, and independent of potential of **O**, where the slope is proportional to K_3 and $[\mathbf{O}]^0$. Figure 2.6 shows a plot of k_{cat} where the half-lives are those reported in Figure 2.4. Fitting each set of half-lives corresponding to a given oxidant, we find that the plots are approximately linear. Values for the slope should equal k_4K_3, where k_4 is the specific rate of electron transfer for the propagation step, and K_3 is the η^2/κ^1 equilibrium constant for the carbonyl. If this holds true, we expect that as the carbonyl changes from aldehyde to ketone to ester or amide, K_3 decreases and the observed rate of substitution decreases. This is what is observed. Further, as the difference in redox

potential for the alkene and ketone complex increases, so too should the rate of the substitution reaction. *The reaction rate should depend on the potential of the alkene complex*. By this logic, electron-rich alkenes exchanging with electron-poor carbonyls should be the most rapid type of chain-growth substitution reaction.

Comparing the iron oxidants in Figures 2.6 and 2.7, it appears that they are almost identical in catalyzing the exchange. Comparing the low concentrations (~0 mM to 1 mM) and higher concentrations done in triplicate (1, 2.5, and 4 mM) in Figure 2.7, the data between the two oxidants is in good agreement. The k' slope values for the k_{cat} vs [**O**] graphs are approximately the same when comparing ferrocenium and permethylferrocenium at the same range of concentrations (0.038 and 0.39 min^{-1} respectively for the low concentrations and 0.0069 vs 0.0074 min^{-1} for the high concentrations). At lower concentrations, it appears that the change in rate of reaction is increasing faster than the higher concentrations (i.e. larger increase k' values at lower [**O**]). This observation is given with the reservation that the data is inconsistent.

If it was the case that the mechanism involved reaction 5 as a key step, where **O** was truly acting as a catalyst, then the reaction rate should be highly variable on the potential of **O** and **R**. With the ~0.5 V difference in reduction potentials of the oxidants, the ferrocenium and permethylferrocenium should display wildly different reaction rates. Looking at outer-sphere, electron transfer mechanisms, like Marcus theory, the change in reaction rate based on changes in ΔG is exponentially related.[19-20] The half of a volt change between the ferrocenium and permethylferrocenium should give orders of magnitude different reaction rates if there was actually a dependence on the oxidation strength.

If the final reduction step is truly independent of the oxidant and step 5 is almost completely shut off, the reaction rate will be independent of oxidant strength. The apparent insensitivity between these two oxidants helps to support our previous assumption that the catalyzed reaction rate is dependent not on oxidation strength, but on the K_3k_4 term. This is what is qualitatively seen.

Once cobaltocenium is taken into consideration, the mechanism possibly becomes more complicated. Looking at the k' slopes at low [**O**], the rate of reaction is slower than the iron systems. Once higher [O] are taken into account however, the k' for the cobalt system is higher than the iron congeners. The increased rate of reaction could imply a more complicated mechanism for the cobalt catalyst. The conjugate cobaltocene (**R**) might be sufficiently reducing to be able to afford the use of the redox catalysis (step 5) process. The possible combination of the final reduction caused by both oxidation of the cobaltocene byproduct of the initiation step and the chain process (step 4) could allow the reaction to proceed faster than the iron systems at higher concentrations (>3.5 mM, Table 2.2). Relatively weaker ferrocene and permethylferrocene are assumed to not be strong enough to reduce the Mo(I) species, which precludes redox catalysis (step 5). With all of this stated, it should be noted that the rates of reaction, k', for the cobaltocenium are still relatively close to the iron systems. If there was an effect of oxidation power on k' then the increase for an operative electron process should be orders of magnitude higher, not double the value (0.023 min^{-1} vs 0.011 min^{-1}, figure 2.6).

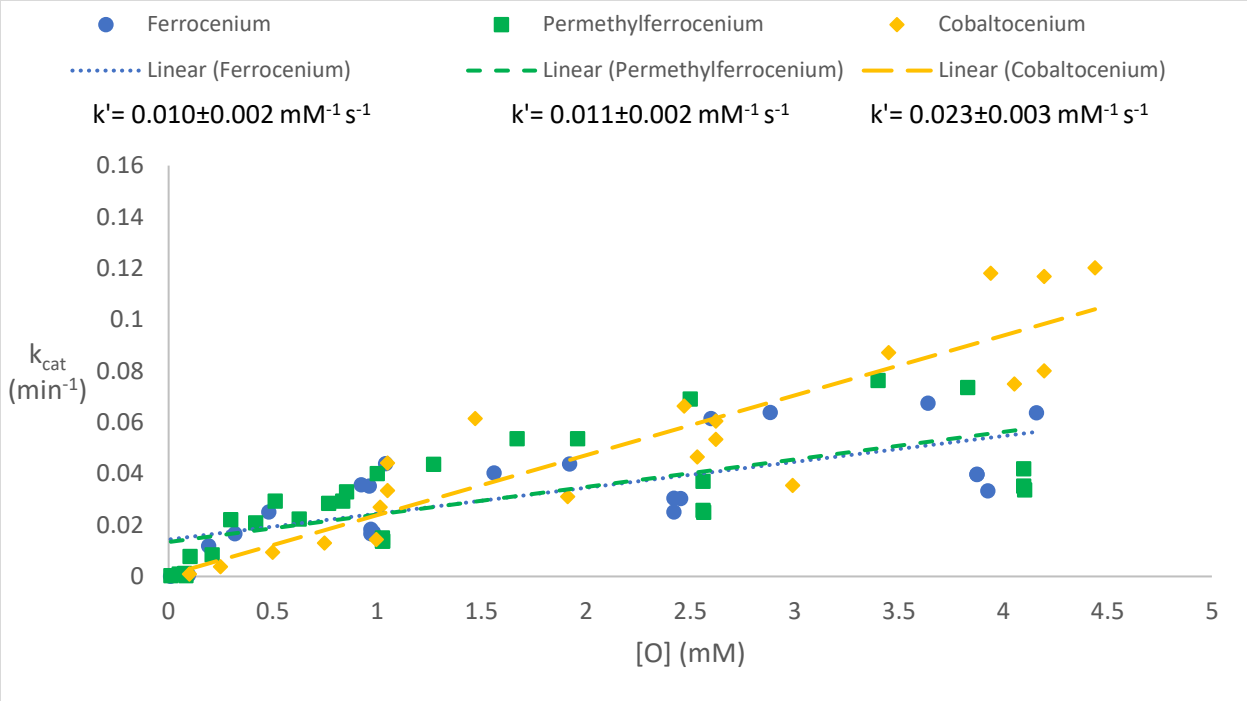


Figure 2.6: A plot of k_{cat} vs time, for the redox catalyzed substitution of pinene for acetone with the ferrocenium, permethylferrocenium, and cobaltocenium salts

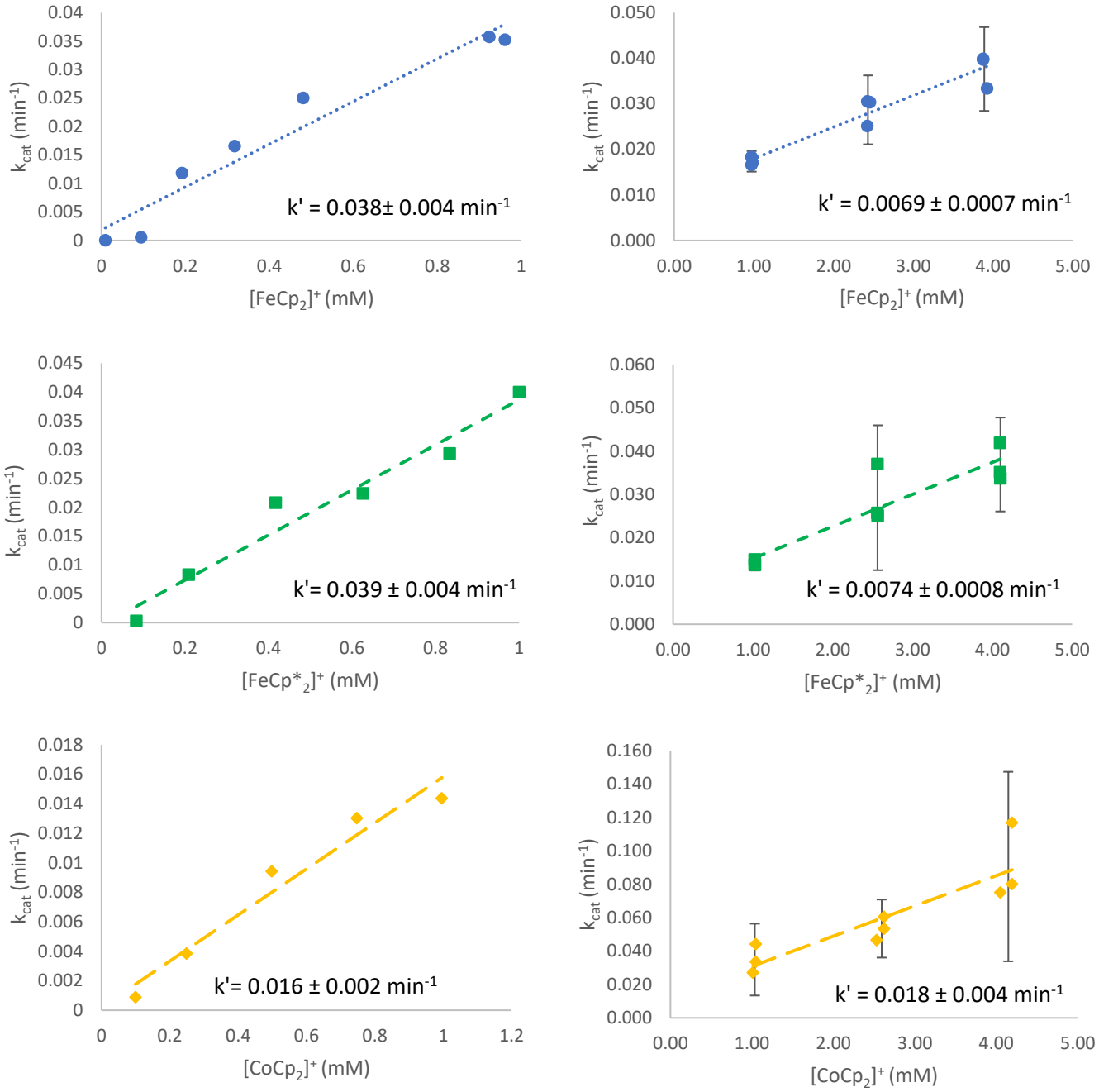


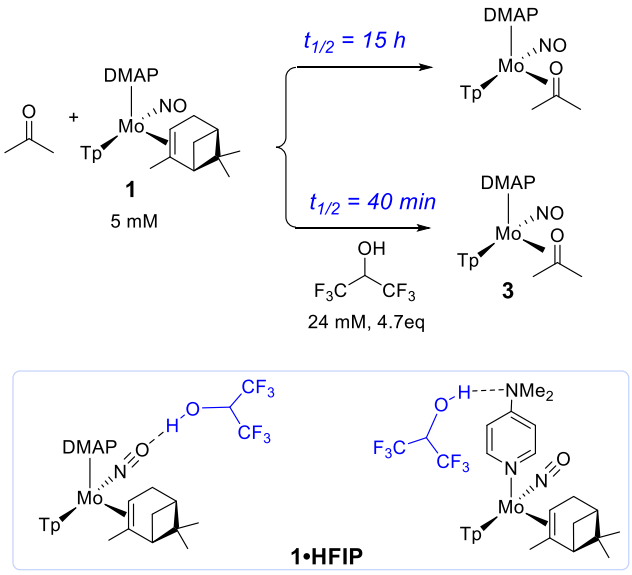
Figure 2.7: Comparison of the k_{cat} of the three metallocene oxidants at low and high concentrations for two different preparations of the molybdenum pinene complex **1**. The test higher concentrations are done in triplicate with a 95% confidence interval added.

It is possible that both steps are active in the mechanism, but the percentage of each process (steps 4 and 5) for the total final reduction might change based on the reduction strength of **R**. Once this assumption is made, the overall mechanism for this reaction becomes significantly more complicated and we cannot determine what the actual overall process is. It is likely that there is a non-zero order dependence on the catalyst. The proposed electron chain process is a good basis for further experimentation.

Overall, this methodology allows for accelerated exchanges of ketones and aldehydes. While the mechanism is not completely defined, we have shown that the reaction rate is relatively independent of oxidant strength but dependent on [**O**]. While the iron systems seem to be in good agreement with these assertions, the cobaltocenium seems to change the mechanism that is operative. We are not sure why the cobaltocenium changes the reaction rate, but the possible addition of the catalytic reduction (step 5) might account for it. However, it is important to note that all of the k' described are relatively consistent when compared to others in the same range (vide supra, 0.0069 min^{-1} to 0.023 min^{-1}).

2.2.4: Lewis acid catalysis

In addition to the redox pathway outlined above, it was noted that hydrogen donors can also promote an acceleration of the ligand exchange reaction for {MoTp(NO)(DMAP)}. In the case of Hexafluoroisopropanol (HFIP), the ligand exchange can be accelerated with rates similar to those observed with the metallocene salts, albeit at much higher concentrations. When the pinene complex **1** in acetone solution is treated with roughly 25 mM (~ 5 eq) of the strong H-donor HFIP, the half-life for substitution is reduced from 15 h to 40 minutes at 25°C.



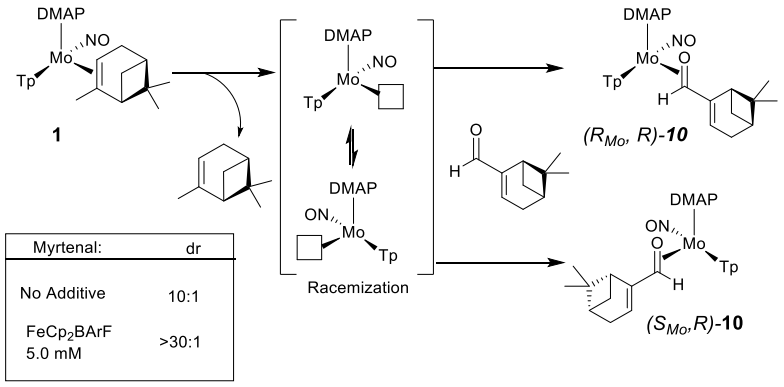
Scheme 2.4: HFIP mediated substitution of pinene for acetone via activation of either NO or DMAP ligands.

It is thought that the HFIP forms a strong hydrogen bond with either the nitrosyl[21] or DMAP[15] ligand of **1**, thereby reducing electron density at the metal, and weakening the back-bonding interaction with the pinene ligand. A similar acceleration of exchange was not observed for the cyclopentene complex, but the replacement of this alkene for acetone is likely to be thermodynamically unfavorable.

A complication arises for the HFIP-induced substitution reactions when monitored by cyclic voltammetry. In addition to an anodic peak corresponding to the product acetone complex (**3**), two additional features, an $E_{p,a}$ = +250 mV and an $E_{1/2}$ = -1800 mV, grow in larger amounts instead of desired product. This pair of electrochemical signals match complexes of the form Mo(I)Tp(NO)(DMAP)(X), where X = Br, I. Judging from CV and NMR data, the amount of desired product **3** is only ~10-25% yield. The remainder of the Mo is oxidized by the alcohol to what is likely MoTp(NO)(DMAP)(κ^1-$OCH(CF_3)_2$). Even with the bulkier fluorinated alcohol $HOC(CF_3)_3$, oxidation occurs with similar product yields. These observations suggest that the accelerated ligand exchange may be a result of an adventitious oxidant that initiates the chain propagation mechanism (vide supra) rather than the proposed H-donation. However, neither mechanism can be ruled out.

2.2.5: Conservation of the Mo asymmetric center

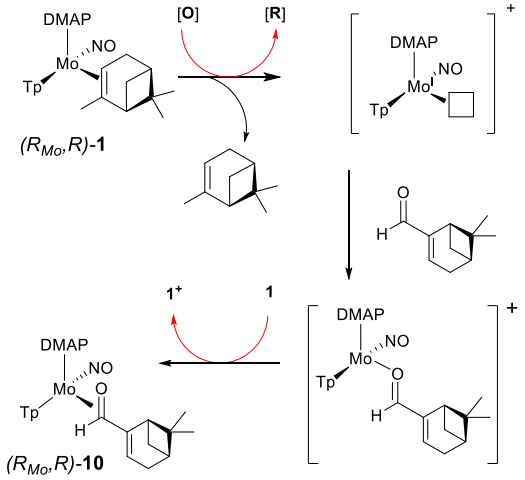
Coordination of a chiral ligand to the chiral molybdenum center forms diastereomers. In previous work, it was noted that the α-pinene complex is synthesized as a single diastereomer.[11] The synthesis of an enantiopure metal complex is important for subsequent synthesis of enantiopure organic products. However, in contrast to the rhenium[22] and tungsten systems[23], uncatalyzed conversion from the synthetically inert molybdenum pinene complex **1** to a more synthetically versatile aromatic ligand occurs with epimerization of the metal stereocenter.[11] After the pinene ligand dissociates, the purported five-coordinate intermediate partially racemizes. For example, the treatment of the pinene complex (R_{Mo}, *R*)-**1** (>30 R_{Mo}: 1 S_{Mo}) with *R*-myrtenal produces a 10:1 R_{Mo}:S_{Mo} mixture of the two diastereomers of the Mo-*R*-myrtenal complex (**10**) overnight at 25°C.



Scheme 2.5: Normal racemization during uncatalyzed substitution for the {MoTP(NO)(DMAP)} five-coordinate intermediate reported by *R*-myrtenal vs the retention of sterochemistry with a catalyzed exchage.

However, addition of ferrocenium catalyzes the ligand exchange reaction to be nearly instantaneous ($t_{1/2}$ <1 min at 25°C) at conditions listed in Scheme 2.**5**. With the expedited reaction, the myrtenal complex diastereomer ratio is increased to >30:1, demonstrating complete retention of the

configuration of the metal stereocenter. As discussed previously,[11] computational studies of the Mo(0) and Mo(I) square pyramidal intermediates indicate that the barrier to epimerization is approximately 3 kcal/mol higher for Mo(I), thus the ligand displacement reaction via the higher oxidation state plays a key role in retention of the stereocenter. The conversion of the pinene complex **1** into the myrtenal complex **10** can also be accelerated by HFIP with retention of the molybdenum stereocenter (>30:1).

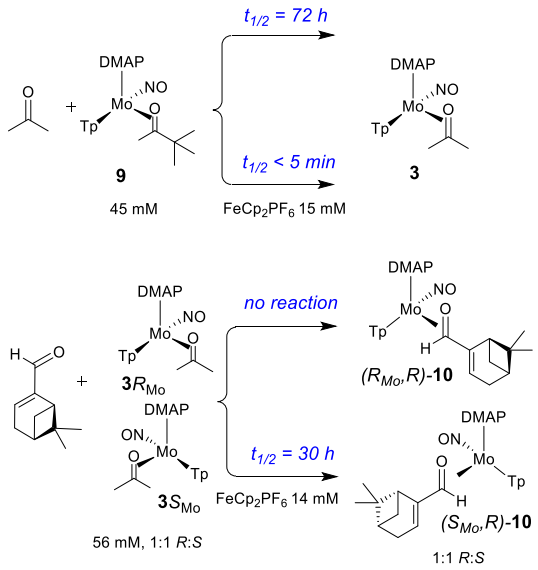


Scheme 2.6: The redox-promoted conversion of pinene complex **1** to myrtenal complex **10** with retention of the molybdenum stereocenter.

2.2.6: Ketone displacement

As a general rule, η^2-ketone complexes of {MoTp(NO)(DMAP)} are more stable than their η^2-arene analogs.[8] Attempts to exchange acetone for cyclopentene yields no discernible trace of the cyclopentane complex (**11**) after monitoring the reaction solution by ^{1}H NMR over multiple days. Addition of HFIP or $FeCp_2^+$ does not alter this outcome. In order to exchange acetone with another ligand, large concentrations of a thermodynamically favorable ligand such as an aldehyde, as well as a catalyst need to be used. The conversion of the acetone complex **3** to the myrtenal complex **10** is an example of this. A myrtenal solution of **3** yields barely discernible quantities of the myrtenal complexes after three days. However, the addition of $FeCp_2$ BArF (13.7mM, 0.25 eq) accelerates the reaction to the point that the half-life of the reaction is 30 hours (Scheme 2.7). In an effort to bias a ketone to be more labile, a ketone with

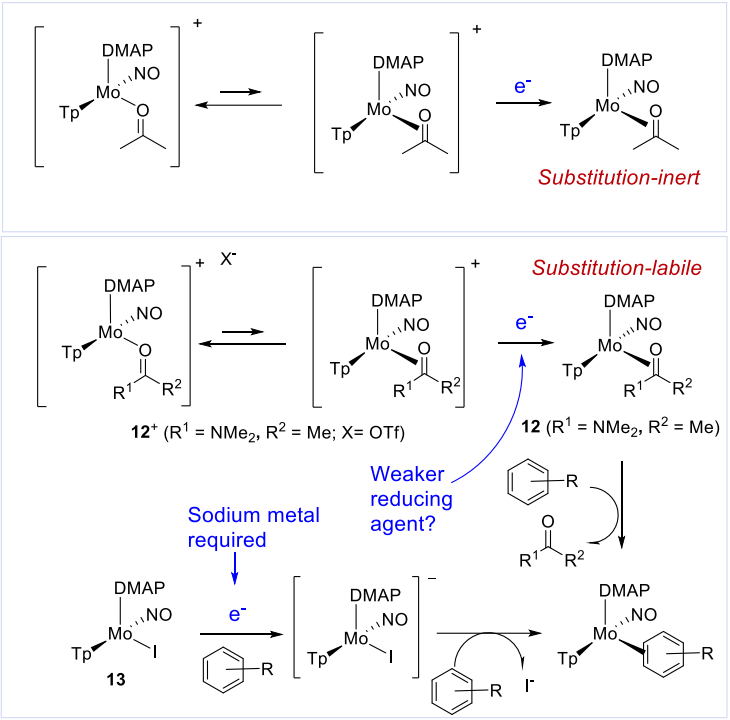
steric bulk near the binding carbonyl, pinacolone, was tested. When the pinacolone complex **9** was dissolved in acetone, the half-life for exchange was determined to be around 3 days. Upon addition of a significant concentration of catalyst (15 mM, 0.25 eq) in acetone, the exchange reaction time was reduced to less than 5 minutes (Scheme 2.7).



Scheme 2.7: Ketone to ketone or aldehyde exchange of the {MoTP(NO)(DMAP)} system catalyzed by ferrocenium

2.2.7: Application for magnesium reductions

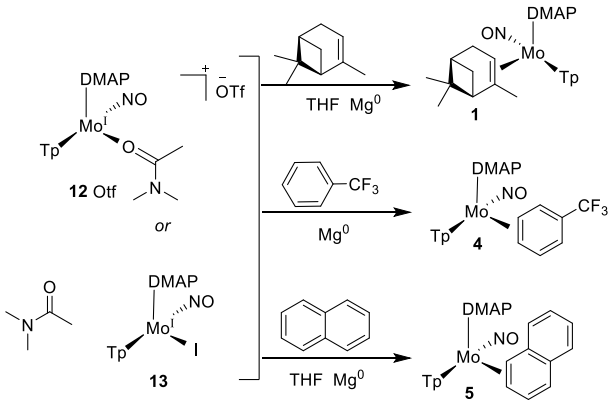
Studies described above rely on the ability of Mo(I) complexes of carbonyl ligands existing as an κ^1/η^2 equilibrium, where although the dihapto-coordinate form may be in minority, its much greater reduction potential and the rapid equilibrium between the two isomers provide a pathway for electron-transfer. We posited that a sufficiently sterically hindered carbonyl might still facilitate reduction, but that the corresponding Mo(0) complex was substitution labile (Scheme 2.8). Such a system could provide access to Mo(0) complexes using reducing agents less powerful than sodium metal, currently used for Mo(I) to Mo(0) reductions in these systems.



Scheme 2.8: proposed reduction pathway for the [Mo-DMA](OTf) salts.

Although the pinacolone complex **9** proved to be as slow to exchange as **1**, despite the bulky t-butyl group, it was known that Mo(0) complexes could undergo ligand exchange in DMA solvent without interference by the amide. The Mo(I)-DMA complex was prepared and isolated as the stable Mo(I) salt [MoTp(NO)(DMAP)(κ^1-DMA)]OTf (**12** OTf). This paramagnetic complex is characterized by a Mo(I/0) reduction potential with $E_{1/2}$ = -1200 mV. This peak is approximately 200 mV more positive than the MoTp(NO)(DMAP)(I) complex used as the precursor to Mo-η^2-arene complexes.[15] While this potential is right at the the range that untreated magnesium metal can normally access in non-aqueous solvents (~ -1.3 V,[24] NHE), our hope was that it had access to a transient η^2 isomer (**12**) which is expected to have a much more positive reduction potential. While the use of zinc metal provided evidence for a very slow reduction from **11** to the Mo-acetone complex (**3**), subsequent tests with arenes were unproductive.

However, magnesium powder, even without any pretreatment of the surface, was able to reduce the Mo(I)-DMA complex to the corresponding Mo(0)- η^2- α-pinene (**1**), trifluorotoluene (**4**), and naphthalene (**5**) complexes. As an example, the naphthalene complex **5** can be prepared on a 17 g scale in 70% overall yield from MoTp(NO)(DMAP)(I) (**13**), using unactivated magnesium powder (325 mesh), *provided* that DMA (0.2% v/v) was included in the reaction mixture. Compared to a comparable sodium reduction,[15] the magnesium reduction of **11** was completed in approximately the same time with 50% higher yield. Without the DMA additive, no product was seen after a week of monitoring. The ability to access compounds of the form MoTp(NO)(DMAP)(η^2-arene) without the need for pyrophoric metals constitutes a significant practical advance.



Scheme 2.9: Generation of Mo(0) arene and alkene complexes through magnesium powder reduction.

2.3: Conclusions

Electron transfer catalyzed substitutions (i.e. electron transfer chain) processes have been well documented.[25,2, 26] Whereas much of the earlier studies focused on κ^1-bound ligands, this study has demonstrated the role of this important mechanism for organometallic reactions in the context of dihapto-coordinated carbonyl ligands, particularly as the incoming ligand. The large difference in

reduction potentials brought about by the change in coordination mode from κ^1 to η^2 possibly provides the thermodynamic driving force required to propagate a proposed electron chain transfer process.[27]

2.4 References

1. Astruc, D., Ligand Substitution Reactions. In *Organometallic Chemistry and Catalysis*, Astruc, D., Ed. Springer Berlin Heidelberg: Berlin, Heidelberg, 2007; pp 121-134.

2. Howell, J. A. S.; Burkinshaw, P. M., Ligand substitution reactions at low-valent four-, five-, and six-coordinate transition metal centers. *Chemical Reviews* **1983,** *83* (5), 557-599.

3. Bengali, A. A.; Leicht, A., Kinetic and Mechanistic Study of the Displacement of η2-Coordinated Arenes from Cp*Re(CO)2(η2-C6H5R) (R = H, CH3, C(CH3)3): Evidence for a Dissociative Mechanism and Estimation of the Re−(η2-Arene) Bond Strength. *Organometallics* **2001,** *20* (7), 1345-1349.

4. Harman, W. D.; Sekine, M.; Taube, H., Substituent effects on .eta.2-coordinated arene complexes of pentaammineosmium(II). *Journal of the American Chemical Society* **1988,** *110* (17), 5725-5731.

5. Taube, H., Substitution Reactions of Ruthenium Ammines. *Comments on Inorganic Chemistry* **1981,** *1* (1), 17-31.

6. Isied, S. S.; Taube, H., Rates of Substitution in Cis and Trans Ruthenium(II) Aquotetraammines. *Inorg. Chem.* **1976,** *15*, 3070.

7. Meiere, S. H.; Brooks, B. C.; Gunnoe, T. B.; Sabat, M.; Harman, W. D., A Promising New Dearomatization Agent: Crystal Structure, Synthesis, and Exchange Reactions of the Versatile Complex TpRe(CO)(1-methylimidazole)(η2-benzene) (Tp = Hydridotris(pyrazolyl)borate). *Organometallics* **2001,** *20* (6), 1038-1040.

8. Myers, J. T.; Smith, J. A.; Dakermanji, S. J.; Wilde, J. H.; Wilson, K. B.; Shivokevich, P. J.; Harman, W. D., Molybdenum(0) Dihapto-Coordination of Benzene and Trifluorotoluene: The

Stabilizing and Chemo-Directing Influence of a CF3 Group. *Journal of the American Chemical Society* **2017,** *139* (33), 11392-11400.

9. Graham, P. M.; Meiere, S. H.; Sabat, M.; Harman, W. D., Dearomatization of Benzene, Deamidization of N,N-Dimethylformamide, and a Versatile New Tungsten π Base. *Organometallics* **2003,** *22* (22), 4364-4366.

10. Mocella, C. J.; Delafuente, D. A.; Keane, J. M.; Warner, G. R.; Friedman, L. A.; Sabat, M.; Harman, W. D., Coordination Chemistry and Properties of Unusually π-Basic Molybdenum Fragments. *Organometallics* **2004,** *23* (16), 3772-3779.

11. Shivokevich, P. J.; Myers, J. T.; Smith, J. A.; Pienkos, J. A.; Dakermanji, S. J.; Pert, E. K.; Welch, K. D.; Trindle, C. O.; Harman, W. D., Enantioenriched Molybdenum Dearomatization: Dissociative Substitution with Configurational Stability. *Organometallics* **2018,** *37* (23), 4446-4456.

12. Harman, W. D.; Sekine, M.; Taube, H., Redox Promoted Linkage Isomerizations of Aldehydes and Ketones on Pentaammineosmium. *J. Am. Chem. Soc.* **1988,** *110*, 2439.

13. Astruc, D., Electron-Transfer Chain Catalysis in Organotransition Metal Chemistry. *Angewandte Chemie International Edition in English* **1988,** *27* (5), 643-660.

14. Toma, Š.; Šebesta, R., Applications of Ferrocenium Salts in Organic Synthesis. *Synthesis* **2015,** *47* (12), 1683-1695.

15. Myers, J. T.; Dakermanji, S. J.; Chastanet, T. R.; Shivokevich, P. J.; Strausberg, L. J.; Sabat, M.; Harman, W. D., 4-(Dimethylamino)pyridine (DMAP) as an Acid-Modulated Donor Ligand for PAH Dearomatization

Organometallics **2017,** *36* (3), 543-555.

16. Myers, J. T.; Shivokevich, P. J.; Pienkos, J. A.; Sabat, M.; Myers, W. H.; Harman, W. D., Synthesis of 2-Substituted 1,2-Dihydronaphthalenes and 1,2-Dihydroanthracenes Using a Recyclable Molybdenum Dearomatization Agent. *Organometallics* **2015,** *34* (14), 3648-3657.

17. Burfield, D. R.; Smithers, R. H., Desiccant Efficiency in Solvent Drying. 3. Dipolar Aprotic Solvents. *J. Org. Chem.* **1978,** *43*, 3966.

18. Harman, W. D.; Sekine, M.; Taube, H., Redox-promoted linkage isomerizations of aldehydes and ketones on pentaammineosmium. *Journal of the American Chemical Society* **1988,** *110* (8), 2439-2445.

19. Marcus, R. A., On the Theory of Oxidation-Reduction Reactions Involving Electron Transfer. I. *The Journal of Chemical Physics* **1956,** *24* (5), 966-978.

20. Stubbe, J.; Nocera, D. G.; Yee, C. S.; Chang, M. C. Y., Radical Initiation in the Class I Ribonucleotide Reductase: Long-Range Proton-Coupled Electron Transfer? *Chemical Reviews* **2003,** *103* (6), 2167-2202.

21. Sharp, W. B.; Legzdins, P.; Patrick, B. O., O-Protonation of a Terminal Nitrosyl Group To Form an η1-Hydroxylimido Ligand. *Journal of the American Chemical Society* **2001,** *123* (33), 8143-8144.

22. Meiere, S. H.; Valahovic, M. T.; Harman, W. D., Strategy for the Resolution of a Chiral Dearomatization Agent:{TpRe(CO)(1-methylimidazole)} Coordination of α-Pinene (Tp = Hydridotris(pyrazolyl)borate). *Journal of the American Chemical Society* **2002,** *124* (50), 15099-15103.

23. Lankenau, A. W.; Iovan, D. A.; Pienkos, J. A.; Salomon, R. J.; Wang, S.; Harrison, D. P.; Myers, W. H.; Harman, W. D., Enantioenrichment of a Tungsten Dearomatization Agent Utilizing Chiral Acids. *Journal of the American Chemical Society* **2015,** *137* (10), 3649-3655.

24. Lossius, L. P.; Emmenegger, F., Plating of magnesium from organic solvents. *Electrochimica Acta* **1996,** *41* (3), 445-447.

25. Hershberger, J. W.; Klingler, R. J.; Kochi, J. K., Electron-transfer catalysis. Radical chain mechanism for the ligand substitution of metal carbonyls. *Journal of the American Chemical Society* **1982,** *104* (11), 3034-3043.

26. Geiger, W. E., Organometallic Electrochemistry: Origins, Development, and Future. *Organometallics* **2007,** *26* (24), 5738-5765.

27. Astruc, D., Transition-metal radicals: chameleon structure and catalytic function. *Accounts of Chemical Research* **1991,** *24* (2), 36-42.

Chapter 3:
Molecular Recognition Within Terpenes:
Redox and H-bond Promoted Isomerizations and the Selective Binding of Complex Alkenes

Adapted from a manuscript (in preparation):

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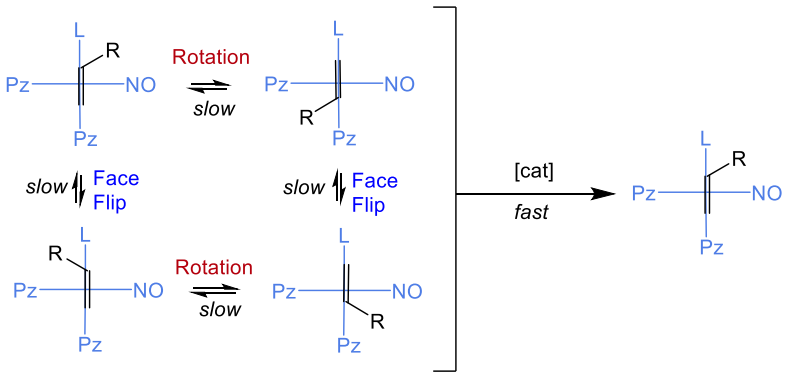
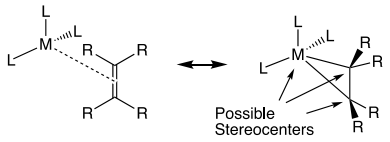
Abstract:



A method for resolution of coordination diastereomers of alkene complexes of the type MoTp(NO)(DMAP)(η^2-alkene) (where Tp = hydridotris(pyrazolyl)borate and DMAP = 4-(dimethylamino)pyridine) and WTp(NO)(PMe_3)(η^2-alkene) has been elucidated and explored. In contrast to the usual fluxional nature of aromatic ligands associated with these metal systems, alkene compounds form as a mixture of kinetic isomers. While the molybdenum system's weaker bonds allow for the isomers to eventually funnel to the thermodynamic isomer while dissolved in an inert solvent (trifluorotoluene), the tungsten analogs remain trapped in the ratio of isomers from synthesis under the same condition. In both metals, it was found that addition of a catalyst, either a fluorinated alcohol or metallocene salt, reduces the number of isomers in solution. Initial observations of accelerated exchanges to isolated alkene bonds was also found, although these were accompanied by significant decomposition.

3.1: Introduction

Since Zeise's discovery in 1830,[1] the ability of a transition metal to bind an alkene through interactions of π orbitals has become a mainstay of organometallic chemistry. When bound to a transition metal, alkenes can participate in a wide range of reactions including nucleophilic or electrophilic addition, migratory insertion, and hydride abstraction.[2-3] Depending on the characteristics of the metal and alkene, the interaction between metal and alkene can be substantial, with the complex taking on features of a metallocyclopropane in which the bound carbons take on tetrahedral geometry (Dewar–Chatt–Duncanson ; equation 3.1). Depending on the nature of the ligands (L) and alkene substituents (R), the metal and bound alkene carbons can each become an independent stereogenic center.



Eqn 3.1.

Our interest in controlling the regiochemistry and stereochemistry for dihapto-coordination of alkenes, as well as for η^2-polyenes and η^2-aromatics, stems from our program to use these systems as a foundation for the preparation of novel organic compounds.[4-6] Our approach, as well as that of others, relies on a rigid enantiomeric scaffold,[7-13] formed between the metal and a prochiral alkene. However, when more than one binding site is available, the strong metal-alkene interactions often required to promote organic reactions can lead to kinetic trapping of undesired isomers. As pioneering work by Gladysz et al demonstrated,[14-15] even an alkene as simple as propene can form up to eight different isomers (four pairs of enantiomers) when coordinated to an asymmetric transition metal complex.

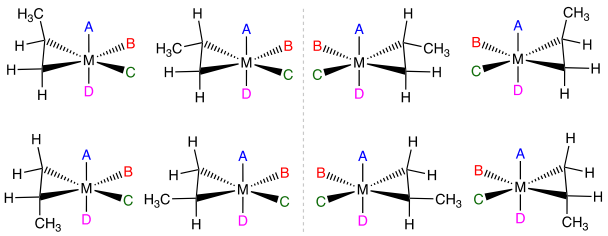


Figure 3.1: Eight isomers resulting from propene complexed to an asymmetric transition metal fragment.

For molecules with more than one alkene functional group, the situation becomes more complicated, owing to the possibility of constitutional isomers. Consider, for example, the dienes *(R)*-limonene or taxadiene (Figure 3.2), where a single enantiomer of these terpenes give rise to 16 possible isomers when dihapto-coordinated to an asymmetric metal fragment. For the triene humulene or the arene cadalene, *24 and 44 η ^{2}-coordinated isomers are possible, respectively*, even though these hydrocarbons themselves are achiral.

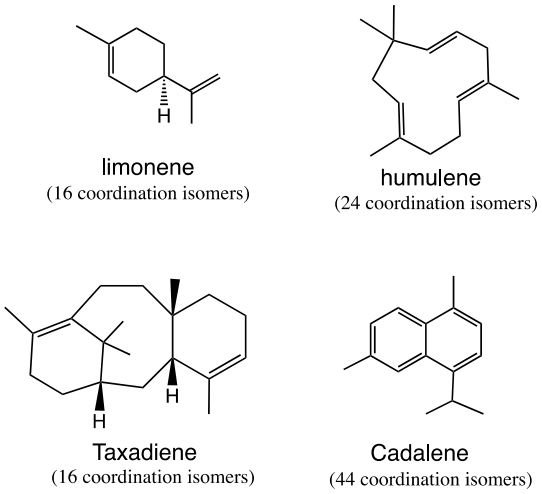


Figure 3.2: Examples of a diene, triene, and arene that could form dihapto-coordinated π complexes with a metal.

Our attention is currently focused on the chemistry of {MoTp(NO)(DMAP)} and {WTp(NO)(PMe_3)};[4] These Group 6 transition metal fragments function as powerful π-bases, capable of forming highly stabilized complexes with alkenes and arenes. For complexes of arenes, constitutional isomerization is facile at ambient temperatures, and binding selectivity usually is governed by thermodynamic factors.[4] However, for alkenes and non-aromatic polyenes, even in cases where thermodynamic factors favor one isomer over others, attempts to coordinate alkenes often result in complex isomeric mixtures. Attempts at equilibrating mixtures through heating typically results in ligand displacement or complex decomposition (vide infra), similar to what others have observed.[15] How then can one avoid the kinetic traps associated with dihapto-coordination of complex polyalkenes with π-basic transition metal complexes? We hypothesized (Figure 3.3) that the complex could be activated by transiently removing electron density from the metal, either by Lewis acid coordination of the nitrosyl group or by one-electron oxidation of the metal. With such action, the metal-alkene bond strength could be compromised to the point that the π-bond is released.

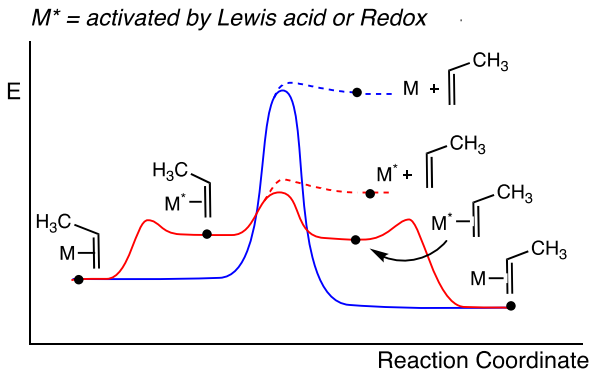


Figure 3.3: Reaction coordinate for the proposed Lewis-acid- or Redox-promoted isomerization of an alkene complex.

Our hope was that isomerization of the activated complex (M*) would not only have a lower activation barrier (Figure 3.3, red curve) than unactivated (blue), but that isomerization could happen without complete displacement of the ligand (dash). Returning the metal to its deactivated state would then complete a catalytic cycle. The following is an account of our findings.

3.2: Results and Discussion

3.2.1: Propene: mapping out the steric profile of a π-base

In our initial study,[16] the complex ReTp(MeIm)(CO)(η^2-propene) was prepared as a racemic mixture of four diastereomers (Figure 3.4). The {ReTp(CO)(MeIm)} fragment features a HOMO capable of significant back-bonding into the π* orbital of the propene.[5] Strong π-interactions with the CO stabilize two of the dπ orbitals, leaving the HOMO oriented in a plane perpendicular to the Re-CO bond axis. As a result, the alkene must be oriented parallel to the Re-N_{MeIm} bond axis. With these constraints, there is a significant barrier for both bond rotation (~12 kcal/mol) and face-flipping (~32 kcal/mol),[16] where either action would disrupt the Re-propene back-bonding interaction (Figure 3.4). At ambient temperatures, interconversion of rotamers is facile, but an intramolecular face-flip isomerization, such as initially proposed by Gladysz et al,[17] requires temperatures so high that decomposition occurs. This problem is even more pronounced with the Group 6 π-bases {WTp(NO)(PMe_3)} and {MoTp(NO)(DMAP)}, where the rotational barrier is expected to be much higher, owing to the greater difference in energy between the HOMO and the other two dπ orbitals capable of π bonding with the alkene.[4]

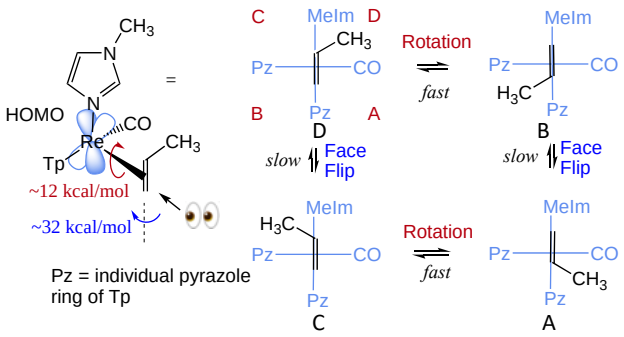


Figure 3.4: The four diastereomers of the rhenium propene complex ReTp(CO)(MeIm)(η^2-propene).

Propene complexes for both the molybdenum (**14A**-**D**) and tungsten (**15A**-**D**) systems were modeled using DFT (calculations of the complexes used B3LYP method. The tungsten used the SDD basis set. The molybdenum system used a hybrid basis set, where the metal used the LZNL2DZ set and all other molecules used 6-31 G(d)). Of the four diastereomers for each system, the isomer placing the methyl group in the C quadrant, **14**/**15** C, is the most unstable (Figure 3.5), owing to steric interactions with the pyrazole ligand trans to the NO. For the tungsten system, steric interactions in the C quadrant are compounded by the PMe_3 group (5 kcal/mol calculated for tungsten vs. 2.7 kcal/mol calculated for the molybdenum). For both systems, the three remaining isomers are of similar energy, thus plans to synthesize these compounds were ceased as there does not appear to be a thermodynamically dominant isomer like there is in the case of [ReCp(NO)(PPh_3)(η^2-propene)]$^+$.[15, 17] Nonetheless, these modeling studies verify the general steric profile for the W and Mo systems as being similar to their ReTp(CO)(MeIm)(η^2-propene) predecessor.[16]

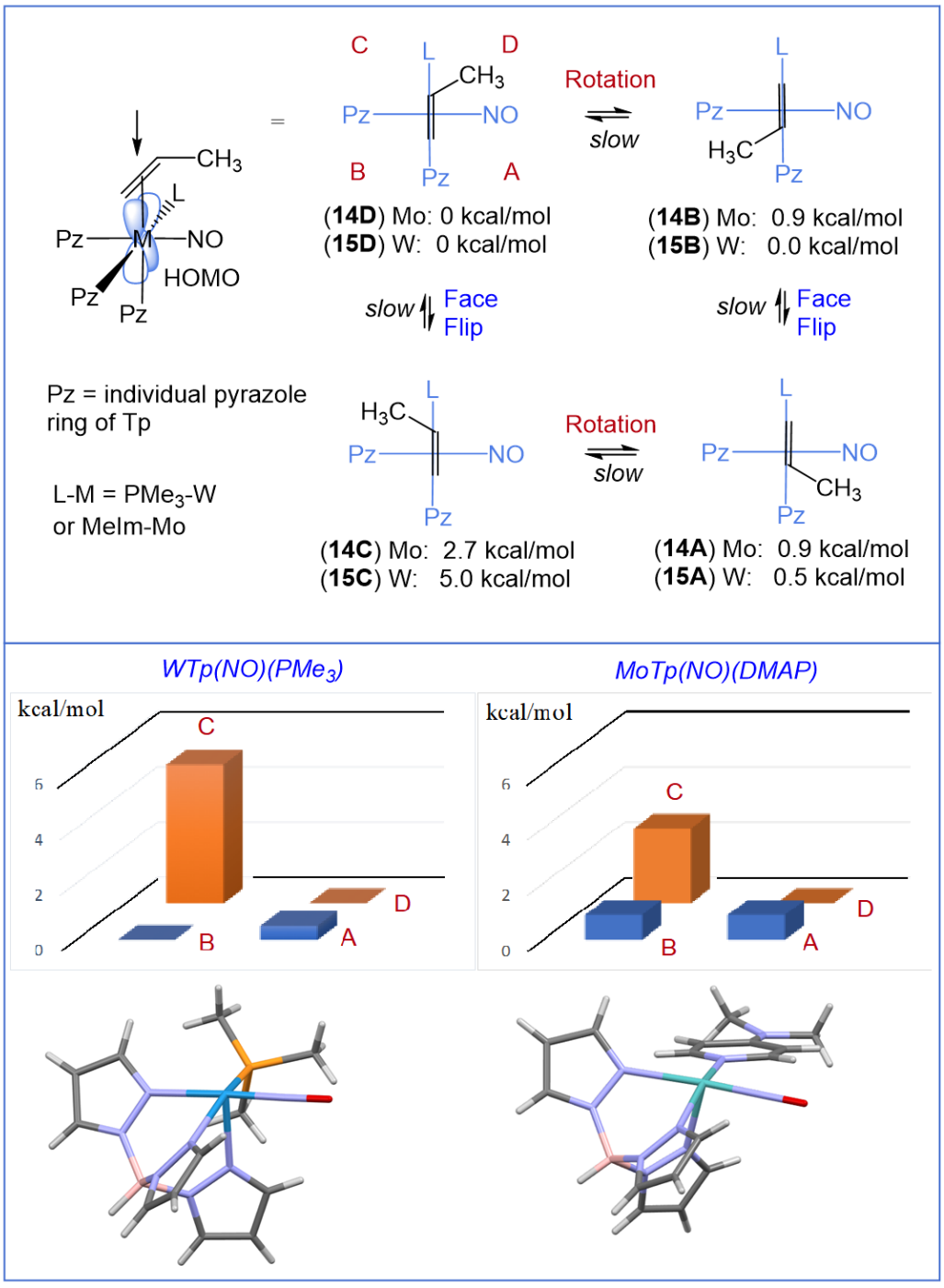


Figure 3.5: Relative energies for the four diastereomers of group 6 propene complexes and the methyl steric profiles for MoTp(NO)(DMAP)(η^2-propene) and WTp(NO)(PMe_3)(η^2-propene).

3.2.2: *Trans*-3-hexene: "face-flip" isomerization

The hydrocarbon *trans*-3-hexene was chosen as a test case in which only two (face-flip) diastereomers were possible, as rotation about the metal-π bond does not generate a unique isomer. Further, it appeared that only one of these isomers avoids placing an ethyl group in the C quadrant, and thus, this isomer should be thermodynamically dominant. The {MoTp(NO)(DMAP)} synthon[18] MoTp(NO)(DMAP)(η^2-α, α, α-trifluorotoluene) was dissolved in THF along with an excess of 3-hexene and allowed to mix. An NMR spectrum taken of the crude reaction mixture reveals the kinetic ratio is close to 1:1. The resulting complex hexene complex **16** was isolated by precipitation into pentanes (experimental) after chromatography in moderate yield (55%) as a mixture of diastereomers with **16A**:**16B** ratios varying from 1:1 to 2:1, depending on the extent of precipitation. A similar process was used to prepare the tungsten complex **17**, this time using the {WTp(NO)(PMe_3)} synthon WTp(NO)(PMe_3)(η^2-benzene).[19] In contrast to its molybdenum congener, initial precipitation (pentane) from the reaction solution yielded only isomer **17B**. Isolation of **17A** required additional repeats of the pentane precipitation steps to isolate. A ^{31}P NMR spectrum indicated that **17A** and **17B** were formed in the reaction in a 1:1 ratio, and therefore the apparent preference for **17B** in the isolated solid is attributed to solubility differences between the two diastereomers. Structural assignments for **16A**, **16B**, **17A**, and **17B** were made on the basis of NOESY and COSY data, and the upfield shift of the bound alkene proton in quadrant **B**, (~1.8 ppm) which resides in a pocket flanked by pyrazole rings (Figure 3.5). Similar to that observed for rhenium,[16, 20] kinetic ratios of prochiral alkene complexes with these Mo and W systems (1:1 for the trans-hexene) tend to be significantly lower than the thermodynamic ratios (>30:1) (vide infra).

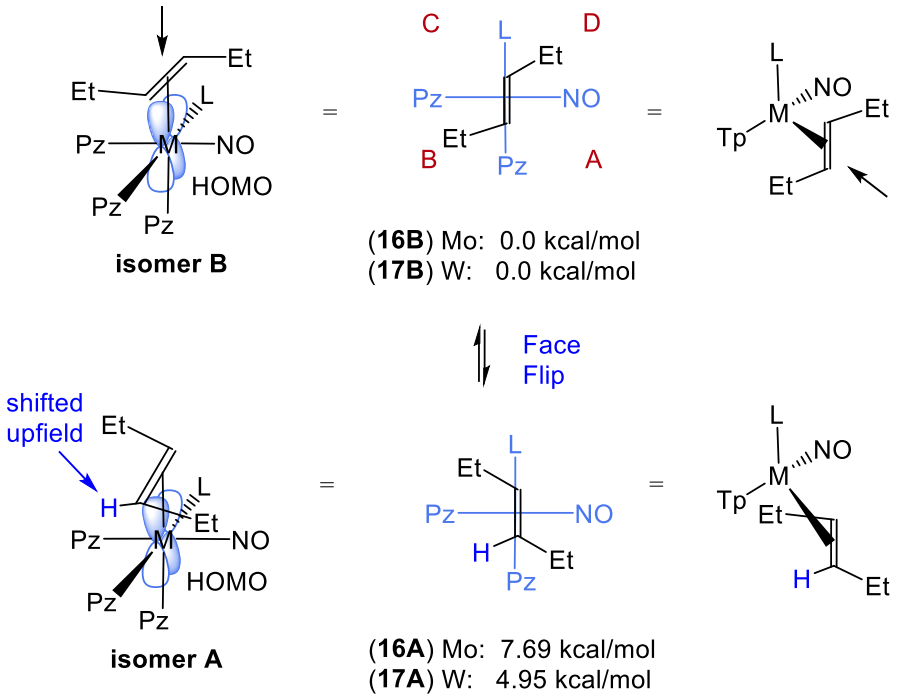


Figure 3.6: The relative energies (calculated) for the two diastereomers of the trans-3-hexene complexes **3** and **4** shown from different perspectives (used herein).

As a control, a 2:1 mixture (**16A**:**16B**) of the molybdenum hexene complex was dissolved in acetone-d_6 and allowed to stand. Over the course of several days, ^{1}H NMR spectra reveal a gradual loss in the signals corresponding to **16A** ($t_{1/2}$ ~ 4 d). However, this was accompanied by the formation of a significant amount of the acetone complex **3**. From the available data, we could not determine how much isomerization occurred over this timeframe, compared to **16** ligand exchange to **3**. Repeating this reaction in acetone-d_6 with an internal standard (DMF-d_7) resulted in almost no change in the ratio of isomers that were detected after 72 hours at 25 °C.

The hypothesis that we aimed to test was that addition of an additive that could decrease electron density at the metal could hasten the isomerization from one face of the hexene ligand to the other. We envisioned this could be accomplished either by interaction of the basic nitrosyl ligand, or by transient oxidation of the metal (Figure 3.7). Reagents that function as oxidants often also function as Lewis Acids

and vice-versa. Metallocene salts were used as oxidants while fluorinated alcohols were tested as Lewis acids.

In choosing a catalytic oxidant, we needed a moiety that would be incapable of stoichiometrically oxidizing the molybdenum. A cyclic voltammogram of the **16A**/**16B** mixture in DMA shows a single anodic wave at 32 mV (vs. NHE). Upon return scan, the only cathodic peak present is one at -1200 mV, corresponding to the DMA complex [MoTp(NO)(DMAP)(κ^1- *O*-DMA)]$^+$. This compound was verified by its independent synthesis and crystal structure (chapter 4). Permethylferrocenium (E = 0.04 V, NHE) has a potential near **16** and cobaltocenium (E = -0.78 V, NHE) has a potential more negative of **16**. In both cases the potential should allow for a small quantity of the oxidized form of the alkene complex **16A**$^+$ to be present. We found that both were capable of promoting the isomerization, but as expected, the higher the potential, the more rapid the isomerization ($T_{1/2}$ $FeCp_2^{*+}$ ~ 1 hour (25^{o}C, 11 mM, 0.2 eq), $T_{1/2}$ $CoCp_2^+$ ~4 hours (25^{o}C, 85 mM, 0.43 eq)). As shown in Figure 3.7, addition of only 0.25 eq (11 mM) of permethylferrocenium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (BArF) allows for complete conversion of the mixture of **16** to only **16B** in less than 3 h ($t_{1/2}$ ~40 min). Earlier examples of redox-promoted linkage isomerizations have mostly involved sigma-bound heteroatoms.[21-24]

Addition of a Lewis acid, or even strong H-donor solvent, was also found to accelerate the isomerization of the hexene coordination diastereomers (**16A** to **16B**; Figure 3.7). For example, a solution containing 0.28 M of the fluorinated alcohol 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP) allows for similar conversion rate ($t_{1/2}$ ~ 40 min) with only minimal formation (5%) of the acetone complex **3**. Similar behavior was seen with nonafluoro-t-butanol. Lewis acids, like BF_3 and $Zn(OTf)_2$ (0.1 eq), also resulted in catalysis for the isomerization on a similar timescale, but were accompanied by significant decomposition as determined by presence of large amounts of free trans-3-hexene by ^{1}H NMR.

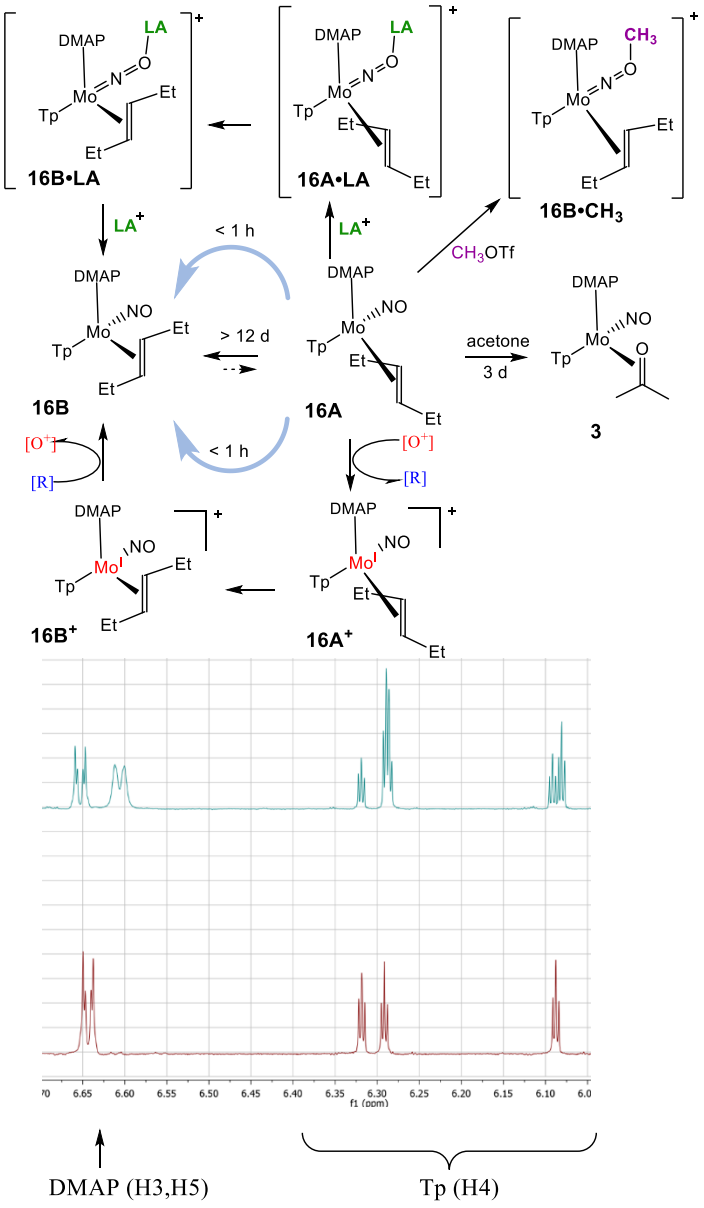


Figure 3.7: The acceleration of the isomerization of **16A** to **16B** without formation of acetone complex using either Lewis acid (LA) or redox catalyst [O$^+$]. Inset: ^{1}H NMR of starting mixture 3A/3B and after addition of [FeCp*$_2$](BArF) (only **16B**).

In order to support the notion that the Lewis acid coordinates to the nitrosyl group, we next attempted a reaction in which the methylating agent CH_3OTf was added to a solution of **16A** and **16B** in a deuterated solvent. Within minutes, an ^{1}H NMR spectrum was taken that showed complete conversion

to a single isomer with concomitant methylation of the nitrosyl group. While we were unable to determine the sequence of these two events, a signal at 4.11 ppm integrating to 3 protons and a full set of hexene signals shifted downfield support the formation of **16B•CH$_3$** (Figure 3.7).[25] While there is decomposition associated with methyl triflate addition, there is about a 65% NMR yield of the methylated analog to 3B.

Guided by DFT calculations, the mechanism for the transformation has been postulated to occur via two possible pathways. The first pathway proceeds through a weakly coordinated hydrogen sigma complex (Figure 3.8a) which lies 58 kcal/mol above the ground state. The second, at 55 kcal/mol above the ground state, consists of an oxidative addition into one of the alkene C-H bonds (Figure 3.8b). Both these pathways are at least 6 kcal lower than complete dissociation.

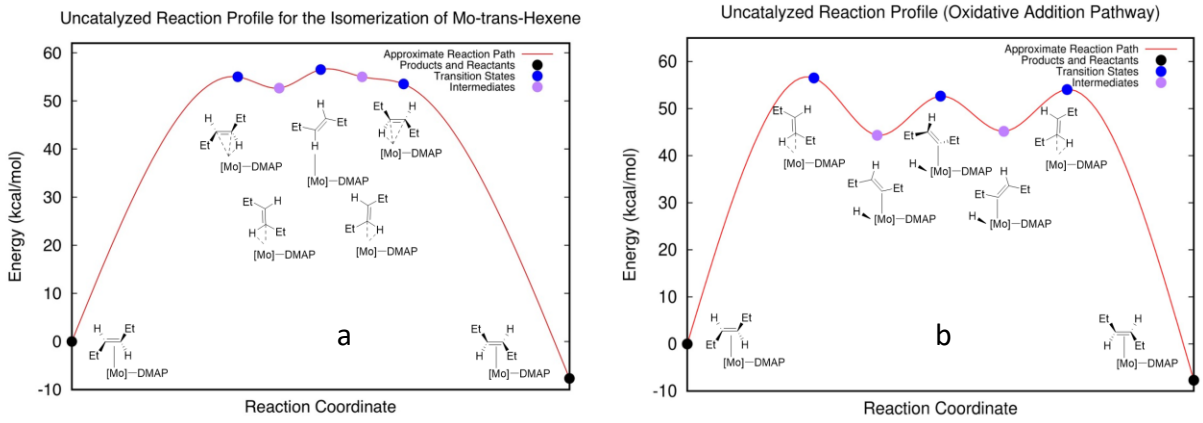


Figure 3.8: Reaction Coordinate diagram for the two possible face-flip isomerization of Mo(0)-trans-hexene complex **16A** and **16B**. a: The isomerization via a hydrogen sigma complex. b: The isomerization via an oxidative addition into a C-H bond.

When one electron is removed, the reaction pathway energy barrier drops to 27 kcal/mol. The sigma transition state complex (Figure 3.9) mimics the first purported reaction pathway (Figure 3.8a), but the barrier to isomerization has dropped by half. The decrease in calculated activation energy is supported by the decreased half-life of isomerization (vide supra).

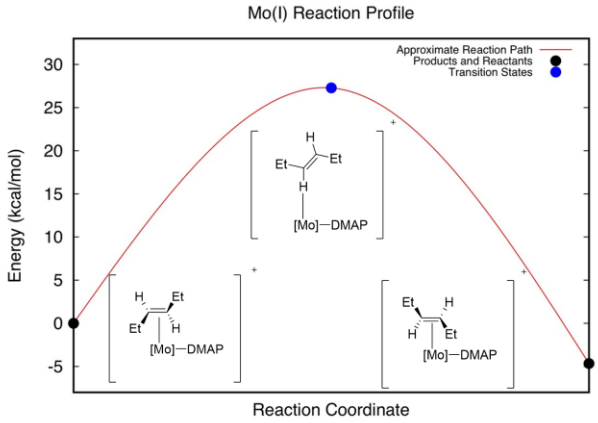


Figure 3.9: Reaction Coordinate diagram for the face-flip isomerization of Mo(I)-trans-hexene complex **16A** and **16B**.

The tungsten version of the 3-hexene complex acts differently from the molybdenum analog. As a contrast to the apparent single E_{pa} of **16A** and **16B**, the E_{pa} for **17A** is more negative than the $E_{1/2}$ for **17B** (**17A**: E_{pa}: 180 mV, 17**B**: $E_{1/2}$: 294 mV). In addition, when isolated **17A** is oxidized during the course of a CV, **17B** is generated in situ. Oxidation of isolated **17B**, in contrast, gives no generation of **17A**. In theory, the generation of **17B** by CV oxidation proves that the oxidation of **17A** can cause conversion to the more stable product. Attempts to catalytically isomerize or methylate **17A** exactly like **16A** all lead to failure. Use of small amounts of metallocene salts (~0.1 eq), multiple equivalents of fluorinated alcohols, (>~5 eq) or methyl triflate all lead to the same 1:1 mixture of products, with only slight deviation. Addition of a full equivalent of a stronger oxidant, like ferrocenium, removes all trace of **17**. Use of half an equivalent of permethylferrocenium relative to **17A** allows for full conversion to **17B** within 30 seconds of catalyst addition (Figure 3.10) with little decomposition (<5%). It appears that this isomerization is catalytic with clean conversion of the unstable **17A** isomer to the more stable **17B**.

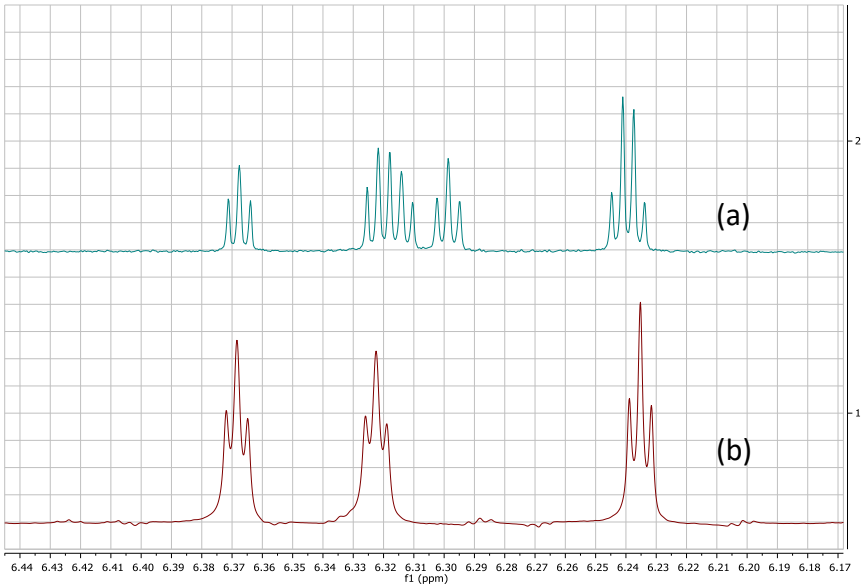


Figure 3.10: The initial 1:1 mixture of the diastereomers of **17** (a) and the resolution of only **17B** by permethylferrocenium(b).

3.2.3: 1,3-Cyclohexadienes: constitutional isomerization for conjugated dienes

Previously, we have reported that both {MoTp(NO)(DMAP)} and {WTp(NO)(PMe_3)} react with 1,3-cyclohexadiene to form multiple diastereomers (Figure 3.11 **A** through **D**). Through a process of protonation to form the π-allyl complex followed by deprotonation, the diene isomer **A** can be selectively prepared for both metal systems.[26-27]

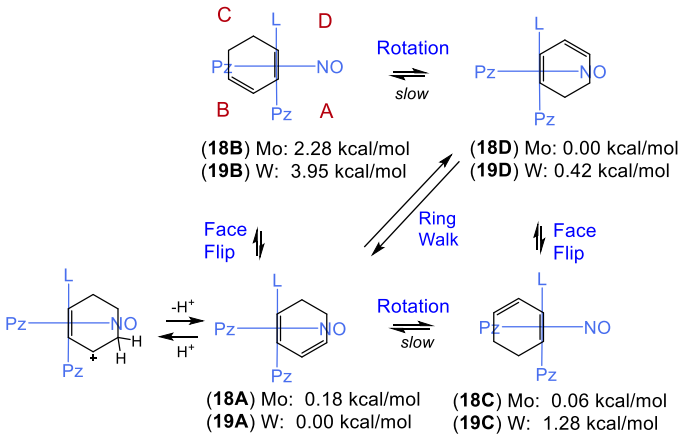


Figure 3.11: Cyclohexadiene complex diastereomers of molybdenum (**18**) and tungsten (**19**) with various isomerization mechanisms.

We envisioned a process in which a "ring-walk" (intrafacial isomerization) from **D** to **A** could be accomplished via a redox-catalyzed mechanism similar to the face-flip (interfacial isomerization) described above. For the tungsten system, DFT calculations identify an η^4-diene transition state (**19**$^{+}$*****; Figure 3.12) on the reaction coordinate between the two η^2-diene isomers for the W(I) complex $[WTp(NO)(PMe_3)(\eta^2\text{-}1,3\text{-cyclohexadiene})]^+$ (**19A**$^+$ and **19B**$^+$) that is roughly 12 kcal above the ground state **7A**$^+$.

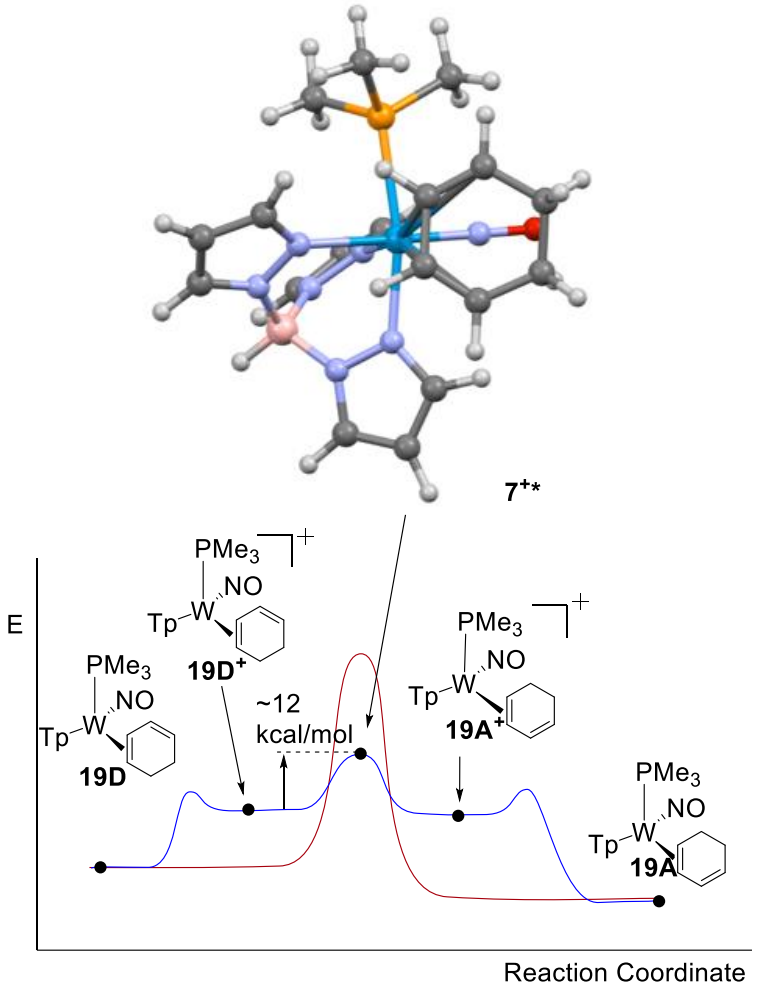


Figure 3.12: Energy barriers for intrafacial isomerization of a 1,3-substituted cyclohexadiene.

Unfortunately, DFT studies reveal that the two diastereomers A and D are virtually isoergic, regardless of metal, and therefore the parent 1,3-cyclohexadiene lacks the thermodynamic driving force needed to test our hypothesis. Furthermore, the interconversion of A and D isomers could occur via a combination of face-flip (interfacial isomerization) and rotation, rather than the intended "ring-walk" (Figure 3.12). Thus, we opted instead to investigate the substituted cyclohexadiene complex **20**, which could be prepared solely as its kinetic isomer (**20A**) from benzene.[25] The *3,4*-η^2-diene complex **8A** was determined to be roughly 2.5 kcal/mol less stable than its *1,2*-η^{2}isomer **20B**. This linkage isomerization

was accomplished with 0.1 equivalent of the mild oxidant ([Fe(Cp^*)$_2$] (Tf_2N)). Complex **20A** has an $E_{p,a}$ = 0.54 V, whereas the permethylferrocenium cation has a Fe(III)/Fe(II) couple with an $E_{1/2}$ = +0.04 V (DMA). Of note, stirring a solution of **20A** in air also effected the isomerization of **20A** to **20B** (Figure 3.13). An X-ray molecular structure determination of a single crystal of **20B** provided confirmation of the purported isomerization.[25] In contrast to that observed for molybdenum, the action of HFIP did not have a noticeable effect on the isomerization, nor did cobaltocenium bistriflimide. Of note, aside from these group 6 complexes, dihapto-coordinated 1,3-diene complexes remain uncommon.[28-29]

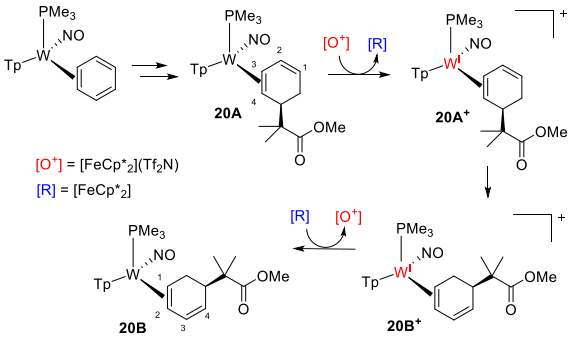


Figure 3.13.: Redox-catalyzed intrafacial isomerization of a 1,3-substituted cyclohexadiene.

3.2.4: *(R)*-Limonene: an unconjugated diene

The monoterpene (*R*)-limonene provides an example of a diene in which the two alkene binding sites are distinct and unconjugated. Further, the terpene is chiral and obtainable in high ee (98 % from Sigma-Aldrich). In total, 16 different isomers are possible (Figure 3.14). Of these, 10 can be considered thermodynamically unstable, as they have a carbon extending into the C quadrant (red, Figure 3.14). Based on DFT calculations, another four isomers (in orange) are between 2-4 kcal/mol destabilized, compared to the two most stable isomers (in green). Both low-energy isomers have the methyl group extending into quadrant A and the cyclohexene ring extending into quadrant B. Correspondingly, their energies differ by less than 0.1 kcal/mol for molybdenum and 0.2 kcal/mol for tungsten.

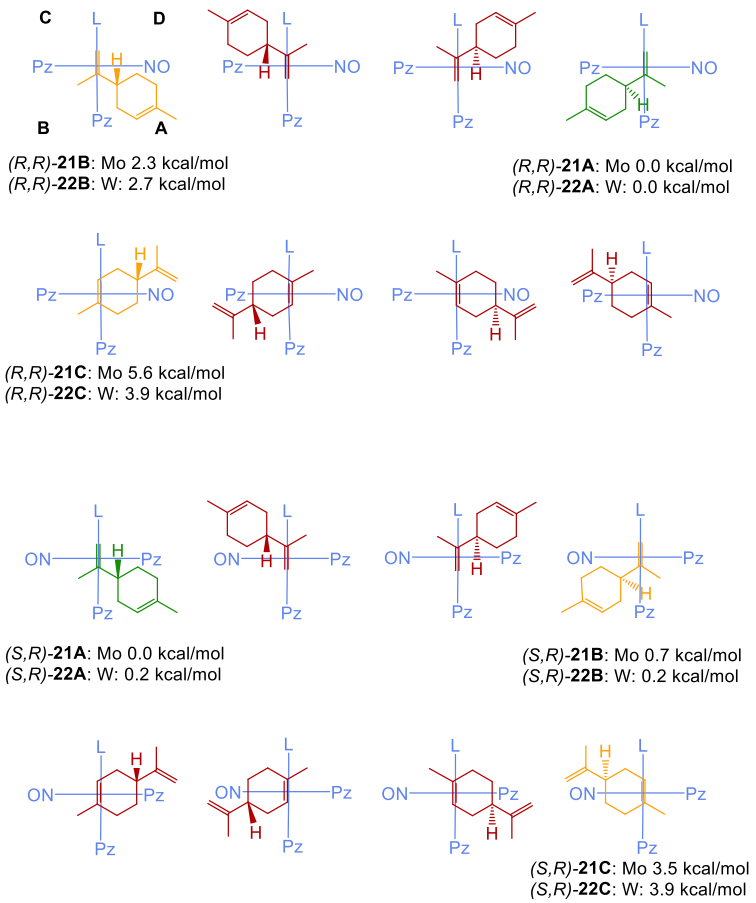


Figure 3.14: Sixteen possible isomers shown for the limonene complexes (**21** and **22**).

When the molybdenum limonene complex was synthesized from a racemic metal source such as MoTp(NO)(DMAP)(η^2-TFT) or reduction of MoTp(NO)(DMAP)(I), multiple pairs of diamagnetic complexes were formed according to the NMR spectrum of the isolated product mixture (Figure 3.15,a). We found the Pz4 region of the NMR spectrum (5.9 – 6.4 ppm) to be relatively free of other signals, thus it proved to be a valuable window for determining the number of diamagnetic complexes present in solution. Remarkably, when the complex mixture was treated with 5.5 equivalents of nonafluoro-tert-butyl alcohol (F-^{t}BuOH) or with HFIP in trifluorotoluene, the isomer mixture converged into just two isomers within 45 minutes (Figure 3.15, b). When either MoTp(NO)(DMAP)(η^2-(*R*)- α-pinene) ((*R*,*R*)-**1**) or MoTp(NO)(DMAP)(η^2-(*S*)- α-pinene) ((*S*,*S*)-**1**) was added to (*R*)-limonene with HFIP present, *a single*

major compound (Figure 3.15, c, d) was synthesized, with minor amounts (~10:1) of the other metal diastereomer present, as well as an unknown side product (~20%).

Finally, crystals obtained from the diastereomeric mixture of *(R,R)*-**21A** and *(S,R)*-**21A** were grown and analyzed. The analysis confirmed the postulated structure (Figure 3.16), but showed significant disorder in the limonene ring, owing to it packing in the P-1 space group. Because the P-1 space group requires an inversion center, it also requires both enantiomers of the limonene to be present, which would call into question the validity of the P-1 fitting. Attempts to solve the structure in lower symmetry (P1), required to conserve the *R* stereocenter of the limonene, did not fully resolve the issue of disorder. Our efforts to grow crystals from enantioenriched versions of **21A** via α-pinene complexes (*S*,*S*)-**21** or (*R*,*R*)-**21** resulted in the same P-1 symmetry structure as that prepared from a racemic source of {MoTp(NO)(DMAP)}. Unfortunately, we could not confirm if the same crystal structure is from epimerization of metal stereocenter during crystal growth or if the minor diastereomers was incorporated into crystal growth in a 1:1 ratio. Although we do not think it is likely that the free (*R*)-limonene epimerized under these conditions, it is a possibility that cannot be ruled out.

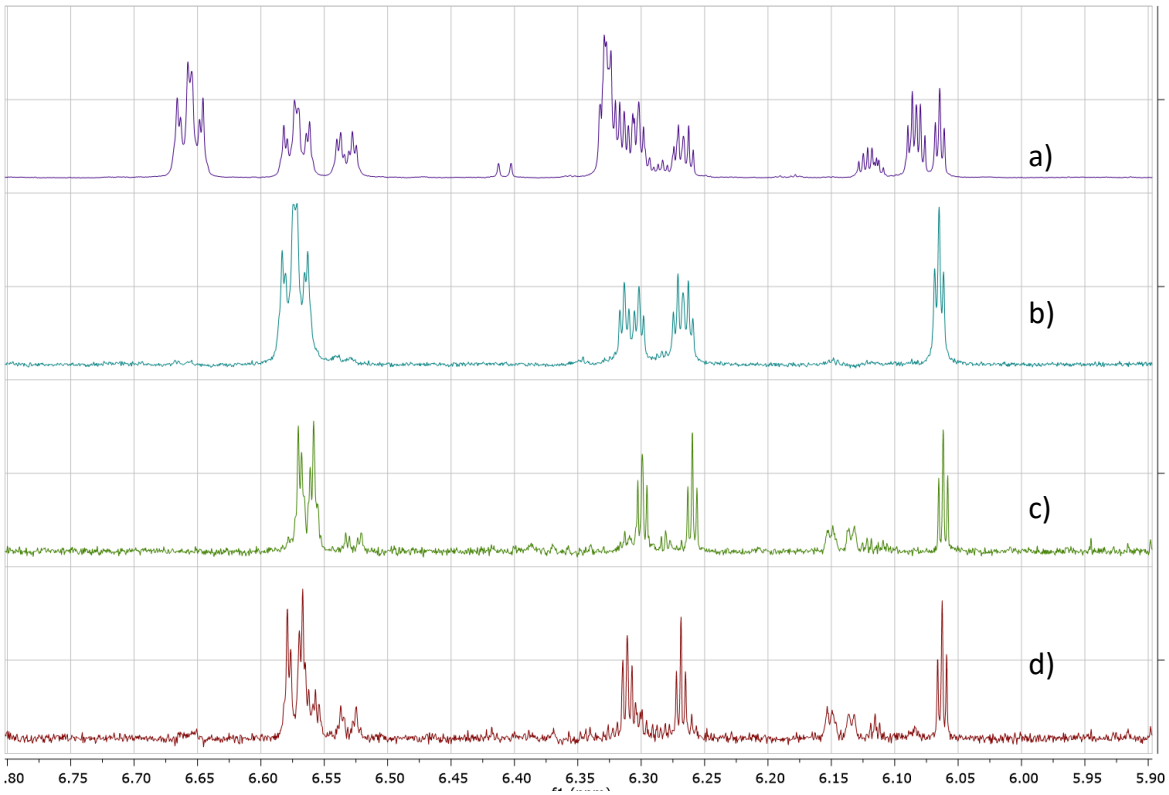


Figure 3.15: NMR data for the Mo-limonene complex **21** showing Tp H4 and DMAP protons for:

a) initial mixture of isomers b) 1:1 mixture of (*S,S*)-**21** and (*R,R*)-**21** redox catalyst addition c) *(S,R)*-**21A,** prepared from *(S,S)*-**1** d) *(R,R)*-**21A,** prepared from *(R,R)*-**1**.

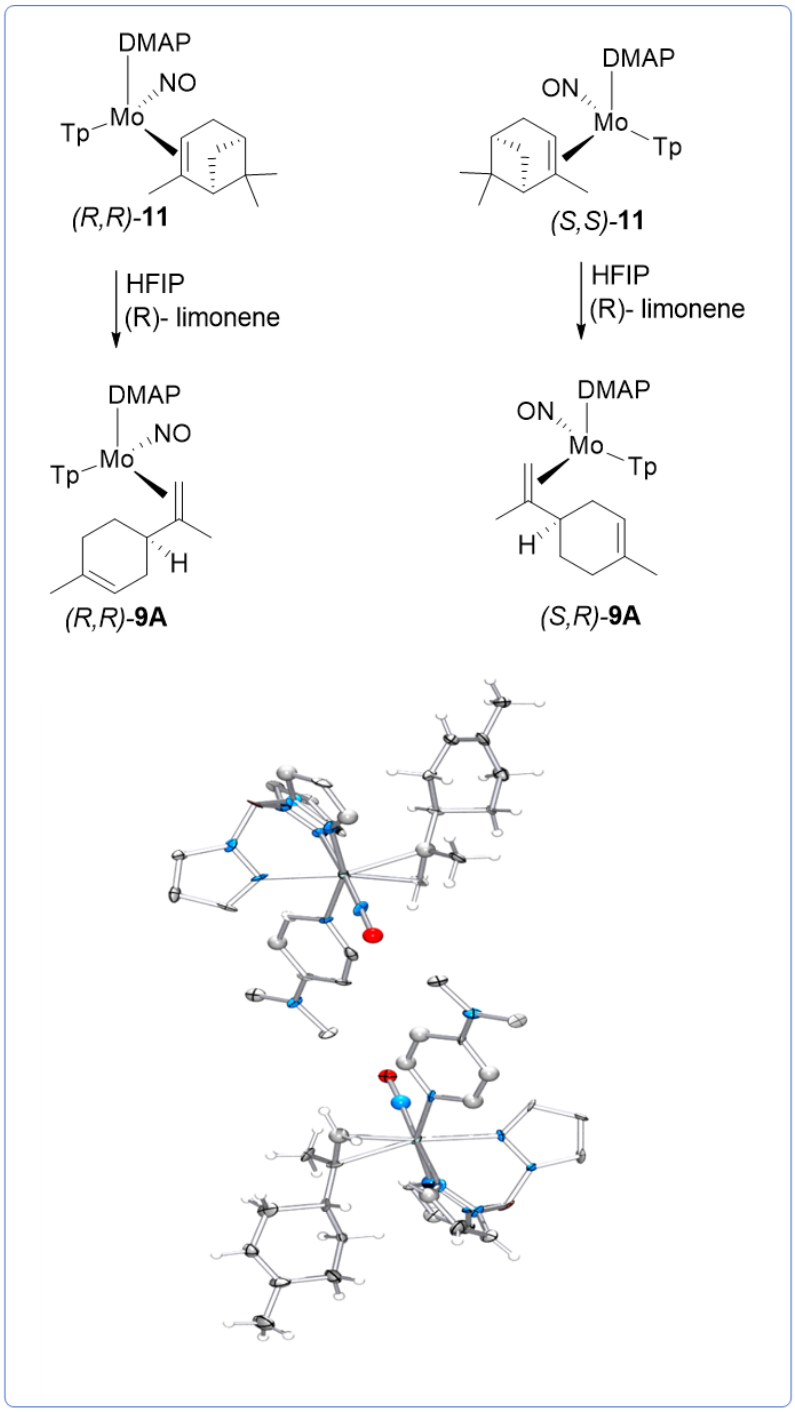


Figure 3.16: *(S,R)*-**9A** prepared from *(S)*-α-pinene, and *(R,R)*-**9A**, prepared from *(R)*-α-pinene, and a solid state structure of a diastereomeric mixture of **9A**.

Combining WTp(NO)(PMe_3)(η^2-benzene) with (*R*)-limonene in DME again results in the formation of multiple isomers (~10 according to ^{31}P NMR spectra). Initial attempts to isolate a solid from the reaction solution caused a selective precipitation of a single diastereomer, *(S,R)*-**22A** (3% mass recovered), the tungsten analog to the molybdenum compound *(S,R)*-**21A**. Further preparations of **22** allowed for a mixture of isomers to be collected. Attempts to isomerize the mixture of 10 isomers using redox catalysts or HFIP, done exactly like **9**, failed to cause the mixture to converge as it did in the molybdenum system. Use of a half equivalent of permethylferrocenium causes reduction to fewer isomers, but still many more diastereomers than were seen with the Mo analog (**21**). Interestingly, small crystals formed from a dilute pentane solution of **22** were shown to be a 1:1 mixture of (*R*,*R*)-**22A** to(*S*,*R*)-**22A**. Since only a few crystals (<5 mg) were made over the course of a month, this preparation is unfortunately not viable for large scale synthesis of the resolved complex.

Only a few limonene complexes have been reported,[30-33] and only in one case was the limonene bound in a dihapto fashion.[30] For the complex MoCp*(NO)(CO)(limonene), a mixture of isomers was reported.[30]

3.2.5: Humulene: an unconjugated triene

The achiral sesquiterpene α-humulene can bind to the metal centers and allows for a racemic mixture of 12 isomers (**23**, **24**) based on the three individual alkene binding sites. These are shown for the R form of the metal fragments in Figure 3.17.

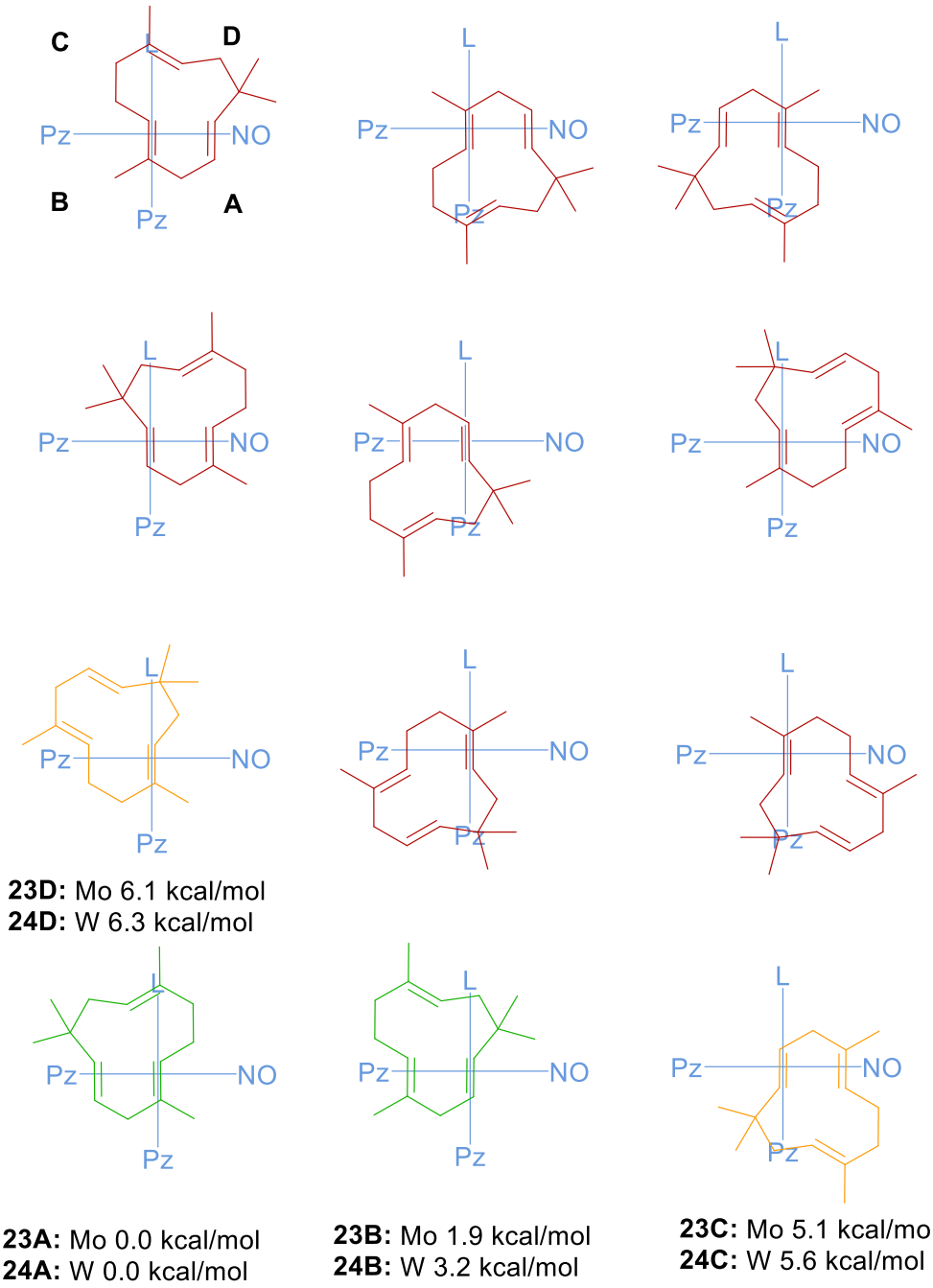


Figure 3.17: The twelve possible isomers possible when humulene binds to the R configuration of either {MoTp(NO)(DMAP)} (**23**) or {WTp(NO)(PMe_3)} (**24**). DFT calculations were carried out on the four lowest energy isomers (isomers with no substituent projecting into the C quadrant).

Of the twelve possible isomers, the four isomers that do not place a substituent into quadrant C were modeled and optimized (yellow, green). These four isomers are shown with their relative calculated energies in Figure 3.17. For both the molybdenum and tungsten systems, isomers A and B were found to be the lowest energy (green).

As expected, when humulene was combined with either MoTp(NO)(DMAP)(η^2-trifluorotoluene) or WTp(NO)(PMe_3)(η^2-benzene), numerous isomers are initially formed. Remarkably, when the molybdenum mixture was precipitated out of solution, isolated, redissolved in trifluorotoluene, and treated with either a metallocene oxidant (permethylferrocenium BArF, 0.25 eq) or fluorinated alcohol (HFIP, >2 eq.), ^{1}H NMR data shows that the number of isomers in solution converges to just one major product (**23A**, Figure 3.18). Two minor complexes, thought to be coordination diastereomers, were detected (~ 5%), as well as a moderate amount of oxidation (~30%).

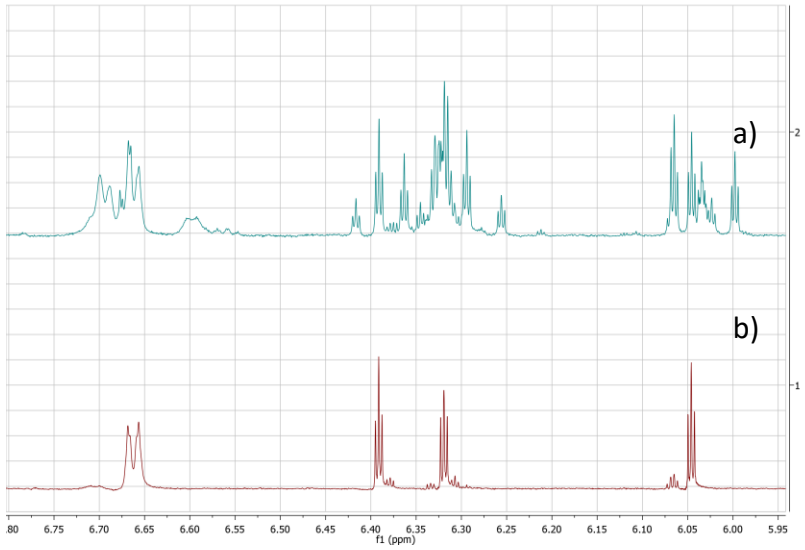


Figure 3.18: Formation of a mixture of isomers of the form MoTp(NO)(DMAP)(η^2-humulene) (**23**) (a) and its conversion to one major isomer (**23A**)(b).

Unfortunately, unambiguous assignment of all of the ring protons, even from a full 2D NMR analysis suite, including COSY, NOESY, HSQC, and HMBC spectra, proved to be difficult. To aid in the characterization of **23**, the initial mixture of the humulene complexes was methylated, analogous to the procedure used for the hexene complex **16**. Since the methylation of the nitrosyl oxygen creates a triflate salt, the complex **23A•CH$_3$** is easier to isolate via precipitation with ether and pentane (~75%). The added methyl group also helped to separate the chemical shifts of the numerous humulene ring protons and facilitated the characterization of the humulene conformation and binding location via 2D NMR data (see Figure 3.19).

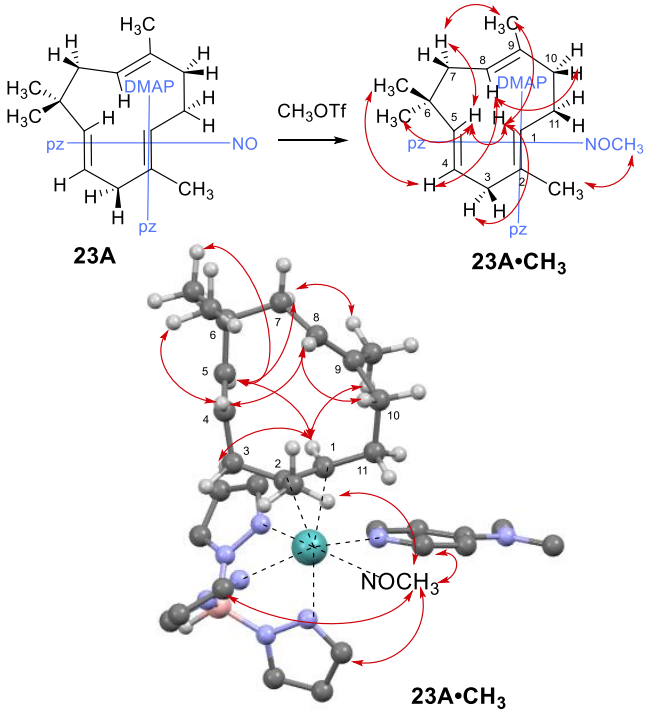


Figure 3.19: The conversion of **12A** MoTp(NO)(DMAP)(η^2-humulene) to its methylated form **12 A•CH$_3$**. DFT simulation of **12** shows a humulene ring conformation consistent with NOESY interactions (red).

The tungsten humulene analog **24** is also formed as a mixture of at least 10 isomers. Precipitation from solution provides an isolated solid, that according to ^{31}P data, still contains approximately the same ratio of isomers. Letting the compound mixture **24** sit in trifluorotoluene for a week does not change the isomer ratio. Like the hexene and limonene, attempts to mirror the Mo isomerization did not cause the resolution of the most stable compound out of the mess of diastereomers. The addition of half of an equivalent of permethylferrocenium allows for resolution to one major compound (Figure 3.20). The single isomer (**24A**) matches the most stable molybdenum structure (**23A**), shown in Figure 3.19. Unfortunately, there is a significant amount of free humulene in the reaction mixture. While it is possible that there is some isomerization present, it appears that most of the simplification of the NMR is due to decomposition of the unstable isomers.

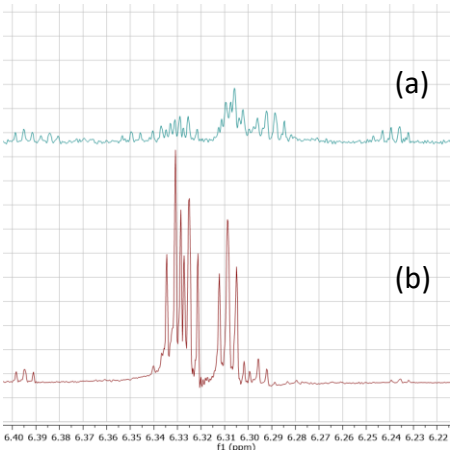


Figure 3.20: Simplification of **24** (a) via permethylferrocenium addition to yield **24A** as the major product (b).

3.2.6: Alkene-to-alkene substitution

In addition to intramolecular isomerization, it was noted that intermolecular alkene-to-alkene exchange can be catalyzed with a fluorinated alcohol. Conversion of the Mo-pinene complex **11** to other alkene complexes normally takes several days to fully exchange if the reaction solution is homogenous.

If the Mo complex is not soluble in solution, the exchange takes far longer. Consider for example cyclopentene, which is incapable of dissolving the molybdenum pinene complex. The addition of THF as a cosolvent creates a homogeneous solution, but substitution still takes several days to complete ($t_{1/2}$ ~ 15 h). However, upon treating a suspension of **1** in neat cyclopentene with a few equivalents of HFIP (0.2 M) or other fluorinated alcohol, the solution becomes homogeneous and the substitution is complete (>99%) in less than 15 minutes. This increase in reaction rate is unfortunately accompanied by a large amount (>50%) of decomposition as indicated by a side product with an $E_{p,a}$ at 250 mV and $E_{1/2}$ at -1800 mV The mechanism that provides this acceleration is thought to be similar to that enabling isomerization, where the HFIP interacts with the NO ligand on the complex, weakening the back bonding interaction with the pinene ligand (Figure 3.21).

Earlier work in our group found that the pinene complex **1** is a good synthon for {MoTp(NO)(DMAP)}, providing access to a broad range of compounds through substitution.[34] However, this substitution is accompanied by complete loss of stereochemical retention. The earlier finding (vide supra) that α-pinene reacted with limonene in the presence of HFIP to provide mostly one diastereomer of the limonene complex (Figure 3.14) suggested that under the influence of HFIP, configurational retention was being achieved at room temperature. We recently reported a method for determining stereochemistry of the Molybdenum system using *(1R)*-myrtenal and a small amount of a redox catalyst.[35] We queried whether this was a general feature of alkene to alkene substitution reactions for the molybdenum system. To test this, we first used the pinene complex **1** to prepare cyclopentene complex **11.** This was followed by a second substitution with *(1R)*-myrtenal. Both substitution reactions were carried out under the influence of HFIP. Remarkably, this one adjustment to the reaction conditions provided a considerable amount of retention in the final product (>30 Mo_R:1 Mo_S stating from 11*R*). Oxidation of the molybdenum was unavoidable, with usually ~10-25% yield of reactions. While we do not fully understand the reason for increased retention of the molybdenum stereocenter, the ligand exchange is thought to be dissociative,[4,]

[35] and that the barrier to isomerization of the purported square-pyramidal intermediate[35] is being raised by action of the HFIP.

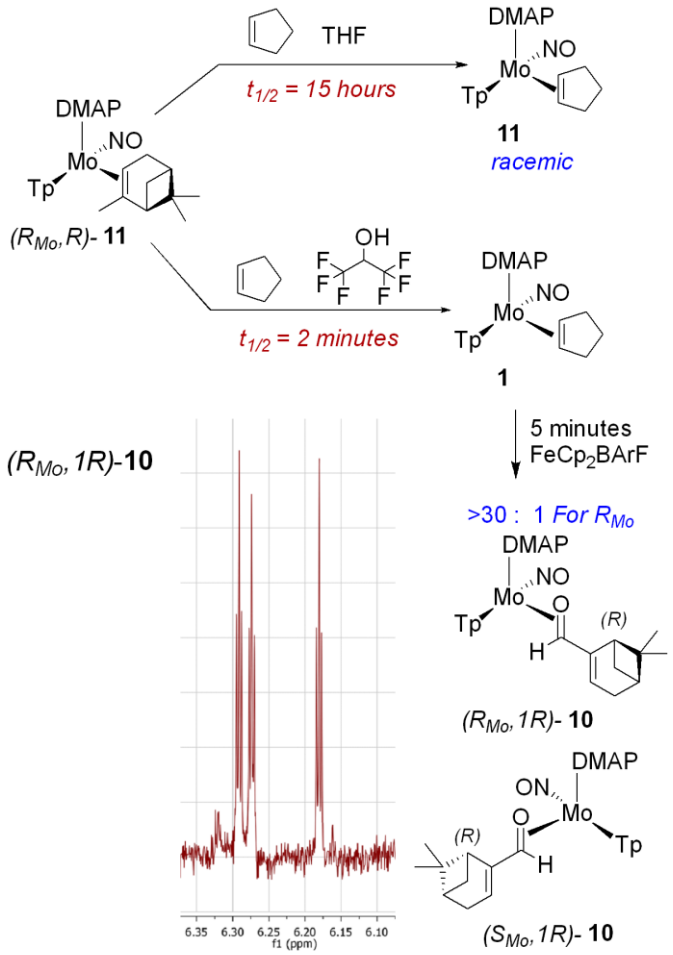


Figure 3.21: The HFIP-promoted substitution of pinene for cyclopentene. The inset NMR is of the myrtenal test[34] done to the enantioenriched **11.**

3.3: Conclusions

The dihapto-coordination afforded by the {MoTp(NO)(DMAP)} and {WTp(NO)(PMe_3)} fragments is a useful tool for dearomatization and organic modifications.[4] With alkene complexes with multiple coordination diastereomers, use of metallocene salts, fluorinated alcohols, and methylating agents was

found to help resolve isomers. In addition, use of the alcohols was found to help promote exchanges to alkene compounds with retention of the molybdenum metal center's enantiopurity.

With these protected terpenes and terpenoids, the next step could follow two different pathways. One is to functionalize the unbound alkene bonds.[25] The other possible route is to hydride abstract from a carbon adjacent to the bound alkene.[36] Further functionalization on terpene cores is an interesting prospect, especially with protection of one alkene by the metal.

3.4: References

1. Zeise, W. C., Von der Wirkung zwischen Platinchlorid und Alkohol, und von den dabei entstehenden neuen Substanzen. *Annalen der Physik* **1831,** *97* (4), 497-541.

2. Hartwig, J. F., *Organotransition metal chemistry : from bonding to catalysis*. 2010.

3. Crabtree, R. H., *The organometallic chemistry of the transition metals*. John Wiley: New York, 2001.

4. Liebov, B. K.; Harman, W. D., Group 6 Dihapto-Coordinate Dearomatization Agents for Organic Synthesis. *Chemical Reviews* **2017,** *117* (22), 13721-13755.

5. Keane, J. M.; Harman, W. D., A New Generation of Pi-Basic Dearomatization Agents. *Organomet.* **2005,** *24*, 1786-1798.

6. Harman, W. D., The Activation of Aromatic Molecules with Pentaammineosmium(II). *Chem. Rev.* **1997,** *97*, 1953-1978.

7. Garnier, E. C.; Liebeskind, L. S., Organometallic enantiomeric scaffolding: general access to 2-substituted oxa- and azabicyclo[3.2.1]octenes via a Brønsted acid catalyzed [5 + 2] cycloaddition reaction. *Journal of the American Chemical Society* **2008,** *130* (23), 7449-7458.

8. Amouri, H., *Chirality in transition metal chemistry : molecules, supramolecular assemblies and materials*. Chichester, U.K. : Wiley, 2008.: 2008.

9. Faller, J. W.; Nguyen, J. T.; Ellis, W.; Mazzieri, M. R., Resolution of CpMo(NO)X(.eta.3-2-methallyl) complexes and their enantioselective reactions with an aldehyde. *Organometallics* **1993,** *12* (4), 1434-1438.

10. Davies, S. G., The Chiral Auxiliary [C5H5Fe(CO)(PPh3)] for Asymmetric Synthesis. *Aldrichchimica Acta* **1990,** *23*, 31-37.

11. Bauer, E. B., Chiral-at-metal complexes and their catalytic applications in organic synthesis. *Chemical Society Reviews* **2012,** *41* (8), 3153-3167.

12. Wong, H.; Garnier-Amblard, E. C.; Liebeskind, L. S., Organometallic Enantiomeric Scaffolding: A Strategy for the Enantiocontrolled Construction of Regio- and Stereodivergent Trisubstituted Piperidines from a Common Precursor. *J. Am. Chem. Soc. 133* (19), 7517-7527.

13. Gladysz, J. A.; Boone, B. J., Chiral Recognition In Pi Complexes of Alkenes, Aldehydes, and Ketones with Transition Metal Lewis-Acids - Development of a General Model For Enantioface Binding Selectivities. *Angew. Chemie. Int. Ed.* **1997,** *36(6)*, 551.

14. Bodner, G. S.; Fernández, J. M.; Arif, A. M.; Gladysz, J. A., Selective Binding of One Enantioface of Monosubstituted Alkenes to the Chiral Transition Metal Lewis Acid $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$. *J. Am. Chem. Soc.* **1988,** *110*, 4082.

15. Bodner, G. S.; Peng, T.-S.; Arif, A. M.; Gladysz, J. A., Synthesis, Structure, and Reactivity of Chiral Rhenium Alkene Complexes of the Formula $[(h^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C = CHR)]^+X^-$. *Organometallics* **1990,** *9*, 1191.

16. Meiere, S. H.; Harman, W. D., Binding Selectivity of Dihapto-Coordinated Olefins, Ketones, and Aldehydes Utilizing the Asymmetric π-Basic Metal Fragment {TpRe(CO)(1-methylimidazole)} (Tp = Hydridotris(pyrazolyl)borate). *Organometallics* **2001,** *20* (18), 3876-3883.

17. Peng, T.-S.; Gladysz, J. A., Mechansim of Equilibration of Diastereomeric Chiral Rhenium Alkene Complexes of the Formula $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C=CHR)]^+BF_4^-$. The Metal Traverses between Alkene Enantiofaces without Dissociation! *J. Am. Chem. Soc.* **1992,** *114*, 4174.

18. Myers, J. T.; Smith, J. A.; Dakermanji, S. J.; Wilde, J. H.; Wilson, K. B.; Shivokevich, P. J.; Harman, W. D., Molybdenum(0) Dihapto-Coordination of Benzene and Trifluorotoluene: The Stabilizing and Chemo-Directing Influence of a CF3 Group. *Journal of the American Chemical Society* **2017,** *139* (33), 11392-11400.

19. Welch, K. D.; Harrison, D. P.; Lis, E. C.; Liu, W.; Salomon, R. J.; Harman, W. D.; Myers, W. H., Large-Scale Syntheses of Several Synthons to the Dearomatization Agent {TpW(NO)(PMe3)} and Convenient Spectroscopic Tools for Product Analysis. *Organometallics* **2007,** *26* (10), 2791-2794.

20. Peng, T.-S.; Pu, J.; Gladysz, J. A., Syntheses and Structures of Unsymmetrically 1,1- and 1,2-Disubstituted Alkene Complexes of the Chiral Rhenium Lewis Acid [(.eta.5-C5H5)Re(NO)(PPh3)]+: Enantioface Binding Selectivities and Conformational Equilibria. *Organometallics* **1994,** *13* (3), 929-940.

21. Tomita, A.; Sano, M., Linkage Isomerizations of (Sulfoxide)ammineruthenium Complexes Induced by Electrochemical Processes. *Inorganic Chemistry* **1994,** *33* (25), 5825-5830.

22. Sano, M.; Taube, H., Molecular hysteresis. *Journal of the American Chemical Society* **1991,** *113* (6), 2327-2328.

23. Harman, W. D.; Sekine, M.; Taube, H., Redox-promoted linkage isomerizations of aldehydes and ketones on pentaammineosmium. *Journal of the American Chemical Society* **1988,** *110* (8), 2439-2445.

24. Harman, W. D.; Taube, H., Redox Coupled Linkage Isomerizations with η^2-Coordinated Anilines. *J. Am. Chem. Soc.* **1988,** *110*, 5403.

25. Wilson, K. B.; Smith, J. A.; Nedzbala, H. S.; Pert, E. K.; Dakermanji, S. J.; Dickie, D. A.; Harman, W. D., Highly Functionalized Cyclohexenes Derived from Benzene: Sequential Tandem Addition Reactions Promoted by Tungsten. *The Journal of Organic Chemistry* **2019**.

26. Harrison, D. P.; Nichols-Nielander, A. C.; Zottig, V. E.; Strausberg, L.; Salomon, R. J.; Trindle, C. O.; Sabat, M.; Gunnoe, T. B.; Iovan, D. A.; Myers, W. H.; Harman, W. D., Hyperdistorted Tungsten Allyl Complexes and Their Stereoselective Deprotonation to Form Dihapto-Coordinated Dienes. *Organometallics* **2011,** *30* (9), 2587-2597.

27. Liu, W.; You, F.; Mocella, C. J.; Harman, W. D., A New Approach to Promoting Sluggish Diels-Alder Reactions: Dihapto-Coordination of the Diene. *J. Am. Chem. Soc.* **2006,** *128* (5), 1426-1427.

28. Peng, T. S.; Wang, Y.; Arif, A. M.; Gladysz, J. A., Synthesis, structure, and reactivity of .eta.2-1,3-diene and enyne complexes of the chiral rhenium Lewis acid [(.eta.5-C5H5)Re(NO)(PPh3)]+: ozonolysis within a metal coordination sphere. *Organometallics* **1993,** *12* (11), 4535-4544.

29. Spera, M. L.; Chin, R. M.; Winemiller, M. D.; Lopez, K. W.; Sabat, M.; Harman, W. D., Sequential Electrophile/Nucleophile Additions for η^2-Cyclopentadiene Complexes of Osmium(II), Ruthenium(II), and Rhenium(I). *Organometallics* **1996,** *15*, 5447.

30. Doetz, K. H.; Lyon, C.; Rott, J., Reactions of complex ligands. XXX. A general route to pentaalkylcyclopentadienyl(carbonyl)(nitrosyl)(olefin) complexes of molybdenum. *J. Organomet. Chem.* **1988,** *345* (1-2), 117-24.

31. Johnson, B. F. G.; Lewis, J.; Yarrow, D. J., Reactivity of coordinated ligands. XVII. (π-Cyclopentadienyl)rhodium complexes of cyclic monoterpenoids. *J. Chem. Soc., Dalton Trans.* **1974,** (10), 1054-8.

32. Ullah, S. S.; Molla, M. E.; Begum, N., Synthesis and reactions of limonenetricarbonyliron. *Indian J. Chem., Sect. A* **1984,** *23A* (12), 992-4.

33. Vekki, D. A.; Uvarov, V. M.; Bel'skii, V. K.; Skvortsov, N. K., Reaction of platinum complexes with (+)-α-pinene and (+)-limonene. Synthesis, molecular structure, and catalytic activity of dichloro(η4-[p-mentha-1,8{9}-diene])platinum(II). *Russ. J. Gen. Chem.* **2006,** *76* (8), 1288-1294.

34. Shivokevich, P. J.; Myers, J. T.; Smith, J. A.; Pienkos, J. A.; Dakermanji, S. J.; Pert, E. K.; Welch, K. D.; Trindle, C. O.; Harman, W. D., Enantioenriched Molybdenum Dearomatization: Dissociative Substitution with Configurational Stability. *Organometallics* **2018,** *37* (23), 4446-4456.

35. Shivokevich, P. J.; Myers, J. T.; Smith, J. A.; Pienkos, J. A.; Dakermanji, S. J.; Pert, E. K.; Welch, K. D.; Trindle, C. O.; Harman, W. D., Enantioenriched Molybdenum Dearomatization: Dissociative Substitution with Configurational Stability. *Organometallics* **2018**.

36. Lis, E. C.; Delafuente, D. A.; Lin, Y.; Mocella, C. J.; Todd, M. A.; Liu, W.; Sabat, M.; Myers, W. H.; Harman, W. D., The Uncommon Reactivity of Dihapto-Coordinated Nitrile, Ketone, and Alkene Ligands When Bound to a Powerful π-Base. *Organometallics* **2006,** *25* (21), 5051-5058.

Chapter 4:
Magnesium Metal Reductions for Dearomatization: Divergent Synthesis of Group 6 Dearomatization Agents

Adapted from a manuscript (in preparation):
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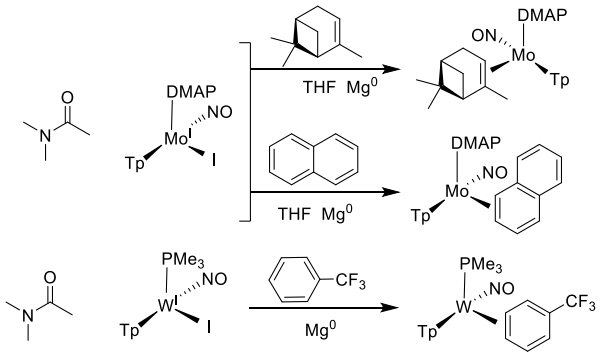
Abstract:

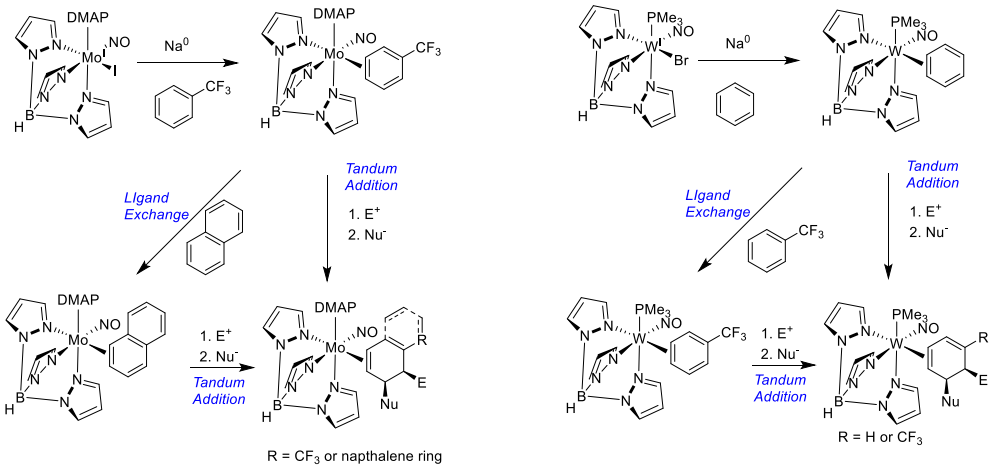


The dearomatization complexes MoTp(NO)(DMAP)(η^2-alkene/aromatic) (where Tp = hydridotris(pyrazolyl)borate and DMAP = 4-(dimethylamino)pyridine) and WTp(NO)(PMe_3)(η^2-alkene/aromatic) have been successfully synthesized using the bench stable reducing agent magnesium instead of sodium metal. The development of said reduction process is described herein. This process is reliant on the presence of N,N-dimethylacetamide (DMA, at least 0.3 eq). The coordination of DMA was found to be necessary for this milder reduction. This is believed to be due to the formation of a transient DMA complex that increases the reduction potential to a more positive voltage through a suspected κ^1/η^2 equilibrium. Utilizing this newly found, sodium free, reduction process, synthesis of MoTp(NO)(DMAP)(η^2-naphthalene) was made on a 17 g scale. This constitutes an approximate 50% increase in yield over the reported sodium reduction with the ability to reclaim the unreacted magnesium for future reductions. Initial findings show this process to be applicable to the synthesis of WTp(NO)(PMe_3)(η^2-PhCF_3) and optimization to scales on par with previous sodium conditions are ongoing (>15 g isolable product).

4.1: Introduction

The negative reduction potential of sodium (~-3 V, standard electrode potential) makes the metal a versatile one-electron donor, which has led to its ubiquitous use in synthetic chemistry. Reactions like acyloin condensation,[1] Bouveault-Blanc reduction,[2] and Wurtz and Wurtz-Fittig reactions[3] all use sodium metal to perform simple organic transformations. The Birch reduction[4] is noteworthy in that it uses sodium in a dearomatization reaction to form functionalized rings from aromatics. Another application for sodium metal in dearomatization is in a one electron reduction to form stable dihapto complexes of aromatic ligands for the electron rich chiral metal scaffolds {MoTp(NO)(DMAP)}[5-7] and {WTp(NO)(PMe_3)}[8] (Figure 4.1). Once the η^2 complexes of type [M]-(η^2-alkene/aromatic) (where [M] is either {MoTp(NO)(DMAP)} or {WTp(NO)(PMe_3)}) are formed, the excess sodium is isolated away from the reaction solution and disposed of (Scheme 4.1).

Since the reduction is the only synthetic step that requires sodium for these metal complexes, ligand exchanges can be done to afford dearomatized products with functional groups that are sodium-incompatible. Complexes of bound aromatics like benzene[9] and trifluorotoluene[5] make labile starting materials (Scheme 4.1). Once these aromatics are dearomatized through a sodium reduction, the labile ligand can be exchanged to other ligands, dearomatizing the second ligand without sodium present. Pyrroles,[10] amines,[11] pyridines,[12] and other normally sodium-reactive ligands can be dearomatized and functionalized this way.



Scheme 4.1: General reaction scheme for one electron reductions of the Mo(I) and W(I) precursors and functionalization of the unsaturated ring.

Initial development of the π-basic pentaammineosmium system, $\{Os(NH_3)_5\}^{2+}$, showed that the reduction to dihapto-coordinated products could be done with magnesium.[13-14] The Os(II) core has the proper electron density to coordinate aromatics (reduction potential ~ 0 V, NHE) in a d^6 metal electron configuration.[15] While developing the molybdenum and tungsten systems, dihapto-coordination at the d^6, M(0) electron configuration was found to require a ligand set that decreases the analogous M(I) reduction potential.[7, 16] Unfortunately, this potential shift pushes the reduction potential of the M(I) species outside the reducing ability of magnesium (~-1.3 V vs NHE, DMA[17]) (vide infra). This necessitated the shift to the harsher sodium reduction conditions.

One benefit of the magnesium reductions over sodium mediated reactions is ligand compatibility. With sodium reductions, phenols,[18] pyridines,[19-20] and ligands containing ketones[5] cannot be bound due to the reduction of the ligand prior to reduction of the metal. As stated before, these ligands can be bound and functionalized through exchanges with the synthetic precursors. Magnesium is able to withstand some functional groups that are incompatible with sodium. Reductions to ketones like acetone can be

done with magnesium (vide infra). In addition, amides like N,N-dimethylacetamide and N,N-dimethylformamide can withstand magnesium, but will react with sodium.[21]

Another benefit is in cost of reaction, magnesium is cheaper than sodium. Based on recent pricing from Sigma-Aldrich, fine magnesium powder (-325 mesh) is approximately $150 for 250 g ($14.59/mol). Sodium dispersion in paraffin can be bought from the same vendor for ~$350 per 500 g (~30 w/t % sodium, 150 g sodium, $53.57/mol). The magnesium is less than a third of the cost per mole. In addition, the magnesium has the ability to reduce two M(I) complexes per metal atom. Even with the increased amount of magnesium used in reductions (vide infra), the ability to recover the magnesium after a reaction allows for recyclability of the magnesium through multiple reductions.

Magnesium has a long history of use as a reducing agent. From Grignards,[22-24] reductive trifluoromethylation,[25] to mixtures of magnesium with methanol for peroxide reductions,[26] reductions with magnesium metal are ubiquitous in chemistry, like sodium.[27-32] The specific use for reductions to achieve dearomatization is limited, but present at least in the $\{Os(NH_3)_5\}^{2+}$ system. [13-14] With a continual effort to improve the sustainability of our research, we sought to develop a synthesis of dearomatization agents, void of pyrophoric reducing agents, with scales matching or exceeding our current capabilities. The goal of this work is to develop a methodology to broadly apply magnesium metal to the one electron reduction of MoTp(NO)(DMAP)(I) or WTp(NO)(PMe_3)(Br) instead of sodium metal.

4.2: Results and Discussion

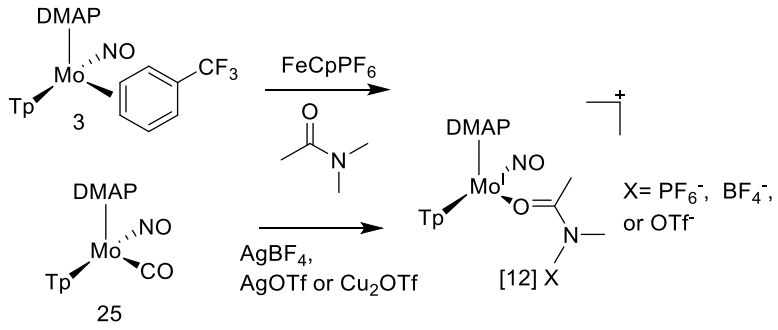
4.2.1: Reductions of the {MoTp(NO)(DMAP)} metal fragment with magnesium

While it was hoped that sodium could simply be substituted with magnesium, this was not the case. Attempts to reduce either MoTp(NO)(DMAP)(I)[7] (**13**) or WTp(NO)(PMe_3)(Br)[9] (**30**) with magnesium

in place of sodium (30 mg **13** or **30**, 60 mg Mg^0 powder, 1 mL TFT) result in no production of the M(0) dihapto-coordinated trifluorotoluene product. The weaker reducing power of the magnesium is simply not able to reduce the halide complexes (~-1350 mV, NHE). In order to accomplish magnesium reductions for our use, alternate synthetic precursors were investigated.

For most dihapto bound compounds of the fragment {MoTp(NO)(DMAP)}, cyclic voltammetry (CV) is an invaluable tool for determination of solution compositions. When DMA is used as the solvent for these experiments, there are repeatable features that appear in CV scans after the after the oxidation of Mo(0)-η^2 arene, alkene, carbonyl or nitrile compounds. An E_{pa} at +900 mV (vs NHE) and $E_{1/2}$ at -1200 mV (vs NHE) are seen after electrochemical oxidation of these complexes with DMA present. Replacement of the DMA for acetonitrile or THF as the CV solvent prevents these signals from growing in. The set of electrochemical responses are purported to be the cation MoTp(NO)(DMAP)(κ^1-O-DMA) ([**12**]$^+$). In order to prove the identity of the Mo(I)-DMA byproduct ([**12**]$^+$), efforts were made to synthesize the complex as an isolated solid. Attempts to isolate Mo(0)-(η^2-DMA) (**12**) by ligand exchange procedures commonly used for the molybdenum system have been unsuccessful, due to instability of diahapto-bound amides.[6] Alternative approaches to prepare stable [MoTp(NO)(DMAP)(κ^1-O-DMA)]$^+$ ([**12**]$^+$) salts were pursued.

Initial oxidations of molybdenum dihapto complexes with ferrocenium hexafluorophosphate ($FeCp_2PF_6$) produced small quantities of the cationic DMA complex [**12**]$^+$. Addition of the oxidant (0.052 g, 0.17 mmol) to a DMA solution of the MoTp(NO)(DMAP)(η^2-trifluorotoluene (TFT)) (**4**) complex (0.10 g, 0.17 mmol, 34 mM) created a complex with a CV signature that matches the previously seen byproduct. Due to the paramagnetic nature of Mo(I) compounds, NMR identification cannot be used. Unfortunately, no crystals of [MoTp(NO)(DMAP)(κ^1-O-DMA)]PF_6 ([**12**] PF_6) suitable for X-ray diffraction were successfully grown for identification.



Scheme 4.2: Synthesis of [MoTp(NO)(DMAP)(κ^1-O-DMA)]X ([**12**] X) from different sources and oxidants.

Alternative methods to make the DMA complex, [**12**]$^+$, from MoTp(NO)(CO)(DMAP) (**25**), a precursor in the synthesis of molybdenum dihapto complexes, were tested. Using silver tetrafluoroborate or triflate as oxidants, clean [MoTp(NO)(DMAP)(κ^1- O-DMA)] BF_4 ([**12**] BF_4) and [MoTp(NO)(DMAP)(κ^1- O-DMA)] OTf ([**12**] OTf) products were obtained in decent yields (48% and 75% yield respectively). The latter can be scaled up to generate 5.2 g of [**12**] OTf. In addition to the silver salt, cheaper copper triflate can be used with similar yield (67%). Both of the complexes synthesized match the CV signatures proposed to be [**12**]$^+$. Crystals of both the triflate and tetrafluoroborate salts of [**12**]$^+$ were grown and characterized (Figure 4.1 and appendix), helping to support the identity of the signals seen in the CV scans.

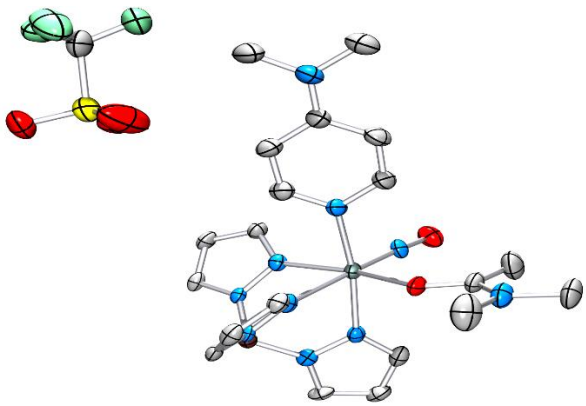
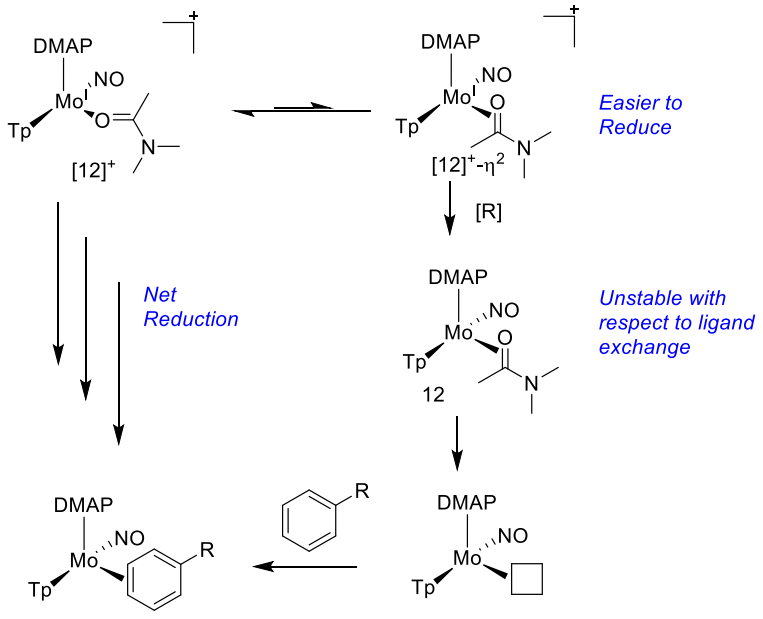


Figure 4.1: Crystal structures of [MoTp(NO)(DMAP)(κ^1-O-DMA)]OTf ([**12**] OTf)

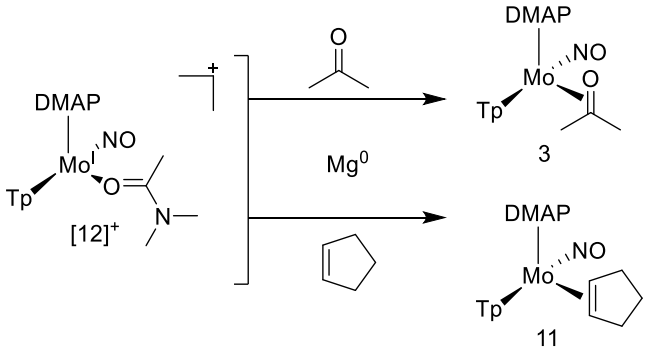
The synthesis of the Mo-DMA salts ([**12**] X, where X is PF_6, BF_4, or OTf) are straightforward. Addition of one equivalent of oxidant to a DMA solution of the CO precursor **25** generates [**12**]$^+$ with a short reaction time (<1 minute) (Scheme 4.2). The isolation, however, is troublesome and inconsistent. Starting with 5 g of **25**, 500 mL or more of precipitating solvent (hexanes, pentane, or diethyl ether) are required to remove the ~5 g of [**12**] X from the DMA reaction solution. Attempts to use water as a precipitating solvent resulted in an intractable mixture. In addition, any precipitation with the DMA present has a high risk of an oil forming instead of a powdered product. As a comparison, the synthesis of the MoTp(NO)(DMAP)(I) complex (**13**), the precursor used for sodium reductions,[5, 7] uses roughly 1 L of diethyl ether for 150 g of product, with little history of oil formation.[7] While scaling up the DMA synthesis might reduce the relative volume of precipitating solvent needed per gram, the volume will likely far exceed that needed for the synthesis of **13**.

With the more positive reduction potential of the Mo(I)-DMA complex ([**12**]$^+$**,** Mo(I/0) $E_{1/2}$= -1270 mV) compared to the iodide precursor **13** (Mo(I/0) $E_{1/2}$= -1430 mV[7]), it was postulated that a weaker reducing agent could afford the same dihapto-bound products as sodium. The thought was based on two separate ideas. The Mo(I/0) reduction potential of [**12**]$^+$ is approximately 150 mV more positive than the reduction potential for the corresponding Mo(I)-iodine complex **13**. The second idea is that there is a slight equilibrium that is formed between the κ^1 and the η^2 forms of metal amide complex ([**12**]$^+$ and [**12**]$^+$-η^2 respectively) in solution (Scheme 4.3). This linkage isomerization is thought to be accompanied by an approximate +1 V shift in reduction potential based on previous Os[33] and current Mo work. The ability to engage in the back-bonding interaction between the metal and ligands allows the η^2 form to become easier to reduce. Once the amide complex is reduced in the η^2 form, the ligand dissociates quickly due to the weak bonding interaction between the Mo(0) center and the amide. This reaction scheme takes advantage of the labile nature of reduced Mo(0)-η^2-DMA complex **12**. The molybdenum center is then able to bind a more stable ligand once the DMA dissociates from the metal.



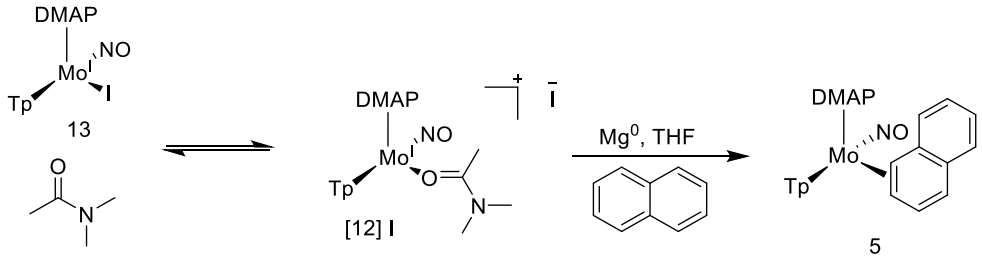
Scheme 4.3: Proposed mechanism for synthesis of Mo(0)-(η^2 products) from Mo-DMA ([**12**]$^+$).

Fine magnesium powder (-325 mesh prior to treatment with iodine or triflic acid, usually two times the mass of Mo(I) used) accomplished the complete conversion of the DMA complex [**12**]$^+$ to MoTp(NO)(DMAP)(η^2-acetone) (**3**)[5] in less than two days according to cyclic voltammetry . A test with cyclopentene (2.5 mL, 25 mmol, 2.9M) in THF (6 mL) with magnesium (1.0 g, cleaned with I_2) generated 0.12 g (60 % yield) of the corresponding MoTp(NO)(DMAP)(η^2-cyclopentene) (**11**) complex (0.25 g [**12**] OTf, 0.36 mmol, 0.42 mM). Comparing the magnesium reduction yield to a sodium reduction to synthesize **11** shows an increase in yield by about 50 %, albeit at a smaller scale (3 g of Mo-iodine (**13**) for a sodium reduction to yield 1.1 g of **11**, 40 % yield vs 0.25 g [**12**] OTf for the magnesium reduction to yield 0.13 g **11**). Small-scale (30 mg [**12**] OTf) experiments to generate the Mo(0) dihapto complexes with trifluorotoluene (**4**), naphthalene (**5**), and α-pinene (**1**) all showed promise and were scaled up (vide infra).



Scheme 4.4: Generation of a reduced Mo(0) species by one electron reduction with a relatively weak metal reducing agent, magnesium.

While investigating other $[MoTp(NO)(DMAP)(DMA)]^+$ ($[\mathbf{12}]^+$) synthesis methods, iodine was used to form a [MoTp(NO)(DMAP)(DMA)] iodide ([**12**] I) salt to directly compare to the standard Mo-iodine complex **13**. Instead of a clean [**12**] I salt, a 1:1 mixture of [**12**] I and **13** formed. Tests with the iodine complex mixture and magnesium saw consumption of both iodine compounds (Scheme 4.5). As stated before, **13** *is not reduced by magnesium metal*. However, addition of DMA (as low as 0.026 mM compared to 82 mM **13**, vide infra) allows for clean conversion of the usually magnesium reduction inert precursor to reduced dihapto complexes (Scheme 4.5).



Scheme 4.5: Proposed equilibrium of the Mo(I) species and reduction of the mixture to stable Mo(0)-η^2-naphthalene (**5**) complex.

Further investigation of the iodine complex mixture showed a possible equilibrium between the two species, [MoTp(NO)(DMAP)(DMA)] iodide ([**12**] I) and MoTp(NO)(DMAP)(I) (**13**). An independent test

of **13** mixing in neat DMA showed formation of [**12**]$^+$ by CV. Exchanges at a Mo(I) oxidation state are possible. Mixing [**12**]$^+$ in DMF causes a complete exchange to the Mo-DMF complex [**8**]$^+$ (seen as an Mo(1/0) $E_{1/2}$ = -1090 mV). Regardless of whether an equilibrium is established or not, some amount of [**12**]$^+$ is generated when **13** is exposed to DMA. To be succinct, the large-scale produced **13** precursor can be used in magnesium reductions through formation of the DMA complex [**12**]$^+$ in situ.

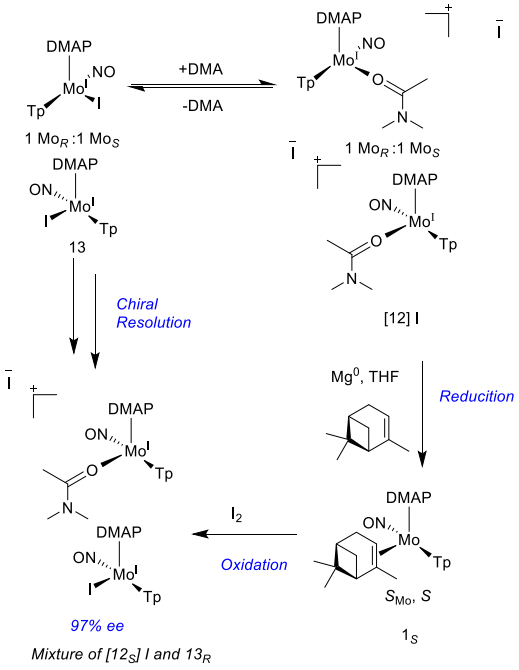
The synthesis of MoTp(NO)(DMAP)(η^2-naphthalene) complex (**5**) (Scheme 4.5) was used as the test case to optimize and scale up the magnesium reduction. The reported sodium reduction starts with 24 g of iodine complex **13** and has a 50 % yield (12 g of **5**).[7] Adapting this reaction to magnesium allowed for a similar large-scale synthesis. The major difference between the two, besides the change in reductant, is the addition of DMA (26 mM in 500 mL THF) to the magnesium reduction. Instead of an equal mass of a 30-35 % w/w Na^0 in paraffin to **13**, twice the mass of **13** in uncleaned magnesium powder (-325 mesh, 48 g magnesium to 24 g of **13**) was used. As a side note, it was found with the molybdenum system, precleaning the magnesium powder was not necessary. Magnesium that had been sitting open to atmospheric air can afford the same reactivity as magnesium powder that had the surface cleaned with either an ether solution of iodine or triflic acid under a nitrogen atmosphere. There is only a qualitative increase in reaction rate with cleaned magnesium over uncleaned magnesium. After a similar work up,[7] the magnesium reaction yielded 70 % product. *This is almost a 50% increase in yield over the sodium reaction with no major changes to the reaction other than use of magnesium and DMA*. In addition, the excess magnesium powder that is used in this reaction could be reclaimed by simply filtering it off prior to work up, allowing for multiple uses of the magnesium powder. To reemphasize an important point: *without the DMA present, no magnesium mediated reduction will occur*.

Efforts to translate the synthesis of the TFT complex MoTp(NO)(DMAP)(η^2-trifluorotoluene) (**4**) from sodium reductions to magnesium proved less than fruitful. The sodium preparation of **4** is heavily influenced by the sodium particles used in the reaction.[34] Under the best conditions with small flecks or

spheres of sodium, the reaction is complete within 16 hours and can yield 37 g of product.[5] The reaction with large flakes of sodium can take 3 days and yield less than 10 g on the same scale. With magnesium, it was hoped that the more uniform particle size would help keep the synthesis consistent. However, the reaction was found to be as inconsistent with magnesium as it was with sodium. Under the best of conditions (3 g iodine complex **13**, ~8 g freshly cleaned magnesium powder, 0.5 M DMA), only about 200 mg of a **4** can be claimed. The isolation of the solid product is also affected heavily by the reaction conditions. With DMA in the reaction solution, the normally insoluble **4** is dissolved. Instead of simply filtering off the solid product and sodium for further purification,[5] the reaction solution was pulled through a silica plug and the product was eluted with 1:1 diethyl ether/THF solution (~400 mL). The resulting filtrate was concentrated and the solid **4** was then precipitated out with pentane. While it is impressive that the labile **4** could be synthesized without the use of sodium metal, the sodium reaction is optimized far better at larger scales. As a result, attempts to scale up the magnesium reduction were suspended. Tests with a lower concentration of DMA might help to change the solubility back to the levels seen in the sodium reductions and might help increase yield. If the labile precursor **4** could be made with magnesium reductions, *all of the molybdenum dihapto-coordinated dearomatization chemistry could, in theory, be done without the need of sodium*.

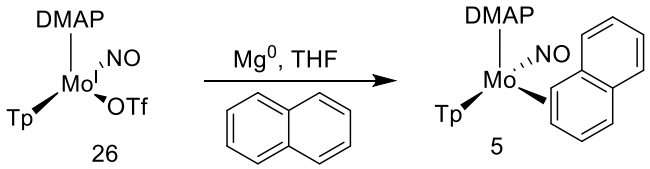
Enantiopure MoTp(NO)(DMAP)(η^2-α-pinene) (**1**) can be formed through a direct sodium reduction from racemic iodine complex **13**.[6] Iodine can then be used to oxidize **1** to form enantioenriched **13**, which can then be reduced at lower temperatures to afford enantiopure aromatic complexes, like the trifluorotoluene complex **4**.[6] *R*-α-pinene can form $\mathbf{1}_R$ which can then become $\mathbf{13}_S$ while *S*-α-pinene forms the other enantiomer with the molybdenum core. This is accomplished currently by two separate reactions, with two separate work-up steps, with about a 40% overall yield.[6] With magnesium reductions, it was hoped that there would be a similar increase in yield to **1** like the large-scale naphthalene reduction. This would subsequently allow for more enantioenriched **13** complex to be made. In addition, it was

hoped that the magnesium reduction and iodine oxidation could be done without isolation between the two reactions (Scheme 4.6). Trying this previously with the sodium reduction would be difficult due to the inconsistent yield of **1**. The inability to measure the amount of reduced Mo complex produced in the sodium reduction precludes accurate addition of the iodine to oxidize the product. With the magnesium reduction, addition of half an equivalent of iodine (I_2) relative to the starting amount of **13** allows for a clean oxidation without significant overoxidation. Due to the residual DMA used in the magnesium reduction to *S*-α-pinene, a mixture of enantioenriched **13**$_R$ and [**12** $_S$] I complexes (>90% ee from 97% ee (*S*)-α-pinene, verified by a myrtenal test from enantioenriched Mo-TFT (**4**) generated from the mixture[6]) can be recovered in about a 45% yield (vide infra). Compared to the two steps of the sodium pathway, *this is an increase of five percentage points with only one work up step*.



Scheme 4.6: Reduction and oxidation of racemic Mo-I (**13**) to form an enantiopure Mo(I) complex mixture ([**12**] I / **13**)

In addition to the use of DMA for magnesium reductions, it was noted that the complex MoTp(NO)(DMAP)(κ ^{1}-OTf) (**26**) could also be reduced with magnesium. The Mo(I/0) reduction of **26** is chemically irreversible by CV at 100 mV/s (E_{pc} = -1400 mV). This indicates that upon reduction, the triflate quickly leaves and is replaced by the CV solvent (DMA), which is seen as the generation of an E_{pa} at -1270 mV (the anodic wave of the $E_{1/2}$ of the [**12**]$^+$) immediately after oxidation of **26**. It is of special note that magnesium reductions of **26** to **5** occur *with or without DMA present* (Scheme 4.7). The reduction potential is more positive than what is reported by the CV because of the faster removal of the triflate. With a possibly much more positive reduction potential, magnesium is strong enough to directly reduce **26** without need to invoke the linkage isomerization mechanism stated above. As of writing this paper, use of **26** as a reduction starting material has not been fully investigated.



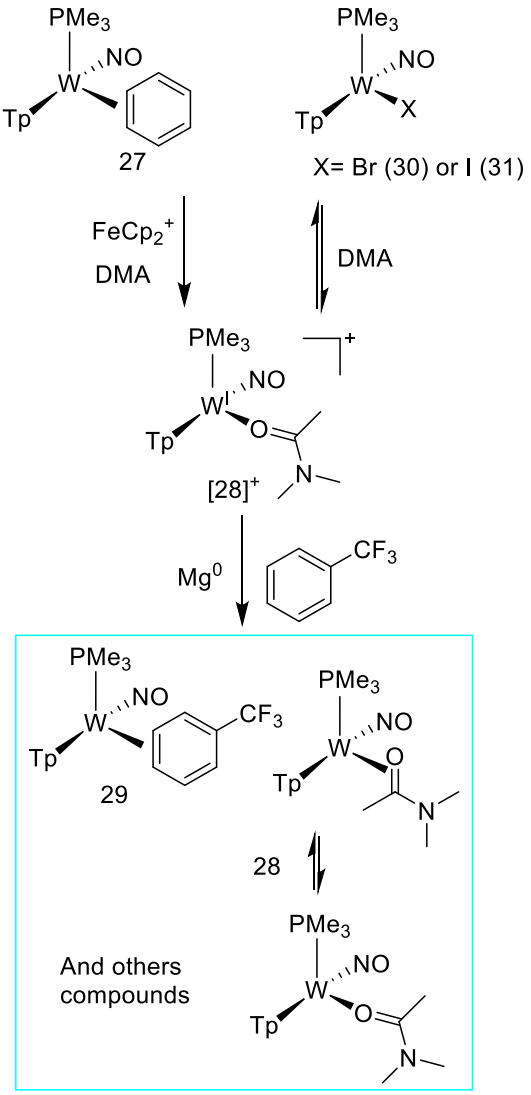
Scheme 4.7: Magnesium reduction of Mo(I)-OTf (**26**) complex in the absence of DMA

4.2.2: Reductions of the {WTp(NO)(PMe$_3$)} metal fragment with magnesium

The alternative to the Mo system, the {WTp(NO)(PMe$_3$)} fragment has an extensive history of dearomatization and further chemical reactivity.[35-38] Initial attempts to apply magnesium to tungsten reductions followed the strategy taken for the molybdenum system. The complex WTp(NO)(PMe$_3$)(η^2-benzene) (**27**) was oxidized with silver triflate in DMA to form (WTp(NO)(PMe$_3$)(κ^1-DMA))OTf ([**28**] OTf, W(I/0) $E_{1/2}$: -1085 mV and W(II/I) E_{pa} : +400 mV). This tungsten DMA complex [**28**] OTf was subjected to a magnesium reduction (2 times the mass of [**28**] OTf in cleaned magnesium powder in neat TFT). As an initial proof of concept, a small quantity of WTp(NO)(PMe$_3$)(η^2-trifluorotoluene) (**29**) complex was formed

from [**28**] OTf (<10% yield). The reaction seemed to stall, with [**28**] OTf never being fully consumed in the reaction solution.

Upon examination of the CV data, it was noted that the tungsten DMA complex seen before work up had in fact been reduced to the W(0)-DMA complex, **28**. The large current uptake at the start of the CV scans and stirring CV scans support this. While the reduction of the oxidized Mo-DMA complex [**12**]$^+$ to the reduced Mo(0)-η^2-DMA complex **12** is the suspected pathway for the molybdenum system, the dissociation of the amide ligand from the W-(0)-η^2-DMA analog **28** is significantly slower than **12**. In the case of **12** and [**12**]$^+$, there is minimal accumulation of the reduced molybdenum form. Instead, the DMA ligand of **12** dissociates and allows binding of the more stable, desired ligand as the reduction is ongoing. The tungsten DMA congener **28** has a relatively slow half-life of exchange (>20 hours). Reduced tungsten DMA complex **28** can be formed from a reduction in neat DMA. After removal of the excess magnesium, addition of trifluorotoluene to the solution of **28** allows exchange to the more stable W-TFT complex **29**, but this exchange proceeds very slowly. After 3-5 days, **28** is still the dominant species by CV. While it might be possible to reduce the tungsten system to form **28** and exchange to a more desirable ligand, the slow overall reaction prevents rapid synthesis of labile synthon complexes.



Scheme 4.8: Production of the W-DMA complex ([**28**]$^+$) and initial attempts at reductions of the [**28**]$^+$ to the W-TFT (**29**) complex in addition to the W(0)-DMA (**28**) complex

One possible method to prevent accumulation of the reduced DMA complex is through use of halide tungsten precursors. Like the molybdenum system, the DMA is important to the overall reduction of the tungsten system, but does not need to be bound initially for the reduction to proceed (Scheme 4.8). There is no reaction, other than decomposition, when WTp(NO)(PMe_3)(X) (where X is Br (**30,** W(I/0) $E_{1/2}$: -1400 mV, W(II/I) E_{pa}: 410 mV) or I (**31**, W(I/0) $E_{1/2}$: -1310 mV, W(II/I) E_{pa}: 410 mV) is mixed with magnesium and TFT. The W-Br complex (**30**) is the standard used for sodium reductions on the tungsten system,[8]

analogous to the Mo-iodine complex **13**. Unfortunately, when **30** is used in a magnesium reduction with TFT *and* DMA present, only **30** and reduced W-DMA complex **28** are present by CV after a week or more of mixing. In fact, CV scans of these reductions lose all signals associated with of **28** and **30** before the peak associated with the TFT product **29** (Epa: +70 mV[8]) appears above the baseline. Use of the tungsten iodine complex **31** in the presence of DMA (~1 M) allows for relatively better magnesium reductions than [**28**]$^+$ or **30**, with cases where little to no reduced DMA complex **28** accumulates over the course of the reduction to **29**.

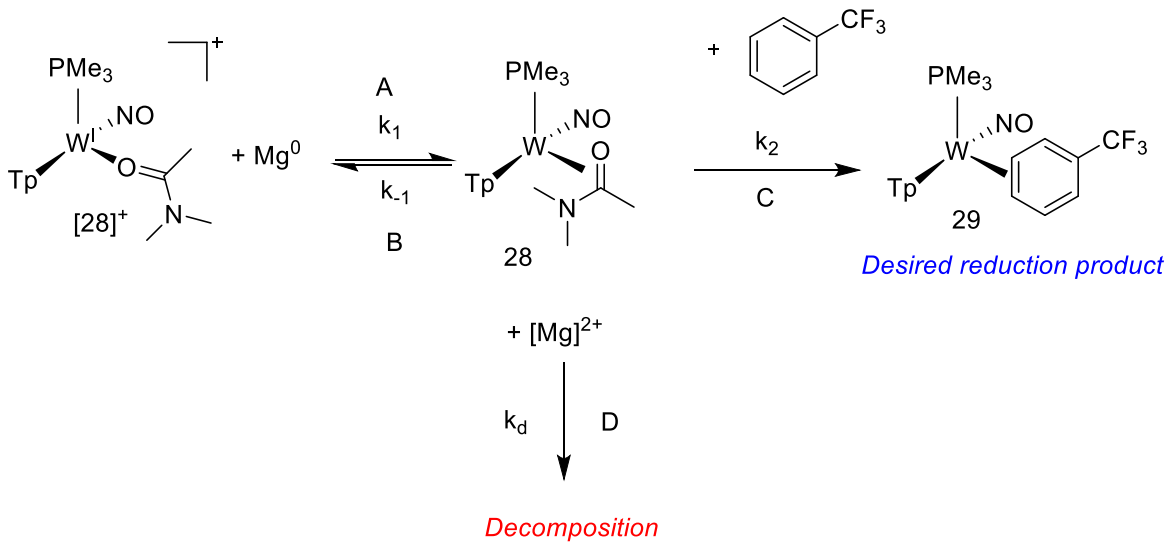
The best conditions shown thus far are very different than what is used with the Mo system. Use of 10 to 20 times the mass of the tungsten iodide complex **31** in uncleaned magnesium and 1 M DMA has been shown to completely eliminate the iodine starting material signals in the CV. If cleaned magnesium (either with I_2 or HOTf in ether) is used, the reaction will almost exclusively generate reduced the DMA complex **28** over the desired W-TFT complex, **29**. Unfortunately, the amount of isolated product is less than 5 % of the theoretical yield. In a reaction with 300 mg of **31**, 3 g of uncleaned magnesium powder, and 1 M DMA in 10 mL of TFT, the reaction appears complete after 5 days, with little to no starting material left by CV. However, only about 10 mg of **29** is able to be isolated from solution. Upon further examination of the CV data of the reaction solution, there is an unexplained E_{pa} at ~+700 mV. The size of this oxidation peak is more than the sum of all the other known tungsten species (**28**, **29**, and **31**) in solution and could possibly be where the vast majority of the missing tungsten is going. As of now, the identity of this peak is not known but it is speculated that it is generated during the reaction and not by oxidation in the CV. The large impurity is removed during work up, but conditions to prevent formation of the unidentified side product have not been found yet.

Other than attempts to synthesize the tungsten trifluorotoluene complex **29**, more labile ligands like benzene, anisole, and dimethoxybenzene were investigated.[9] Again, 10 times the mass of iodine starting material (**31**, 30 mg) in uncleaned magnesium powder (300 mg) was used with 1 M DMA in the

incoming ligand (1 mL of the ligand used as the solvent). While there appears to be a baseline signal of the respective products by CV at early time points (around 24 hours), the slow overall reaction precludes formation of sizable amounts of product prior to decomposition. While the product is formed, the labile nature of the ligand means that it is unstable in solution and will fall apart as the long reduction proceeds. Without the ability to form more stable compounds like **29**, further development of the labile complexes has been halted. If the anisole and benzene complexes could be made from magnesium reductions, *all of the tungsten system's chemistry could be used without sodium*.

Overall, the tungsten magnesium reductions have not been as straightforward as the molybdenum system. Large accumulation of side products, slow reactions, and need for large quantities of magnesium hinder the development of reliable synthesis preparations. There are still a few possible synthetic modifications that can be tested.

As seen with the reduced DMA complexes **12** and **28**, tungsten dihapto complexes have stronger bonding capabilities and longer exchange half-lives than their Mo(0) analogs (e.g. $t_{1/2}$(Mo-TFT, **4**) = 40 mins[5] and $t_{1/2}$(W-TFT, **29**) = 192 h[9] at 25°C). This is due to the third-row transition metal tungsten's higher π basicity relative to the second-row molybdenum, which translates to stronger metal-ligand bonds. The inability of the molybdenum system to form a stable complex with DMA results in a clean exchange of the amide to other desired reduction products. The activation barrier for exchange is assumed to be lower than the molybdenum reduction process (i.e. dissociation of the DMA ligand from **12** is faster than the reduction from [**12**]$^+$ to **12**, Scheme 4.3). It is possible that if the energy barrier to release the DMA at the reduced tungsten oxidation state is higher than the barrier to the initial reduction (i.e. exchanging from **28** to **29** (Scheme 4.9 C, k_2) is slower than reduction of [**28**]$^+$ to **28** (Scheme 4.9 A, k_1)), the reaction will stall and oxidation will become competitive with the final exchange. However, instead of regenerating starting materials (**28** oxidizing back to [**28**]$^+$, Scheme 4.9 B, k_{-1}), the complex instead decomposes to the unknown side product (vide supra, Figure 4.2 D, k_d).



Scheme 4.9: Proposed reaction scheme for reduction of the tungsten system through the DMA complex ([**28**]$^{+}$/**28**) to the TFT complex (**29**).

Lowering the concentration of the magnesium ions in solution could slow the overall rate of decomposition. If the oxidation of the reduced W-DMA complex (**28**) is linked with $[Mg]^{2+}$, then the rates corresponding to k_{-1} and k_d could decrease when the ion is removed from solution. The decreased rate of tungsten oxidation could allow the ligand exchange to be more competitive, possibly pushing the TFT product (**29**) formation to be favorable over decomposition. Addition of ethylenediaminetetraacetic acid (EDTA) or a crown ether could sequester the cation in solution to effectively reduce the concentration. A soluble carbonate or sulfate salt could be added to precipitate out the corresponding insoluble magnesium salt.

Another process that could help is increasing the steric bulk on the amine portion of the amide. Looking at the crystal structures of the Mo-DMA complexes ([**12**]$^{+}$, Figure 4.1 and appendix), it is noted that the orientation of the nitrogen points out over the bulky pyrazole rings of the Tp ligand. When it is reduced to Mo(0)-DMA, it is possible the steric interaction of amine group with the Tp ligand helps to promote the displacement of the ligand. Addition of steric bulk at the carbonyl carbon has been tested

with the molybdenum and tungsten systems. N-Methyl-2-pyrrolidone can be interchanged with DMA with almost no difference in results seen in the reactivity for both metals with DMA. Use of N,N-Dimethylisobutyramide and N,N-dimethylpivalamide in place of the DMA show some promise for the molybdenum system, with baseline generation of the naphthalene complex **5** by CV relative to what appears to be reduced **12** ($E_{1/2}$ ~-1250 mV). Using these two bulky amides with the tungsten system instead shows no generation of products by CV, instead a single unknown $E_{1/2}$ at ~-1270 mV is generated. To reiterate, adding steric bulk to the carbon of the ketone does not help relative to the parent DMA. Adding steric bulk on the amide could allow for the reduction to occur with faster subsequent exchange at the reduced M(0) oxidation state.

Exchanging DMA for N,N-diisopropylacetamide or N,N-ditert-butylacetamide may help with ejection of the ligand at the W(0) state. One concern with this process is that it might yield the same results as increasing the steric bulk on the ketone carbon. It is thought that increasing steric bulk at both sites might decrease the amount of η^2 complex that is in equilibrium with the more stable κ^1 form. With less, or almost none, of the η^2 complex in solution, the reduction, which is speculated to occur on the dihapto form only (vide supra), will not occur.

A third possible option is the use of even weaker reducing agents. Initial tests on the ability to reduce the molybdenum DMA complex [**12**] PF_6 (0.027 g 0.039 mol) to give a dihapto-coordinated product used Zn^0 metal (0.028 g, $E_{1/2}$ = - 500 mV[39]) as the reducing agent in the presence of acetone (d_6, 1 mL) in an attempt to form the molybdenum acetone complex **3**. Over the course of a week, a set of peaks associated with **3** appeared above the noise of a ^{1}H NMR spectrum of the reaction solution. However, the amount of product did not seem to increase after a month. The weaker reducing agent Zn^0 should be tested with reducing the tungsten iodine complex **31** to see if the trifluorotoluene complex **29** can form without significant formation of reduced DMA complex **28** or the unknown side product.

4.3: Conclusions

The development of one electron reductions of metal dearomatization agents with magnesium has been started. The large scale magnesium reduction to generate the MoTp(NO)(DMAP)(η^2-naphthalne) complex has been shown as a preferable alternative to previous sodium metal reductions. A two-step reaction to isolate an enantioenriched Mo(I) precursor has also been found. Initial, small scale success with tungsten metal system, {WTp(NO)(PMe_3)} has been shown, but problems prevent large scale production. Some ideas for possible directions for exploration have been proposed to hopefully fix these issues.

4.4: References

1. Finley, K. T., The Acyloin Condensation as a Cyclization Method. *Chemical Reviews* **1964,** *64* (5), 573-589.

2. An, J.; Work, D. N.; Kenyon, C.; Procter, D. J., Evaluating a Sodium Dispersion Reagent for the Bouveault–Blanc Reduction of Esters. *The Journal of Organic Chemistry* **2014,** *79* (14), 6743-6747.

3. Campbell, J. B.; Dedinas, R. F.; Trumbower-Walsh, S., Preparation of Isoindolones by a Lithium-Iodide Exchange-Induced Intra-molecular Wurtz-Fittig Reaction of o-Iodobenzoyl Chloride/Imine Adducts. *Synlett* **2010,** *2010* (20), 3008-3010.

4. Lei, P.; Ding, Y.; Zhang, X.; Adijiang, A.; Li, H.; Ling, Y.; An, J., A Practical and Chemoselective Ammonia-Free Birch Reduction. *Organic Letters* **2018,** *20* (12), 3439-3442.

5. Myers, J. T.; Smith, J. A.; Dakermanji, S. J.; Wilde, J. H.; Wilson, K. B.; Shivokevich, P. J.; Harman, W. D., Molybdenum(0) Dihapto-Coordination of Benzene and Trifluorotoluene: The Stabilizing and Chemo-Directing Influence of a CF3 Group. *Journal of the American Chemical Society* **2017,** *139* (33), 11392-11400.

6. Shivokevich, P. J.; Myers, J. T.; Smith, J. A.; Pienkos, J. A.; Dakermanji, S. J.; Pert, E. K.; Welch, K. D.; Trindle, C. O.; Harman, W. D., Enantioenriched Molybdenum Dearomatization: Dissociative Substitution with Configurational Stability. *Organometallics* **2018,** *37* (23), 4446-4456.

7. Myers, J. T.; Dakermanji, S. J.; Chastanet, T. R.; Shivokevich, P. J.; Strausberg, L. J.; Sabat, M.; Harman, W. D., 4-(Dimethylamino)pyridine (DMAP) as an Acid-Modulated Donor Ligand for PAH Dearomatization

Organometallics **2017,** *36* (3), 543-555.

8. Ha, Y.; Dilsky, S.; Graham, P. M.; Liu, W.; Reichart, T.; Sabat, M.; Kenae, J. M.; Harman, W. D., Development of Group 6 Dearomatization Agents. *Organometallics* **2006,** *25*, 5184-5187.

9. Welch, K. D.; Harrison, D. P.; Lis, E. C.; Liu, W.; Salomon, R. J.; Harman, W. D.; Myers, W. H., Large-Scale Syntheses of Several Synthons to the Dearomatization Agent {TpW(NO)(PMe3)} and Convenient Spectroscopic Tools for Product Analysis. *Organometallics* **2007,** *26* (10), 2791-2794.

10. Welch, K. D.; Smith, P. L.; Keller, A. P.; Myers, W. H.; Sabat, M.; Harman, W. D., Osmium(II)-, Rhenium(I)-, and Tungsten(0)-Promoted Dipolar Cycloaddition Reactions with Pyrroles: Exploiting the Azomethine Ylide Character of This Heterocycle. *Organometallics* **2006,** *25* (21), 5067-5075.

11. MacLeod, B. L.; Pienkos, J. A.; Myers, J. T.; Sabat, M.; Myers, W. H.; Harman, W. D., Stereoselective Synthesis of trans-Tetrahydroindolines Promoted by a Tungsten π Base. *Organometallics* **2014,** *33* (22), 6286-6289.

12. Delafuente, D. A.; Kosturko, G. W.; Graham, P. M.; Harman, W. H.; Myers, W. H.; Surendranath, Y.; Klet, R. C.; Welch, K. D.; Trindle, C. O.; Sabat, M.; Harman, W. D., Isomerization Dynamics and Control of the η2/N Equilibrium for Pyridine Complexes. *Journal of the American Chemical Society* **2007,** *129* (2), 406-416.

13. Harman, W. D.; Fairlie, D. P.; Taube, H., Synthesis, characterization, and reactivity of the (.eta.2-acetone)pentaammineosmium(II) complex. *Journal of the American Chemical Society* **1986,** *108* (26), 8223-8227.

14. Harman, W. D.; Taube, H., Reactivity of pentaammineosmium(II) with benzene. *Journal of the American Chemical Society* **1987,** *109* (6), 1883-1885.

15. Smith, P. L.; Chordia, M. D.; Harman, W. D., Synthetic Applications of the Dearomatization Agent Pentaammineosmium(II). *Tetrahedron* **2001**, 8203-8225.

16. Liebov, B. K.; Harman, W. D., Group 6 Dihapto-Coordinate Dearomatization Agents for Organic Synthesis. *Chemical Reviews* **2017,** *117* (22), 13721-13755.

17. Lossius, L. P.; Emmenegger, F., Plating of magnesium from organic solvents. *Electrochimica Acta* **1996,** *41* (3), 445-447.

18. Zottig, V. E.; Todd, M. A.; Nichols-Nielander, A. C.; Harrison, D. P.; Sabat, M.; Myers, W. H.; Harman, W. D., Epoxidation, Cyclopropanation, and Electrophilic Addition Reactions at the meta Position of Phenol and meta-Cresol. *Organometallics* **2010,** *29* (21), 4793-4803.

19. Harrison, D. P.; Iovan, D. A.; Myers, W. H.; Sabat, M.; Wang, S.; Zottig, V. E.; Harman, W. D., [4 + 2] Cyclocondensation Reactions of Tungsten,ÄìDihydropyridine Complexes and the Generation of Tri- and Tetrasubstituted Piperidines. *Journal of the American Chemical Society* **2011,** *133* (45), 18378-18387.

20. Harrison, D. P.; Sabat, M.; Myers, W. H.; Harman, W. D., Polarization of the Pyridine Ring: Highly Functionalized Piperidines from Tungsten−Pyridine Complex. *Journal of the American Chemical Society* **2010,** *132* (48), 17282-17295.

21. Young, C. A.; Dewald, R. R., Kinetic studies of the reactions of N,N-dimethylformamide and N,N-dimethylacetamide with sodium in liquid ammonia. *Journal of the American Chemical Society* **1979,** *101* (11), 2884-2888.

22. Kopach, M. E.; Cole, K. P.; Pollock, P. M.; Johnson, M. D.; Braden, T. M.; Webster, L. P.; McClary Groh, J.; McFarland, A. D.; Schafer, J. P.; Adler, J. J.; Rosemeyer, M., Flow Grignard and Lithiation: Screening Tools and Development of Continuous Processes for a Benzyl Alcohol Starting Material. *Organic Process Research & Development* **2016,** *20* (9), 1581-1592.

23. Piller, F. M.; Appukkuttan, P.; Gavryushin, A.; Helm, M.; Knochel, P., Convenient Preparation of Polyfunctional Aryl Magnesium Reagents by a Direct Magnesium Insertion in the Presence of LiCl. *Angewandte Chemie International Edition* **2008,** *47* (36), 6802-6806.

24. Kopach, M. E.; Roberts, D. J.; Johnson, M. D.; McClary Groh, J.; Adler, J. J.; Schafer, J. P.; Kobierski, M. E.; Trankle, W. G., The continuous flow Barbier reaction: an improved environmental alternative to the Grignard reaction? *Green Chemistry* **2012,** *14* (5), 1524-1536.

25. Zhao, Y.; Zhu, J.; Ni, C.; Hu, J., Magnesium Metal-Mediated Reductive Trifluoromethylation of Aldehydes with Phenyl Trifluoromethyl Sulfone. *Synthesis* **2010,** *2010* (11), 1899-1904.

26. Dai, P.; Dussault, P. H.; Trullinger, T. K., Magnesium/Methanol: An Effective Reducing Agent for Peroxides. *The Journal of Organic Chemistry* **2004,** *69* (8), 2851-2852.

27. Maekawa, H.; Noda, K.; Kuramochi, K.; Zhang, T., Catalyst-Free and Solvent-Controlled Reductive Coupling of Activated Vinyl Triflates with Chlorotrimethylsilane by Magnesium Metal and Its Synthetic Application. *Organic Letters* **2018,** *20* (7), 1953-1956.

28. Chattopadhyay, A.; Dubey, A. K., A Simple and Efficient Procedure of Low Valent Iron- or Copper-Mediated Reformatsky Reaction of Aldehydes. *The Journal of Organic Chemistry* **2007,** *72* (24), 9357-9359.

29. Shi, L.; Fan, C.-A.; Tu, Y.-Q.; Wang, M.; Zhang, F.-M., Novel and efficient Ni-mediated pinacol coupling of carbonyl compounds. *Tetrahedron* **2004,** *60* (12), 2851-2855.

30. Hirofumi, M.; Taro, M.; Takeshi, M.; Ikuzo, N., Practical Synthesis of Diethyl Phenylsuccinate by Mg-promoted Carboxylation of Ethyl Cinnamate. *Chemistry Letters* **2011,** *40* (4), 368-369.

31. Maekawa, H.; Okawara, H.; Murakami, T., Reductive carboxylation of aromatic esters by electron transfer from magnesium metal. *Tetrahedron Letters* **2017,** *58* (3), 206-209.

32. Link, A.; Sparr, C., Remote Central-to-Axial Chirality Conversion: Direct Atroposelective Ester to Biaryl Transformation. *Angewandte Chemie International Edition* **2018,** *57* (24), 7136-7139.

33. Harman, W. D.; Sekine, M.; Taube, H., Redox-promoted linkage isomerizations of aldehydes and ketones on pentaammineosmium. *Journal of the American Chemical Society* **1988,** *110* (8), 2439-2445.

34. Myers, J. The Development of a Recyclable Molybdenum Dearomatization Agent. University of Virginia, Department of Chemistry, PHD (Doctor of Philosophy), 2017, Charlottesville, VA, 2017.

35. Wilson, K. B.; Smith, J. A.; Nedzbala, H. S.; Pert, E. K.; Dakermanji, S. J.; Dickie, D. A.; Harman, W. D., Highly Functionalized Cyclohexenes Derived from Benzene: Sequential Tandem Addition Reactions Promoted by Tungsten. *The Journal of Organic Chemistry* **2019**.

36. Wilson, K. B.; Myers, J. T.; Nedzbala, H. S.; Combee, L. A.; Sabat, M.; Harman, W. D., Sequential Tandem Addition to a Tungsten–Trifluorotoluene Complex: A Versatile Method for the Preparation of Highly Functionalized Trifluoromethylated Cyclohexenes. *Journal of the American Chemical Society* **2017,** *139* (33), 11401-11412.

37. MacLeod, B. L.; Pienkos, J. A.; Wilson, K. B.; Sabat, M.; Myers, W. H.; Harman, W. D., Synthesis of Novel Hexahydroindoles from the Dearomatization of Indoline. *Organometallics* **2016,** *35* (3), 370-387.

38. Strausberg, L.; Li, M.; Harrison, D. P.; Myers, W. H.; Sabat, M.; Harman, W. D., Exploiting the o-Quinodimethane Nature of Naphthalene: Cycloaddition Reactions with η2-Coordinated Tungsten–Naphthalene Complexes. *Organometallics* **2013,** *32* (3), 915-925.

39. Gal, D.; Hodes, G.; Lincot, D.; Schock, H. W., Electrochemical deposition of zinc oxide films from non-aqueous solution: a new buffer/window process for thin film solar cells. *Thin Solid Films* **2000,** *361-362*, 79-83.

Chapter 5:

Concluding Remarks

The outcome of this work was the creation of new methods for manipulating the dihapto-coordinated ligands on the {MoTp(NO)(DMAP)} and {WTp(NO)(PMe_3)} metal fragments. A detailed understanding of redox processes has led to several improvements in the dearomatization process. Through use of a redox catalyst, rates of both ligand substitution and isomerization are dramatically increased. Furthermore, significant differences in the redox potential of κ^1/η^2 bound ligands provides a new mechanism for reduction of the M(I)-halide precursors.

The use of redox catalysts for ligand exchanges of the {MoTp(NO)(DMAP)} system have allowed for the exchange process to occur at a small fraction of their normal time. Catalyzed exchanges from the naphthalene ligand of **5** can be done in a day instead of two weeks. Until now, final decomplexation of alkene products from the metal required full oxidation of the metal system. This often resulted in degradation of the organic product. Under catalytic redox conditions, the organic product can be liberated under more mild conditions with generation of a M(0) complex that could possibly be reused. Even if the options for catalyzed exchanges are reduced to ketones and aldehydes, the universal nature of the initiation step has even allowed the normally substitution inert acetone complex (**3**) to be exchanged. The retention of the stereochemistry of the molybdenum fragment {MoTp(NO)(DMAP)} through a Mo(I) oxidation state also had significant consequences. Molybdenum halide precursors of the form MoTp(NO)(DMAP)(I) could be prepared from the MoTp(NO)(DMAP)(η^2-α-pinene) (**1**) complex. With the ability to enantioenrich both metals, tungsten *and* molybdenum can be used for generation of enantiopure novel small molecules.

Isomerization of alkene complexes has important applications for selective synthesis of organic products derived from them. While the trans-hexene complexes are not the most synthetically interesting, they provided a simple model to investigate isomerization methods. Study of the transition pathways helps elucidate the underlying mechanism of both catalyzed and uncatalyzed isomerizations. When *R*-limonene and α-humulene are bound to the metal fragments, only one of the double bonds is

interacting with the metal. In future work, functionalization of the unbound double bonds of the terpene ligands could yield interesting derivatives. By controlling which double bond and at which face of the terpene ligand is bound to the metal, the isomers of any functionalized terpene products can be controlled more easily. Further, the use of the redox-promoted isomerization with the functionalized cyclohexadiene **20** has created a different reactivity pattern.

The last application presented was for magnesium mediated reductions to form dihapto-coordinated complexes of Mo(Tp)(NO)(DMAP)(η^2-alkene/aromatic) and W(Tp)(NO)(PMe_3)(η^2-alkene/aromatic)). The suspected shift of redox potential associated with the κ^1/η^2 equilibrium has allowed for reductions under the more mild magnesium conditions. Use of DMA has allowed for the success of magnesium reductions. The preparation of the naphthalene complex (**5)** has been dramatically improved with magnesium. Conversion of racemic iodine complex (**1)** complex to an enantiopure Mo(I) precursor has been improved as well. Initial experiments for magnesium reductions on the tungsten system have been reported. While magnesium reductions of tungsten complexes are still far from usable, development could lead to increases in yield for tungsten dearomatized products, as seen with the generation of **5**. The wider adoption of these metal systems to organic synthesis might be possible with the milder and more cost-efficient magnesium.

The initial question of “why is the exchange reaction going faster than normal?” has led to several years of work exploring the applications of a redox process. The investigation that started by seeing an accelerated exchange reaction has shown three main advancements. The ability to undergo ligand exchange without epimerization has led to the development of enantioenrichment of the molybdenum core. The use of transient oxidation has led to generation of new reactivity patterns for novel small molecules. And the application of κ^1/η^2 isomerization has allowed for discovery of sodium-free reductions for both the molybdenum and tungsten systems. The methodology presented here has

advanced several aspects of dihapto dearomatization, bringing it one step closer to use as a general tool for organic synthesis.

Chapter 6:

Appendix

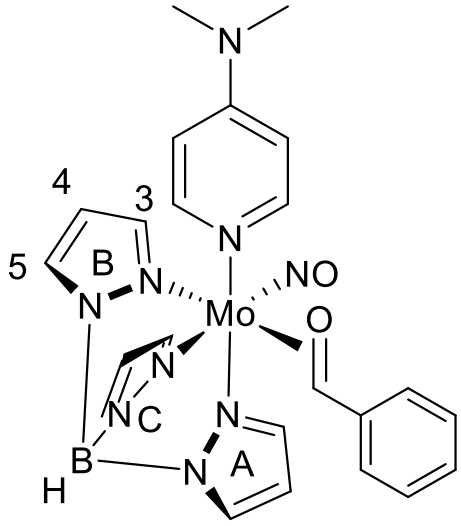
General Methods.

NMR spectra were obtained on a 600 or 800 MHz spectrometer. All chemical shifts are reported in ppm, and proton and carbon shifts are referenced to tetramethylsilane (TMS) utilizing residual ^{1}H or ^{13}C signals of the deuterated solvents as an internal standard. Coupling constants (*J*) are reported in hertz (Hz). Infrared spectra (IR) were recorded as a glaze on a spectrometer fitted with a horizontal attenuated total reflectance (HATR) accessory or on a diamond anvil ATR assembly. Electrochemical experiments were performed under a nitrogen atmosphere. Cyclic voltammetry data were taken at ambient temperature (~25°C) at 100 mV/s in a standard three-electrode cell with a glassy-carbon working electrode, N,N-dimethylacetamide (DMA) or acetonitrile (CH_3CN) solvent (unless otherwise specified), and tetrabutylammonium hexafluorophosphate (TBAH) electrolyte (approximately 0.5 M). All potentials are reported versus NHE (normal hydrogen electrode) using cobaltocenium hexafluorophosphate ($E_{1/2}$=−0.78 V), ferrocene ($E_{1/2}$= +0.55 V), or decamethylferrocene ($E_{1/2}$= +0.04 V) as internal standard. The peak-to-peak separation was less than 100 mV for all reversible couples. Unless otherwise noted, all synthetic reactions were performed in a glove box under a dry nitrogen atmosphere. Deuterated solvents were used as received. Pyrazole (Pz) protons of the hydrido tris(pyrazolyl)borate(Tp) ligand were uniquely assigned (e.g.,“PzB3”) using a combination of two-dimensional NMR data. When unambiguous assignments were not possible, Tp protons were labeled as “Pz3/5 or Pz4”. All *J* values for Pz protons are 2(±0.2) Hz. BH peaks (around 4−5 ppm) are not identified due to their quadrupole broadening; IR data are used to confirm the presence of a BH group (around 2500 cm^{-1}).

Compound

MoTp(NO)(DMAP)(η²-benzaldehyde) (**2**) 117
MoTp(NO)(DMAP)(η²-naphthalene) (**5**) 120
MoTp(NO)(DMAP)(η²-DMF) (**8**) 121
MoTp(NO)(DMAP)(η²-Pinacolone) (**9**) 123
MoTp(NO)(DMAP)(η²-Cyclopentene) (**11**) 125
MoTp(NO)(DMAP)(κ¹-N,N-Dimethylacetamide)⁺ (**12**) 137
Mo$_R$Tp(NO)(DMAP)(I)/[MoTp(NO)(DMAP)(κ¹-DMA)] I (enantioenriched mixture) (**13**/**12**) 166
MoTp(NO)(DMAP)(η²-Propene) (**14**) 167
WTp(NO)(PMe$_3$)(η²-Propene) (**15**) 186
MoTp(NO)(DMAP)(η²-trans-3-hexene) (**16**) 203
(MoTp(NO-Me)(DMAP)(η²-3-Trans-Hexene))(OTf) (**16•CH$_3$**) 227
WTp(NO)(PMe$_3$)(η²-trans-3-hexene) (**17**) 241
MoTp(NO)(DMAP)(η²-1,3-cyclohexadiene) (**18**) 255
WTp(NO)(PMe$_3$)(η²-1,3-cyclohexadiene) (**19**) 275
MoTp(NO)(DMAP)(η²-*R*-limonene) (**21**) 293
Mo$_R$Tp(NO)(DMAP)(η²-*R*-limonene) (*R*,*R*)- **21A** 360
Mo$_S$Tp(NO)(DMAP)(η²-*R*-limonene) (*S*,*R*)- **21A** 363
WTp(NO)(PMe$_3$)(η²-*R*-limonene) (*R*,*R*)- **22A** and (*S*,*R*)- **22A** 366
MoTp(NO)(DMAP)(η²-α-humulene) (**23**) 401
(MoTp(NO-Me)(DMAP)(η²-α -Humulene))(OTf) (**23A•CH$_3$**) 432
WTp(NO)(PMe$_3$)(η² α-humulene) (**24**) 435
MoTp(NO)(DMAP)(κ¹-OTf) (**26**) 463

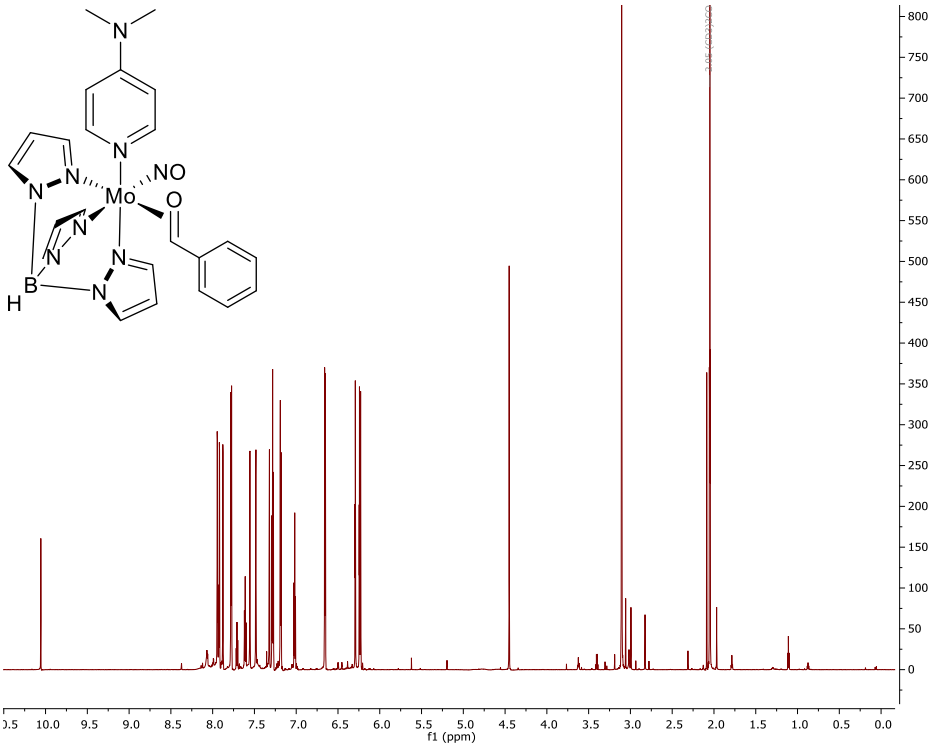
MoTp(NO)(DMAP)(η^2-benzaldehyde) (**2**)



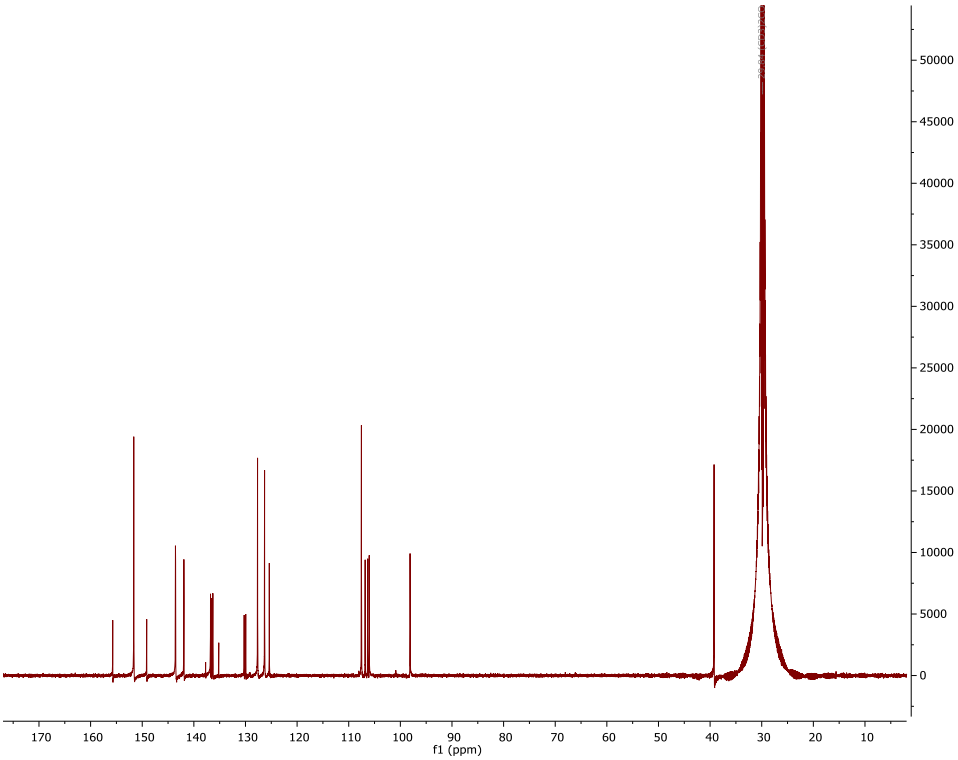
In a 4-dram vial was charged with a stir pea, MoTp(NO)(DMAP)(η^2-α,α,α-trifluorotoluene) (1.1 g, 1.7 mmol) and benzaldehyde (10. g, 98 mmol) were combined. This homogeneous light green mixture was capped and stirred at room temperature for 10 minutes. This reaction mixture was then loaded onto a 60 mL coarse porosity fritted disc 2/3 full with silica gel. This column was washed with diethyl ether (50 mL) and the green band was isolated using THF (100 mL). The green solution was evaporated *in vacuo* to 20 mL and added to chilled pentane (100 mL) yielding a white precipitate which was collected on a 15 mL fine porosity fritted disk. Some product had oiled out on the bottom of the filter flask, and this was dissolved in a minimal amount of DCM (~3 mL) and then added to ~ 50 mL of stirring chilled pentane. A white precipitate was isolated on a 15 mL fine porosity fritted disc washed with chilled pentane (2 x 10 mL), and dried under static vacuum for 2 h yielding **2** (0.52 g, 0.91 mmol, ~50% yield). IR: υ_{NO}: 1580 cm^{-1}, υ_{BH}: 2484 cm^{-1}. CV (THF): E_{pa} = +0.400 V. ^{1}H-NMR (d^6-Acetone, δ): 7.95 (1H, d, Pz3/5), 7.92 (1H, d, Pz3/5), 7.88 (1H, d, Pz3), 7.78 (2H, m, DMAP H2 and H6), 7.56 (1H, d, Pz3/5), 7.48 (1H, d, Pz3/5), 7.32 (1H, d, Pz3), 7.28 (2H, t, *J* =7.84, H3 and H5), 7.19 (2H, d, *J* = 7.31, H2 and H6), 7.02 (1H, t of t, *J* = 7.25, 1.25, H4), 6.65 (2H, m, DMAP H3 and H5), 6.29 (1H, t, Pz4), 6.24 (1H, t, Pz4), 6.23 (1H, t, Pz4), 4.45 (1H, s, aldehyde H), 3.10 (6H, s, DMAP methyls). ^{13}C-NMR (d^6-Acetone, δ). 155.7 (DMAP 4), 151.63 (DMAP 2 and 6), 149.13

(C1), 143.5 (Pz3/5), 143.5 (Pz3/5), 141.9 (Pz3/5), 136.8 (Pz3/5), 136.6 (Pz3/5), 136.3 (Pz3/5), 127.7 (C3 and C5), 126.30 (C2 and C6), 125.4 (C4), 107.6 (DMAP 3 and 5), 106.8 (Pz4), 106.3 (Pz4), 106.0 (Pz4), 98.1 (aldehyde carbonyl C), 39.2 (DMAP methyls). Calculated for $C_{23}H_{26}BMoN_9O_2$: C, 48.70; H, 4.62; N, 22.22. Found: C, 48.32; H: 4.63; N: 20.23. Calculated for $4(C_{23}H_{26}BMoN_9O_2) \bullet CH_2Cl_2$: C, 48.26; H, 4.93; N, 20.89.

^{1}H NMR (d^{6}-Acetone) of **2:** Spectra collected by Jacob A. Smith



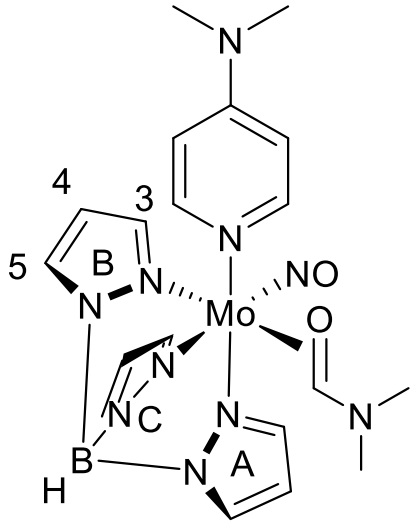
^{13}C NMR (d^{6}-Acetone) of **2:** Spectra collected by Jacob A. Smith



MoTp(NO)(DMAP)(η^2-naphthalene)[8] (5) Alternative Synthesis

In a 1 L round bottom flask charged with a stir egg, MoTp(NO)(DMAP)(I) (24 g, 0.040 mol), THF (500 mL), naphthalene (67 g, 0.508 mol), DMA (1.2 mL) and magnesium powder (48g, 325 mesh) were added. This mixture was allowed to stir at room temperature. After 24 h, Et_2O (500 mL) was added and the reaction mixture was subsequently loaded onto a 600 mL medium porosity fritted disk, ~3/4 full with silica. A yellow band was eluted with 1/: THF/Et_2O (1000 mL), collected as an orange solution, and then evaporated *in vacuo* to ~50 mL. This orange solution was added to stirring pentane (900 mL), forming an orange precipitate. This precipitate was isolated on a 350 mL fine porosity fritted disk, washed with pentane (3X200 mL), and desiccated to yield a yellow solid (17 g, 29 mmol, 70% yield).

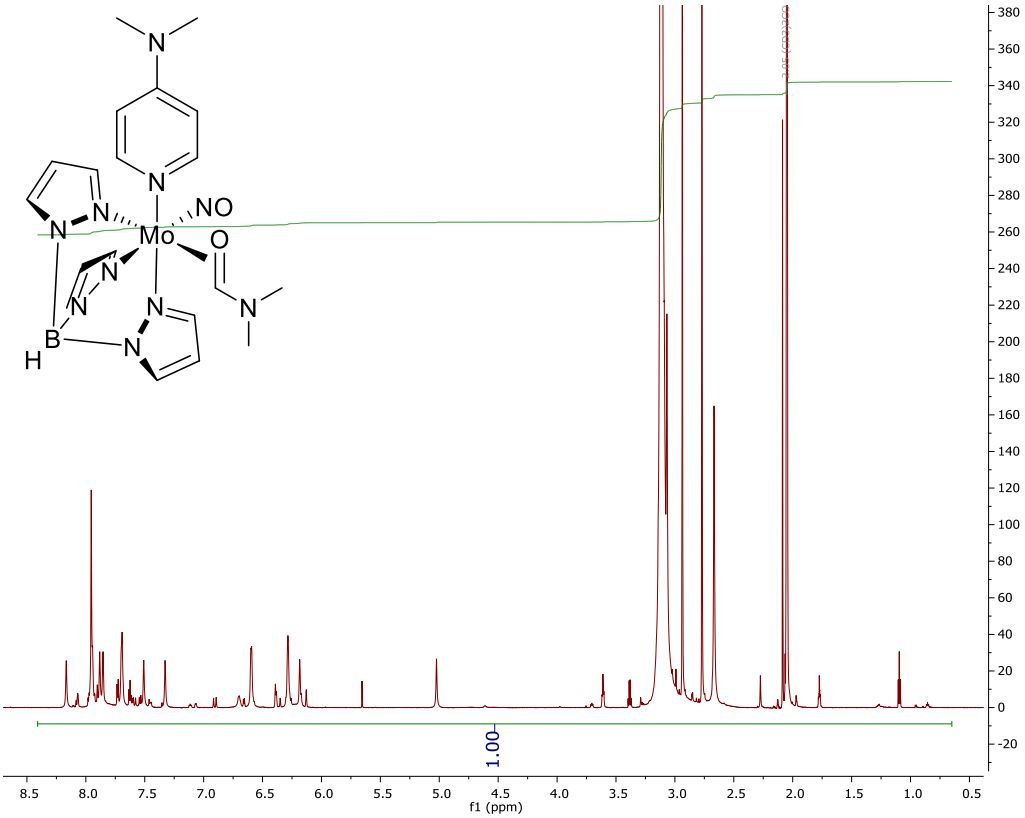
MoTp(NO)(DMAP)(η^2-DMF) (**8**)



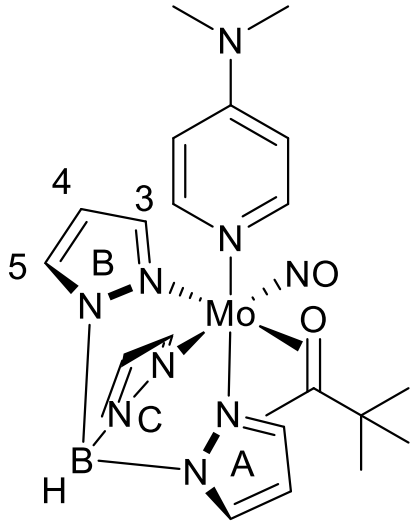
Although full characterization of **7** is not included due to instability, the complex matches the analog, MoTp(NO)(MeIM)(η^2-DMF).[26]

CV: E_{pa}: +790 mV, $E_{1/2}$: -1090 mV.

^{1}H NMR (d^{6}-Acetone) of **8:** Spectra collected by Jacob A. Smith

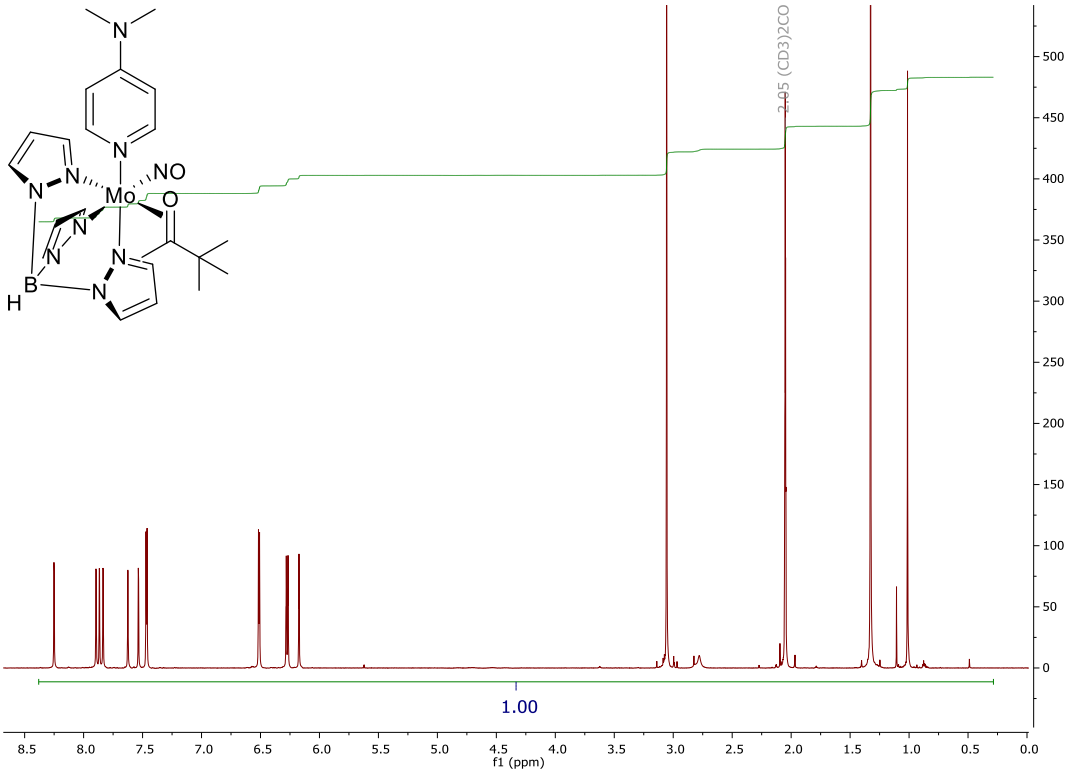


MoTp(NO)(DMAP)(η²-Pinacolone) (**9**)

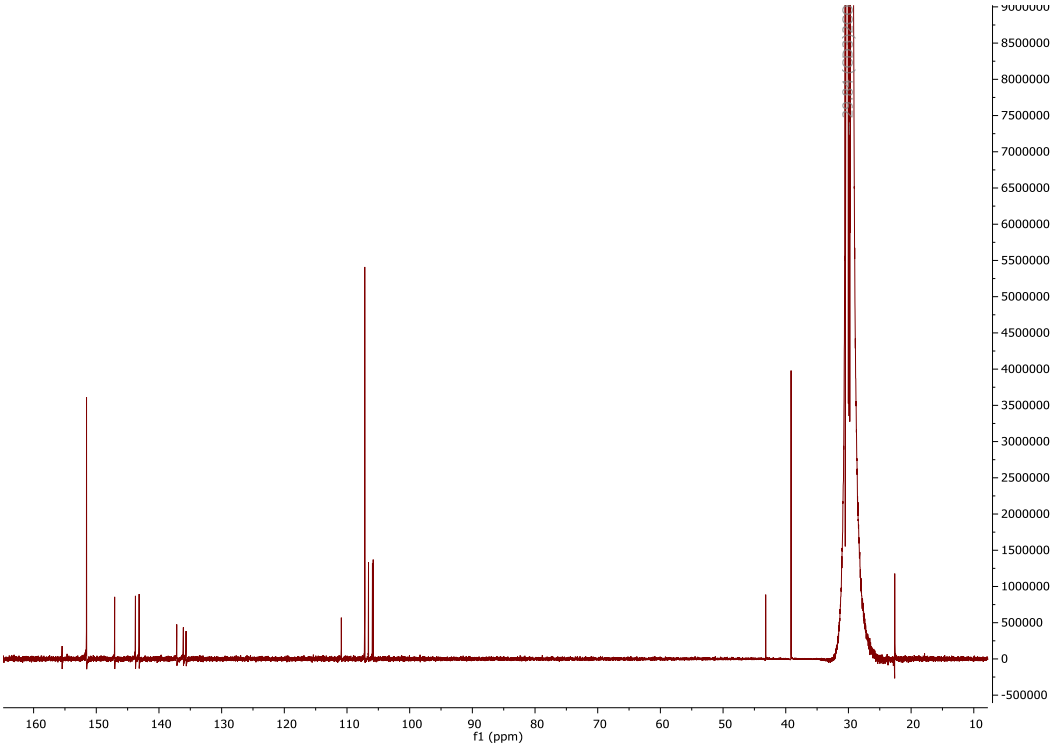


In a 4 dram vial charged with a stir pea, MoTp(NO)(DMAP)(η²-trifluorotoluene) (0.15g, 0.00025 mol) and pinacolone (2.0 mL, 0.015 mol) were combined and was allowed to stir overnight (18 h). The off-white precipitate was then collected on a 15 mL fine porosity fritted disc and washed with hexanes (3 x 10 mL). The solid was desiccated for 2 h under vacuum and collected (0.0729 g, 50%, ~5% paramagnetic material impurity by CV). IR υ_{NO}: 1554.35 Hz, υ_{BH}: 2513.80 Hz. CV E_{pa}: +280 mV (Broad). ^{1}H NMR (d_6-Acetone, δ): 8.25 (1H, d, PzA3), 7.90 (1H, d, PzB5), 7.87 (1H, d, PzC5), 7.83 (1H, d, PzA5), 7.62 (1H, d, PzB3), 7.54 (1H, d, PzC3), 7.46 (2H, m, DMAP H2 and H6), 6.51 (2H, m, DMAP H3 and H5), 6.28 (1H, t, PzA4), 6.27 (1H, t, PzB4), 6.17 (1H, t, PzC4), 3.06 (6H, s, DMAP methyls), 1.33 (9H, s, H 4), 1.01 (3H, s, H1). ^{13}C NMR (d_6-Acetone, δ): 155.5 (DMAP 4), 151.6 (DMAP 2 and 6), 147.1 (PzA3), 143.8 (PzC3), 143.2 (PzB3), 137.2 (PzA5), 136.1 (PzC5), 135.7 (PzB5), 110.9 (C2), 107.2 (DMAP 3 and 5), 106.6 (PzA4), 105.9 (PzB4), 105.8 (PzC4), 43.2 (C3), 39.2 (DMAP methyls), 30.5 (3C, C4 methyls), 22.6 (C1).

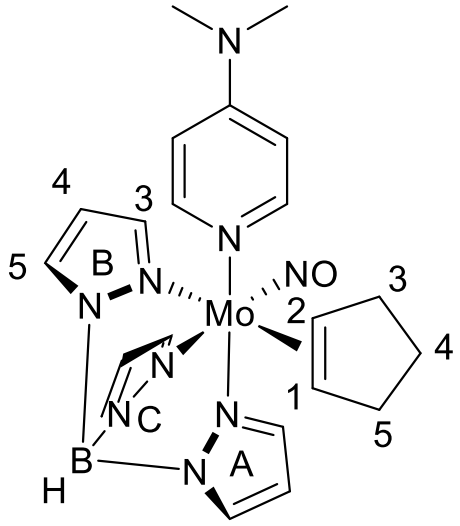
^{1}H NMR (d^{6}-Acetone) of **9**



^{13}C NMR (d^{6}-Acetone) of **9**



MoTp(NO)(DMAP)(η^2-Cyclopentene) (**11**)



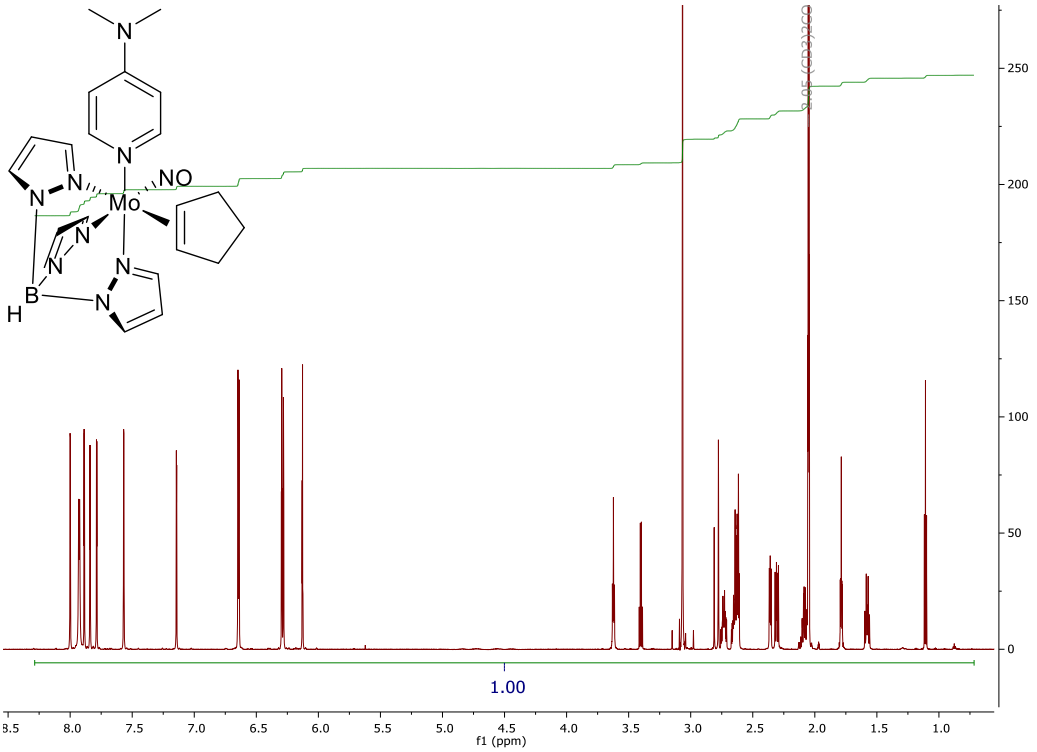
In a 100 mL round bottom charged with a stir egg, sodium dispersion in paraffin wax (3 g, ~35% Na^0 by weight, ~1.1 g Na^0, 0.049 mol) and 100 mL of hexanes were combined. The mixture was capped and allowed to mix vigorously for 18 h. The hexanes were then decanted and the remaining Na^0 was crushed with a spatula to yield smaller grains. The sodium was then combined with about 50 mL of THF, cyclopentene (3.0 g, 0.044 mol), and then MoTp(NO)(DMAP)(I) (3.0 g, 0.0051 mol). The flask was recapped and allowed to mix 1 h. At this time, 50 mL of ether was added to the dark solution and allowed to mix for about 30 seconds. The solution was then added to a 150 mL medium porosity fritted disk about 3/4 full of silica, and the orange band was eluted with 500 mL of ether. The orange ether solution was then concentrated *in vacuo* to about 50 mL causing precipitation of a yellow solid, which was collected on a 60 mL fine porosity fritted disk and washed with pentane (3 x 30 mL). Desiccating for 2 h yielded a fluffy yellow solid (1.1 g, 2.1 mmol, 42% yield). IR: υ_{NO}: 1550 cm^{-1}, υ_{BH}: 2478 cm^{-1}. CV: Epa: 10 mV. ^{1}H NMR (d6-Acetone, δ): 8.00 (1H, d, PzA3), 7.92 (2H, m, DMAP H2 and H6), 7.88 (1H, d,PzC5), 7.84 (1H, d, PzA5), 7.79 (1H, d, PzB5), 7.57 (1H, d, PzC3), 7.14 (1H, d,PzB3), 6.65 (2H, m, DMAP H3 and H5), 6.30 (1H, t, PzC4), 6.28 (1H, t, PzA4), 6.13 (1H, t, PzB4), 3.07 (6H, s, DMAP methyls), 2.74 (1H, m, H4), 2.66 (3H, m, H1, H3 anti from DMAP, and 4), 2.36 (1H, m, H2), 2.31 (1H, m, H3 proximal to DMAP)) , 2.09 (1H, m, H5), 1.57 (1H, m,

H5). ^{13}C NMR (d6-Acetone, δ): 155.0 (DMAP 4), 150.7 (DMAP 2 and 6), 143.0 (PzA5), 142.0 (PzC5), 141.8 (PzB5), 137.1 (PzB3), 136.5 (PzA3), 135.6 (PzC3), 108.4 (DMAP 3 and 5), 106.4 (Pz4), 106.2 (Pz4), 106.2 (Pz4), 76.8 (C1), 71.8 (C2), 39.1 (DMAP Methyls), 36.0 (C4), 35.1 (C3), 23.6 (C5). Anal. Cald: $2(C_{21}H_{28}BMoN_9O) \bullet CH_2Cl_2$: C, 45.17; H, 5.11; N, 22.05. Found for crystals grown in DCM with pentane diffusion: C, 44.66; H, 5.13; N, 21.56.

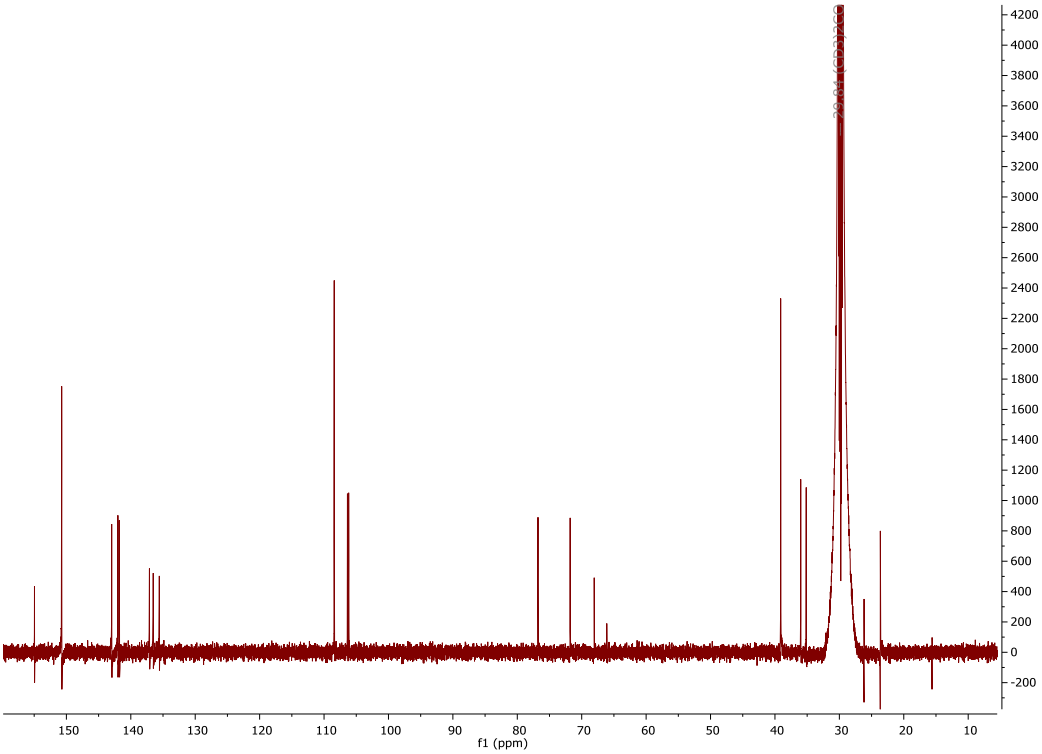
MoTp(NO)(DMAP)(η^2-Cyclopentene) (11) Alternative Synthesis

To a 4 dram vial charged with a stir pea, magnesium powder (1.0 g, 325 mesh) was combined with I_2 (0.033 g, 0.13 mmol) dissolved in 2 mL DMA and mixed by hand until the yellow orange solution became clear. The DMA solution was decanted from the magnesium powder and 2 mL of fresh DMA was added to the Mg^0. The DMA was again decanted and ~10 mL of pentane was added, mixed by hand, and decanted to remove any extra DMA. The freshly cleaned magnesium was then combined with cyclopentene (2.5 mL, 25 mmol) and 6 mL THF. Then [MoTp(NO)(DMAP)(κ^1-DMA)](OTf) (0.25 g, 0.36 mmol) was added to the magnesium suspension and the vial was capped. The solution was allowed to mix for 2 d. After this duration, the solution was added to a 15 medium porosity fritted disk, ~3/4 full of silica, and a yellow band was eluted with about 25 mL of ether. The filtrate was evaporated *in vacuo* to ~10 mL and 100 mL of pentane was added. Again, volume was reduced down *in vacuo* to 50 mL. The bright yellow precipitate was collected on a 15 mL fine porosity fritted disk and washed with pentane (3x10 mL). The solid was desiccated and the product was then collected (0.13 g, 0.24 mmol, ~62 % yield, ~5% starting material impurity).

^{1}H NMR (d^{6}-Acetone) of **11**



^{13}C NMR (d^{6}-Acetone) of **11**



Compound **11** Data collected by Diane A. Dickie

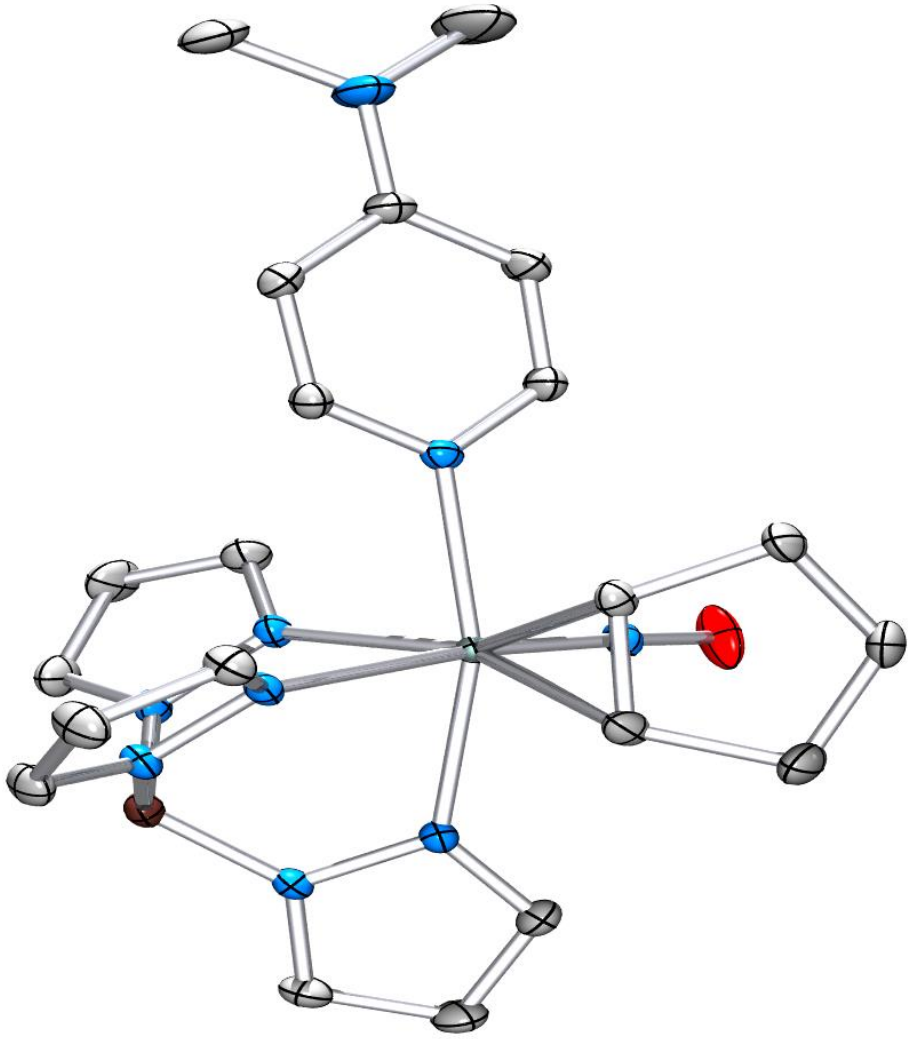


Table 1. Sample and crystal data for $C_{21}H_{28}BMoN_9O$.

Chemical formula	$C_{21}H_{28}BMoN_9O$
Formula weight	529.27 g/mol
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal size	0.254 x 0.488 x 0.548 mm
Crystal habit	yellow block
Crystal system	monoclinic

Space group	P $2_1/n$	
Unit cell dimensions	a = 11.4512(8) Å	α = 90°
	b = 17.1393(12) Å	β = 99.6970(10)°
	c = 12.8859(9) Å	γ = 90°
Volume	2492.9(3) $Å^3$	
Z	4	
Density (calculated)	1.410 g/cm^3	
Absorption coefficient	0.557 mm^{-1}	
F(000)	1088	

Table 2. Data collection and structure refinement for $C_{21}H_{28}BMoN_9O$.

Diffractometer	Bruker Kappa APEXII Duo
Radiation source	fine-focus sealed tube, Mo K_α
Theta range for data collection	2.00 to 29.60°
Index ranges	-15<=h<=15, -23<=k<=22, -17<=l<=17
Reflections collected	29694
Independent reflections	6992 [R(int) = 0.0380]
Coverage of independent reflections	99.9%
Absorption correction	Multi-Scan
Max. and min. transmission	0.8710 and 0.7500
Structure solution technique	direct methods
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2016/6 (Sheldrick, 2016)

Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	6992 / 0 / 304	
Goodness-of-fit on F^2	1.137	
Δ/σ_{max}	0.001	
Final R indices	5787 data; I>2σ(I)	R1 = 0.0319, wR2 = 0.0745
	all data	R1 = 0.0439, wR2 = 0.0805
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0306P)^2+1.8717P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.562 and -1.103 eÅ^{-3}	
R.M.S. deviation from mean	0.091 eÅ^{-3}	

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å²) for $C_{21}H_{28}BMoN_9O$.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
Mo1	0.45237(2)	0.29283(2)	0.50085(2)	0.01097(5)
O1	0.54493(16)	0.17660(10)	0.36276(16)	0.0337(4)
N1	0.37855(15)	0.36692(10)	0.62357(13)	0.0144(3)
N2	0.29731(15)	0.33453(10)	0.67799(14)	0.0153(3)
N3	0.26037(14)	0.25982(10)	0.46170(14)	0.0145(3)
N4	0.19488(14)	0.24452(10)	0.53850(14)	0.0158(3)
N5	0.44976(15)	0.20103(10)	0.62123(14)	0.0144(3)
N6	0.35696(15)	0.19375(10)	0.67504(14)	0.0148(3)

	x/a	y/b	z/c	U(eq)
N7	0.50802(15)	0.22609(10)	0.41761(14)	0.0167(3)
N8	0.39416(14)	0.37451(10)	0.36888(13)	0.0140(3)
N9	0.25785(19)	0.51472(13)	0.10870(17)	0.0300(5)
C1	0.40376(19)	0.43764(12)	0.66621(17)	0.0184(4)
C2	0.3395(2)	0.45102(13)	0.74736(19)	0.0243(5)
C3	0.2732(2)	0.38445(13)	0.75200(18)	0.0212(4)
C4	0.18781(19)	0.25099(13)	0.36982(18)	0.0202(4)
C5	0.07476(19)	0.22934(15)	0.3859(2)	0.0265(5)
C6	0.08352(19)	0.22590(13)	0.49379(19)	0.0219(5)
C7	0.51969(19)	0.13927(12)	0.64786(18)	0.0203(4)
C8	0.4730(2)	0.09160(13)	0.71865(19)	0.0243(5)
C9	0.3707(2)	0.12808(12)	0.73382(17)	0.0200(4)
C10	0.62655(17)	0.32055(13)	0.59998(17)	0.0181(4)
C11	0.60027(17)	0.37690(12)	0.51831(16)	0.0155(4)
C12	0.69253(18)	0.37385(13)	0.44654(18)	0.0206(4)
C13	0.75824(19)	0.29615(14)	0.4742(2)	0.0251(5)
C14	0.7390(2)	0.27676(15)	0.5868(2)	0.0283(5)
C15	0.31706(17)	0.43323(12)	0.37519(17)	0.0161(4)
C16	0.27115(18)	0.48117(12)	0.29276(17)	0.0172(4)
C17	0.30361(18)	0.47049(12)	0.19301(17)	0.0180(4)
C18	0.3863(2)	0.41020(13)	0.18715(17)	0.0202(4)
C19	0.42676(18)	0.36515(12)	0.27375(17)	0.0173(4)
C20	0.2902(3)	0.4999(2)	0.0063(2)	0.0540(9)
C21	0.1650(2)	0.57130(15)	0.1154(2)	0.0330(6)

	x/a	y/b	z/c	U(eq)
B1	0.2512(2)	0.25043(14)	0.65505(19)	0.0160(4)

Table 4. Bond lengths (Å) for $C_{21}H_{28}BMoN_9O$.

Mo1-N7	1.7593(18)	Mo1-C11	2.2061(19)
Mo1-N5	2.2132(17)	Mo1-N8	2.2169(17)
Mo1-C10	2.231(2)	Mo1-N3	2.2439(16)
Mo1-N1	2.2973(17)	O1-N7	1.224(2)
N1-C1	1.342(3)	N1-N2	1.373(2)
N2-C3	1.344(3)	N2-B1	1.546(3)
N3-C4	1.335(3)	N3-N4	1.364(2)
N4-C6	1.346(3)	N4-B1	1.535(3)
N5-C7	1.337(3)	N5-N6	1.369(2)
N6-C9	1.351(3)	N6-B1	1.540(3)
N8-C15	1.350(3)	N8-C19	1.350(3)
N9-C17	1.356(3)	N9-C20	1.452(3)
N9-C21	1.452(3)	C1-C2	1.395(3)
C1-H1	0.95	C2-C3	1.377(3)
C2-H2	0.95	C3-H3	0.95
C4-C5	1.395(3)	C4-H4	0.95
C5-C6	1.378(3)	C5-H5	0.95
C6-H6	0.95	C7-C8	1.396(3)
C7-H7	0.95	C8-C9	1.371(3)
C8-H8	0.95	C9-H9	0.95
C10-C11	1.423(3)	C10-C14	1.525(3)

C10-H10	1.0	C11-C12	1.518(3)
C11-H11	1.0	C12-C13	1.541(3)
C12-H12A	0.99	C12-H12B	0.99
C13-C14	1.540(3)	C13-H13A	0.99
C13-H13B	0.99	C14-H14A	0.99
C14-H14B	0.99	C15-C16	1.375(3)
C15-H15	0.95	C16-C17	1.409(3)
C16-H16	0.95	C17-C18	1.412(3)
C18-C19	1.372(3)	C18-H18	0.95
C19-H19	0.95	C20-H20A	0.98
C20-H20B	0.98	C20-H20C	0.98
C21-H21A	0.98	C21-H21B	0.98
C21-H21C	0.98	B1-H1A	1.11(2)

Table 5. Anisotropic atomic displacement parameters (Å^2) for $C_{21}H_{28}BMoN_9O$.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mo1	0.00999(8)	0.01299(8)	0.01019(8)	0.00047(6)	0.00247(5)	0.00092(6)
O1	0.0343(10)	0.0264(9)	0.0470(12)	-0.0172(8)	0.0254(9)	-0.0023(7)
N1	0.0143(7)	0.0169(8)	0.0129(8)	0.0002(6)	0.0049(6)	-0.0003(6)
N2	0.0160(8)	0.0165(8)	0.0144(9)	-0.0006(6)	0.0060(7)	-0.0008(6)
N3	0.0127(7)	0.0176(8)	0.0135(9)	-0.0003(6)	0.0028(6)	-0.0006(6)
N4	0.0108(7)	0.0201(9)	0.0167(9)	-0.0001(7)	0.0027(6)	-0.0013(6)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N5	0.0132(7)	0.0165(8)	0.0139(8)	0.0006(6)	0.0037(6)	0.0010(6)
N6	0.0146(8)	0.0162(8)	0.0144(9)	0.0021(6)	0.0048(6)	-0.0002(6)
N7	0.0157(8)	0.0169(8)	0.0187(9)	0.0010(7)	0.0066(7)	-0.0011(6)
N8	0.0135(7)	0.0161(8)	0.0120(8)	0.0013(6)	0.0013(6)	-0.0007(6)
N9	0.0370(11)	0.0334(11)	0.0196(11)	0.0112(9)	0.0046(9)	0.0138(9)
C1	0.0220(10)	0.0164(10)	0.0175(11)	-0.0019(8)	0.0050(8)	-0.0019(8)
C2	0.0338(12)	0.0193(11)	0.0223(12)	-0.0045(9)	0.0119(10)	0.0007(9)
C3	0.0256(11)	0.0217(11)	0.0184(11)	-0.0031(8)	0.0102(9)	0.0028(8)
C4	0.0192(10)	0.0252(11)	0.0151(11)	-0.0006(8)	-0.0004(8)	-0.0007(8)
C5	0.0151(10)	0.0348(13)	0.0264(13)	0.0011(10)	-0.0054(9)	-0.0031(9)
C6	0.0122(9)	0.0265(12)	0.0266(12)	0.0023(9)	0.0018(8)	-0.0026(8)
C7	0.0183(10)	0.0202(11)	0.0225(12)	0.0030(8)	0.0041(8)	0.0058(8)
C8	0.0296(12)	0.0190(11)	0.0245(12)	0.0077(9)	0.0055(9)	0.0060(9)
C9	0.0253(11)	0.0186(10)	0.0167(11)	0.0042(8)	0.0051(8)	-0.0013(8)
C10	0.0133(9)	0.0258(11)	0.0144(10)	0.0022(8)	0.0000(7)	-0.0028(8)
C11	0.0126(8)	0.0176(10)	0.0162(10)	-0.0012(8)	0.0022(7)	-0.0026(7)
C12	0.0145(9)	0.0265(11)	0.0218(11)	0.0044(9)	0.0057(8)	-0.0026(8)
C13	0.0133(9)	0.0329(13)	0.0305(13)	0.0033(10)	0.0074(9)	0.0037(9)
C14	0.0143(10)	0.0365(14)	0.0336(14)	0.0125(10)	0.0023(9)	0.0048(9)
C15	0.0162(9)	0.0165(10)	0.0158(10)	-0.0013(8)	0.0036(8)	0.0005(7)
C16	0.0168(9)	0.0151(10)	0.0194(11)	0.0004(8)	0.0017(8)	0.0020(7)
C17	0.0188(9)	0.0175(10)	0.0165(11)	0.0035(8)	-0.0002(8)	-0.0009(7)
C18	0.0242(10)	0.0232(11)	0.0142(10)	0.0011(8)	0.0054(8)	0.0036(8)
C19	0.0181(9)	0.0177(10)	0.0166(10)	0.0005(8)	0.0043(8)	0.0028(7)

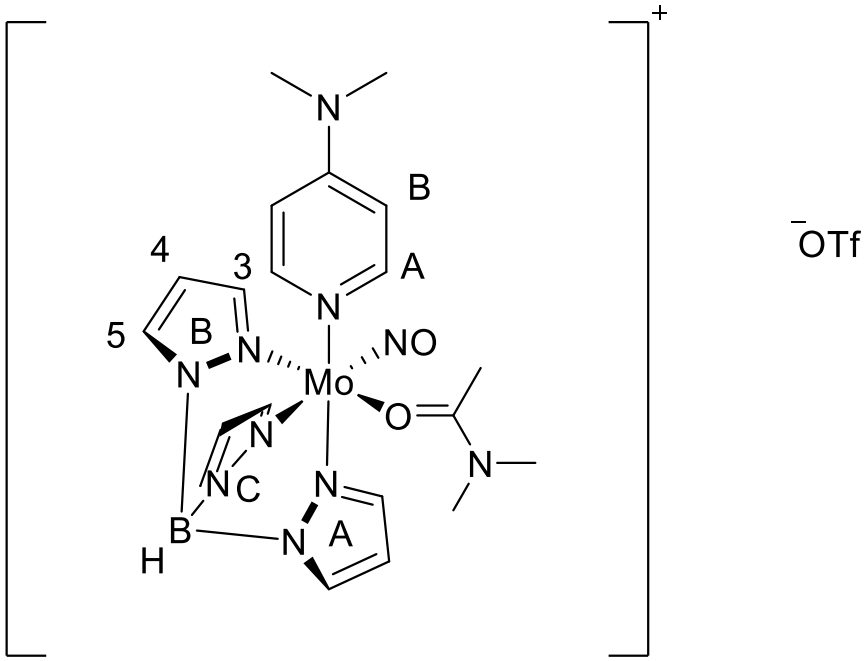
	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C20	0.074(2)	0.067(2)	0.0230(15)	0.0205(14)	0.0122(15)	0.0331(19)
C21	0.0383(14)	0.0266(13)	0.0322(15)	0.0127(11)	0.0009(11)	0.0097(10)
B1	0.0140(10)	0.0181(11)	0.0166(12)	0.0001(9)	0.0049(8)	-0.0007(8)

Table 6. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for $C_{21}H_{28}BMoN_9O$.

	x/a	y/b	z/c	U(eq)
H1	0.4578	0.4736	0.6442	0.022
H2	0.3411	0.4963	0.7902	0.029
H3	0.2196	0.3754	0.7995	0.025
H4	0.2101	0.2584	0.3028	0.024
H5	0.0070	0.2193	0.3342	0.032
H6	0.0211	0.2125	0.5306	0.026
H7	0.5913	0.1292	0.6222	0.024
H8	0.5052	0.0443	0.7495	0.029
H9	0.3181	0.1101	0.7783	0.024
H10	0.6231	0.3397	0.6727	0.022
H11	0.5813	0.4303	0.5419	0.019
H12A	0.7477	0.4186	0.4600	0.025
H12B	0.6544	0.3747	0.3716	0.025
H13A	0.7251	0.2546	0.4246	0.03
H13B	0.8437	0.3019	0.4715	0.03
H14A	0.7288	0.2199	0.5953	0.034
H14B	0.8071	0.2946	0.6392	0.034

	x/a	y/b	z/c	U(eq)
H15	0.2928	0.4420	0.4412	0.019
H16	0.2175	0.5215	0.3031	0.021
H18	0.4141	0.4008	0.1229	0.024
H19	0.4814	0.3246	0.2663	0.021
H20A	0.3759	0.5064	0.0107	0.081
H20B	0.2486	0.5368	-0.0452	0.081
H20C	0.2678	0.4464	-0.0158	0.081
H21A	0.0926	0.5440	0.1254	0.049
H21B	0.1496	0.6018	0.0502	0.049
H21C	0.1903	0.6063	0.1751	0.049
H1A	0.187(2)	0.2352(14)	0.707(2)	0.020(6)

(MoTp(NO)(DMAP)(κ^1-N,N-Dimethylacetamide))(OTf) (**12** OTf)



To a 50 mL RBF charged with a small stir egg, MoTp(NO)(DMAP)(CO) (5 g, 10.2 mmol) was combined with 25 mL DMA. Once the solution was stirring, AgOTf solid (2.6 g, 10 mmol) was added (Caution: CO released during reaction). Once bubbling had ceased, the solution was pulled through a 30 mL medium porosity fritted disk, with a 1 cm layer of Celite to remove the solid silver. The Celite pad was washed with acetone until the green color was washed away (~5 mL). The DMA solution was then added to 600 mL of ether. The ether solution was decanted from the oily solid stuck to the sides of the precipitation flask. The gummy solid was dissolved in 50 mL DCM and then transferred to a 150 mL medium porosity fritted disk. The green solution was then allowed to drip into 1 L of stirring hexanes in a 2 L flask over the course of an hour. The precipitate in the hexane solution was then collected on a 150 mL medium fritted disk and washed with hexanes (3 x 100 mL), ether (2 x 100 mL), and then desiccated for 2 h. The mint green solid was collected (5.2 g, 7.4 mmol, 75% yield). IR: υ_{NO}: 1589 cm^{-1}, υ_{BH}: 2512 cm^{-1}. CV: E_{pa} : 800 mV, $E_{1/2}$: 1,270 mV. Anal. Cald for $C_{21}H_{29}BF_3MoN_{10}O_5S$: C, 36.17; H, 4.19; F, 8.17; N, 20.09. Found: C, 35.97; H, 4.29; F, 7.91; N, 20.08.

[MoTp(NO)(DMAP)(κ^1- O-DMA)] OTf (**12** OTf) **Alternative Synthesis**

To a 50 mL RBF charged with a small stir egg, MoTp(NO)(DMAP)(CO) (5 g, 10 mmol) was combined with 15 mL DMA. Once the solution was stirring, $Cu(OTf)_2$ (1.85 g, 5.1 mmol) was added (Caution: CO released during reaction). Once bubbling had ceased, the solution was pulled through a 150 mL medium porosity fritted disk, with a 1 cm layer of Celite to remove the solid silver. The Celite pad was washed with DMA until the green color was washed away (~5 mL). The DMA solution was added to 500 mL of ether and the green solid was collected on a 150 mL medium porosity fritted disk and washed with ether (3x100 mL). The solid was desiccated and the green product was collected (4.7 g, 6.8 mmol, 67% yield). (0.061 g, 0.085 mmol, ~50 % yield). IR: υ_{NO}: 1589 cm^{-1}, υ_{BH}: 2516 cm^{-1}. CV: E_{pa}: 800 mV $E_{1/2}$: 1270 mV.

[MoTp(NO)(DMAP)(κ^1- O-DMA)] PF_6 (**12** PF_6)

In a 4 dram vial, MoTp(NO)(DMAP)(η^2-Trifluorotoluene) (0.10 g, 0.17 mmol) was dissolved in DMA (5 mL). Ferrocenium hexafluorophosphate (0.052 g 0.17 mmol) was added and the solution as mixed by hand. The green solution was added to 100 mL stirring ether and the resulting green solid was collected on a 30 ml medium porosity frit. The solid was washed with ether (3x20 mL). The green solid was dried and then collected. (0.061 g, 0.085 mmol, ~50 % yield). IR: υ_{NO}: 1589 cm^{-1}, υ_{BH}: 2516 cm^{-1}. CV: E_{pa}: 800 mV $E_{1/2}$: 1270 mV.

[MoTp(NO)(DMAP)(κ^1 -O-DMA)] BF_4 (**12** BF_4)

In a 4 dram vial, MoTp(NO)(DMAP)(CO) (0.10 g, 0.20 mmol) was dissolved in DMA (2mL). Silver Tetrafluoroborate (0.004 g 0.20 mmol) was added (Caution: CO released during reaction) and the solution was mixed by hand. The green solution was filtered through a 1 cm pat of Celite in a 30 mL medium porosity fritted disk to remove the silver metal. The Celite was then washed with ~8 mL DMA to remove the green color. The resulting green DMA solution was added to 100 mL stirring ether. The precipitate was collected on a 60 ml medium porosity frit and was washed with ether (5 x 30 mL). The green solid was

desiccated and then collected (0.063 g, 0.098 mmol 48 % yield). IR: υ_{NO}: 1589 cm^{-1}, υ_{BH}: 2516 cm^{-1}. CV: E_{pa}: 800 mV $E_{1/2}$: 1270 mV.

Compound **12** OTf: Data collected by Diane A. Dickie

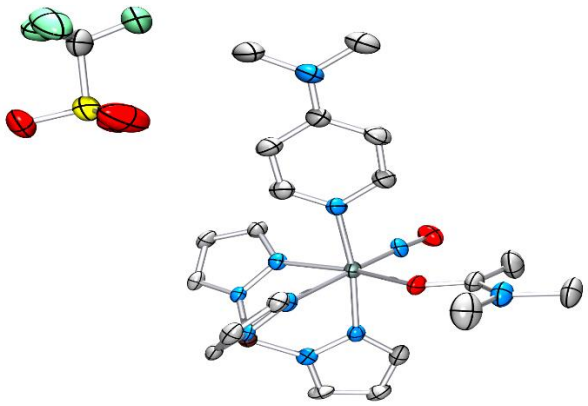


Table 1. Sample and crystal data for $C_{22}H_{29}BF_3MoN_{10}O_5S$.

Chemical formula	$C_{22}H_{29}BF_3MoN_{10}O_5S$	
Formula weight	709.36 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.081 x 0.089 x 0.172 mm	
Crystal habit	green block	
Crystal system	triclinic	
Space group	P 1	
Unit cell dimensions	a = 10.3381(10) Å	α = 104.250(3)°
	b = 10.7776(10) Å	β = 107.755(3)°
	c = 14.4218(13) Å	γ = 91.674(3)°

Volume	1473.8(2) $Å^3$
Z	2
Density (calculated)	1.599 g/cm^3
Absorption coefficient	0.587 mm^{-1}
F(000)	722

Table 2. Data collection and structure refinement for $C_{22}H_{29}BF_3MoN_{10}O_5S$.

Diffractometer	Bruker Kappa APEXII Duo
Radiation source	fine-focus sealed tube (Mo K_α, λ = 0.71073 Å)
Theta range for data collection	1.54 to 27.57°
Index ranges	-13<=h<=13, -14<=k<=14, -18<=l<=18
Reflections collected	6793
Coverage of independent reflections	99.6%
Absorption correction	Multi-Scan
Max. and min. transmission	0.9540 and 0.9060
Structure solution technique	direct methods
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2017/1 (Sheldrick, 2017)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	6793 / 3 / 786
Goodness-of-fit on F^2	1.085
Δ/σ_{max}	0.001

Final R indices	6315 data; I>2σ(I)	R1 = 0.0358, wR2 = 0.0768
	all data	R1 = 0.0403, wR2 = 0.0780
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0208P)^2+3.0052P]$ where $P=(F_o^2+2F_c^2)/3$	
Absolute structure parameter	0.47(6)	
Largest diff. peak and hole	0.898 and -0.886 eÅ^{-3}	
R.M.S. deviation from mean	0.092 eÅ^{-3}	

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for $C_{22}H_{29}BF_3MoN_{10}O_5S$.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
Mo1	0.33525(4)	0.93381(4)	0.22754(3)	0.01320(11)
O1	0.0879(4)	0.8204(5)	0.0507(3)	0.0297(10)
O2	0.2417(4)	0.0416(4)	0.3264(3)	0.0174(8)
N1	0.5213(4)	0.0204(4)	0.3577(3)	0.0145(9)
N2	0.6138(4)	0.9427(4)	0.3938(3)	0.0142(9)
N3	0.4856(5)	0.8432(5)	0.1658(3)	0.0134(9)
N4	0.5904(4)	0.7951(4)	0.2243(3)	0.0156(9)
N5	0.3431(5)	0.7722(5)	0.2937(4)	0.0177(10)
N6	0.4669(5)	0.7295(4)	0.3320(3)	0.0163(9)
N7	0.1890(5)	0.8648(4)	0.1230(4)	0.0185(10)
N8	0.3514(5)	0.1068(4)	0.1783(4)	0.0161(9)

	x/a	y/b	z/c	U(eq)
N9	0.3719(5)	0.4267(5)	0.0620(4)	0.0244(11)
N10	0.1019(4)	0.1490(4)	0.4018(3)	0.0166(9)
C1	0.5641(5)	0.1383(5)	0.4191(4)	0.0177(11)
C2	0.6852(5)	0.1392(6)	0.4957(4)	0.0204(12)
C3	0.7121(6)	0.0132(6)	0.4765(4)	0.0209(12)
C4	0.5056(6)	0.8257(5)	0.0755(4)	0.0165(11)
C5	0.6237(7)	0.7671(6)	0.0761(5)	0.0173(13)
C6	0.6745(6)	0.7496(5)	0.1716(4)	0.0186(11)
C7	0.2474(6)	0.6900(6)	0.2971(5)	0.0237(12)
C8	0.3053(7)	0.5929(6)	0.3372(5)	0.0275(14)
C9	0.4429(7)	0.6204(6)	0.3573(5)	0.0225(14)
C10	0.1255(6)	0.0560(6)	0.3329(4)	0.0151(13)
C11	0.9921(6)	0.9729(6)	0.2669(5)	0.0228(12)
C12	0.8830(6)	0.0566(6)	0.2927(5)	0.0268(13)
C13	0.9587(6)	0.1460(6)	0.3983(4)	0.0224(12)
C14	0.2068(6)	0.2486(5)	0.4748(4)	0.0218(12)
C15	0.2482(6)	0.1826(6)	0.1628(5)	0.0224(14)
C16	0.2511(6)	0.2887(6)	0.1260(5)	0.0233(13)
C17	0.3642(6)	0.3246(5)	0.1002(4)	0.0206(12)
C18	0.4732(6)	0.2483(5)	0.1186(4)	0.0214(12)
C19	0.4632(5)	0.1461(5)	0.1563(4)	0.0175(11)
C20	0.4715(7)	0.4375(6)	0.0119(5)	0.0291(14)
C21	0.2623(7)	0.5086(6)	0.0469(5)	0.0323(15)
B1	0.6007(6)	0.7991(6)	0.3347(5)	0.0160(12)

	x/a	y/b	z/c	U(eq)
Mo2	0.55373(4)	0.70967(4)	0.73711(3)	0.01284(11)
O3	0.4323(4)	0.4817(4)	0.5599(3)	0.0250(9)
O4	0.6569(4)	0.6118(4)	0.8416(3)	0.0180(8)
N11	0.6634(4)	0.8794(4)	0.8625(3)	0.0147(9)
N12	0.5935(4)	0.9797(4)	0.8913(3)	0.0138(9)
N13	0.4742(5)	0.8568(4)	0.6637(3)	0.0142(9)
N14	0.4345(4)	0.9642(4)	0.7182(3)	0.0143(9)
N15	0.3883(5)	0.7399(4)	0.8008(4)	0.0136(9)
N16	0.3563(5)	0.8619(4)	0.8328(4)	0.0163(9)
N17	0.4746(5)	0.5748(4)	0.6333(3)	0.0169(9)
N18	0.7327(5)	0.7066(4)	0.6878(4)	0.0197(10)
N19	0.0611(5)	0.6834(5)	0.5741(4)	0.0262(11)
N20	0.7835(5)	0.4689(4)	0.9084(3)	0.0164(9)
C22	0.7932(5)	0.9102(5)	0.9259(4)	0.0175(11)
C23	0.8073(6)	0.0289(6)	0.9938(4)	0.0218(12)
C24	0.6789(6)	0.0701(5)	0.9703(4)	0.0175(11)
C25	0.4556(5)	0.8704(5)	0.5731(4)	0.0173(11)
C26	0.4053(6)	0.9874(6)	0.5645(5)	0.0175(12)
C27	0.3917(5)	0.0422(5)	0.6582(4)	0.0180(11)
C28	0.2958(6)	0.6597(5)	0.8122(4)	0.0183(11)
C29	0.2037(6)	0.7291(6)	0.8502(4)	0.0204(12)
C30	0.2445(6)	0.8563(6)	0.8611(5)	0.0163(13)
C31	0.6774(6)	0.4966(5)	0.8417(4)	0.0154(12)
C32	0.5909(6)	0.3754(5)	0.7712(4)	0.0210(12)

	x/a	y/b	z/c	U(eq)
C33	0.651(2)	0.2698(16)	0.8136(14)	0.027(3)
C34	0.7913(6)	0.3306(5)	0.8958(5)	0.0222(12)
C35	0.8915(6)	0.5631(6)	0.9826(5)	0.0235(12)
C36	0.7863(7)	0.5949(6)	0.6615(5)	0.0194(14)
C37	0.8936(6)	0.5824(6)	0.6266(5)	0.0235(13)
C38	0.9567(5)	0.6903(6)	0.6127(4)	0.0188(11)
C39	0.9040(5)	0.8080(5)	0.6408(4)	0.0180(11)
C40	0.7966(5)	0.8111(5)	0.6778(4)	0.0173(11)
C41	0.1086(7)	0.7920(7)	0.5465(6)	0.0426(19)
C42	0.1189(6)	0.5621(7)	0.5494(5)	0.0343(16)
B2	0.4424(6)	0.9799(6)	0.8291(5)	0.0158(12)
S1	0.89567(15)	0.42398(14)	0.23020(11)	0.0221(3)
F1	0.7372(4)	0.3432(4)	0.3208(4)	0.0431(11)
F2	0.6641(3)	0.4953(3)	0.2532(3)	0.0275(8)
F3	0.8313(4)	0.5373(5)	0.3912(3)	0.0486(12)
O5	0.8134(5)	0.3363(5)	0.1370(3)	0.0374(12)
O6	0.0072(4)	0.3718(4)	0.2915(4)	0.0308(10)
O7	0.9296(6)	0.5527(5)	0.2257(5)	0.0424(14)
C43	0.7774(6)	0.4519(6)	0.3025(4)	0.0266(13)
S2	0.09161(15)	0.31643(14)	0.73761(11)	0.0220(3)
F4	0.1257(4)	0.0734(4)	0.7249(4)	0.0406(10)
F5	0.9404(5)	0.1286(4)	0.7528(5)	0.0512(14)
F6	0.1338(6)	0.1831(4)	0.8714(3)	0.0559(13)
O8	0.2363(5)	0.3346(5)	0.7549(4)	0.0376(11)

	x/a	y/b	z/c	U(eq)
O9	0.0087(5)	0.2828(5)	0.6337(4)	0.0397(12)
O10	0.0400(5)	0.4088(4)	0.8044(3)	0.0300(10)
C44	0.0742(7)	0.1695(6)	0.7738(5)	0.0320(15)
C33A	0.692(3)	0.272(2)	0.7919(19)	0.027(3)

Table 4. Bond lengths (Å) for $C_{22}H_{29}BF_3MoN_{10}O_5S$.

Mo1-N7	1.762(5)	Mo1-O2	2.100(4)
Mo1-N3	2.161(5)	Mo1-N8	2.171(5)
Mo1-N5	2.175(5)	Mo1-N1	2.220(5)
O1-N7	1.212(6)	O2-C10	1.244(7)
N1-C1	1.329(7)	N1-N2	1.358(6)
N2-C3	1.342(7)	N2-B1	1.551(7)
N3-C4	1.349(7)	N3-N4	1.359(6)
N4-C6	1.349(7)	N4-B1	1.553(7)
N5-C7	1.329(8)	N5-N6	1.372(6)
N6-C9	1.352(7)	N6-B1	1.539(8)
N8-C15	1.362(7)	N8-C19	1.370(7)
N9-C17	1.357(7)	N9-C20	1.443(8)
N9-C21	1.453(7)	N10-C10	1.312(7)
N10-C14	1.455(7)	N10-C13	1.465(7)
C1-C2	1.392(8)	C1-H1	0.95
C2-C3	1.372(8)	C2-H2A	0.95
C3-H3	0.95	C4-C5	1.390(8)
C4-H4	0.95	C5-C6	1.379(8)

C5-H5	0.95	C6-H6	0.95
C7-C8	1.383(9)	C7-H7	0.95
C8-C9	1.369(9)	C8-H8	0.95
C9-H9	0.95	C10-C11	1.522(8)
C11-C12	1.541(8)	C11-H11A	0.99
C11-H11B	0.99	C12-C13	1.539(8)
C12-H12A	0.99	C12-H12B	0.99
C13-H13A	0.99	C13-H13B	0.99
C14-H14A	0.98	C14-H14B	0.98
C14-H14C	0.98	C15-C16	1.377(9)
C15-H15	0.95	C16-C17	1.402(8)
C16-H16	0.95	C17-C18	1.412(8)
C18-C19	1.357(8)	C18-H18	0.95
C19-H19	0.95	C20-H20A	0.98
C20-H20B	0.98	C20-H20C	0.98
C21-H21A	0.98	C21-H21B	0.98
C21-H21C	0.98	B1-H1A	1.0
Mo2-N17	1.771(5)	Mo2-O4	2.095(4)
Mo2-N13	2.165(5)	Mo2-N15	2.172(5)
Mo2-N18	2.173(5)	Mo2-N11	2.215(4)
O3-N17	1.220(6)	O4-C31	1.266(7)
N11-C22	1.350(7)	N11-N12	1.368(6)
N12-C24	1.347(7)	N12-B2	1.547(7)
N13-C25	1.307(7)	N13-N14	1.379(6)
N14-C27	1.342(7)	N14-B2	1.543(7)

N15-C28	1.345(7)	N15-N16	1.368(6)
N16-C30	1.341(8)	N16-B2	1.552(8)
N18-C40	1.349(7)	N18-C36	1.357(7)
N19-C38	1.353(7)	N19-C41	1.444(9)
N19-C42	1.463(8)	N20-C31	1.316(7)
N20-C35	1.446(7)	N20-C34	1.464(7)
C22-C23	1.379(8)	C22-H22	0.95
C23-C24	1.381(8)	C23-H23	0.95
C24-H24	0.95	C25-C26	1.397(8)
C25-H25	0.95	C26-C27	1.386(8)
C26-H26	0.95	C27-H27	0.95
C28-C29	1.387(8)	C28-H28	0.95
C29-C30	1.379(9)	C29-H29	0.95
C30-H30	0.95	C31-C32	1.505(8)
C32-C33	1.485(18)	C32-C33A	1.57(3)
C32-H32A	0.99	C32-H32B	0.99
C32-H32C	0.99	C32-H32D	0.99
C33-C34	1.568(19)	C33-H33A	0.99
C33-H33B	0.99	C34-C33A	1.50(3)
C34-H34A	0.99	C34-H34B	0.99
C34-H34C	0.99	C34-H34D	0.99
C35-H35A	0.98	C35-H35B	0.98
C35-H35C	0.98	C36-C37	1.349(9)
C36-H36	0.95	C37-C38	1.403(9)
C37-H37	0.95	C38-C39	1.411(7)

C39-C40	1.370(7)	C39-H39	0.95
C40-H40	0.95	C41-H41A	0.98
C41-H41B	0.98	C41-H41C	0.98
C42-H42A	0.98	C42-H42B	0.98
C42-H42C	0.98	B2-H2	1.0
S1-O5	1.433(5)	S1-O7	1.442(5)
S1-O6	1.445(4)	S1-C43	1.822(6)
F1-C43	1.343(8)	F2-C43	1.335(7)
F3-C43	1.322(7)	S2-O9	1.429(5)
S2-O8	1.438(5)	S2-O10	1.441(4)
S2-C44	1.806(7)	F4-C44	1.326(7)
F5-C44	1.357(8)	F6-C44	1.321(8)
C33A-H33C	0.99	C33A-H33D	0.99

Table 5. Anisotropic atomic displacement parameters ($Å^2$) for $C_{22}H_{29}BF_3MoN_{10}O_5S$.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mo1	0.0115(2)	0.0146(3)	0.0126(3)	0.0019(2)	0.0042(2)	-0.0011(2)
O1	0.017(2)	0.040(3)	0.020(2)	-0.0045(19)	-0.0016(17)	-0.0050(19)
O2	0.0133(18)	0.0214(19)	0.019(2)	0.0030(16)	0.0092(16)	0.0028(16)
N1	0.015(2)	0.015(2)	0.015(2)	0.0044(18)	0.0059(18)	0.0013(18)
N2	0.013(2)	0.016(2)	0.015(2)	0.0057(17)	0.0056(17)	0.0006(17)
N3	0.015(2)	0.014(2)	0.011(2)	0.0052(19)	0.0037(18)	0.0025(19)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N4	0.015(2)	0.018(2)	0.014(2)	0.0046(18)	0.0060(18)	0.0042(18)
N5	0.020(2)	0.019(2)	0.013(2)	0.0020(19)	0.006(2)	0.002(2)
N6	0.024(2)	0.015(2)	0.014(2)	0.0055(19)	0.0104(19)	0.002(2)
N7	0.017(2)	0.016(2)	0.022(3)	0.0017(19)	0.009(2)	-0.0018(19)
N8	0.015(2)	0.019(2)	0.016(2)	0.0071(19)	0.0050(18)	0.0004(18)
N9	0.031(3)	0.020(2)	0.021(3)	0.008(2)	0.003(2)	0.005(2)
N10	0.015(2)	0.019(2)	0.015(2)	0.0015(18)	0.0050(18)	0.0019(18)
C1	0.017(3)	0.019(3)	0.017(3)	0.002(2)	0.008(2)	0.000(2)
C2	0.016(3)	0.024(3)	0.015(3)	-0.001(2)	0.002(2)	-0.008(2)
C3	0.013(2)	0.032(3)	0.013(3)	0.003(2)	0.001(2)	0.000(2)
C4	0.022(3)	0.015(2)	0.010(3)	0.003(2)	0.002(2)	-0.004(2)
C5	0.027(3)	0.020(3)	0.007(3)	0.001(2)	0.009(2)	0.002(3)
C6	0.017(3)	0.014(3)	0.025(3)	0.002(2)	0.008(2)	0.004(2)
C7	0.028(3)	0.022(3)	0.022(3)	0.001(2)	0.014(3)	-0.006(2)
C8	0.042(4)	0.018(3)	0.026(3)	0.002(2)	0.020(3)	-0.009(3)
C9	0.040(4)	0.015(3)	0.016(3)	0.003(2)	0.015(3)	0.001(3)
C10	0.019(3)	0.016(3)	0.009(3)	0.003(2)	0.003(2)	-0.003(2)
C11	0.020(3)	0.025(3)	0.023(3)	0.002(2)	0.010(2)	-0.001(2)
C12	0.016(3)	0.031(3)	0.030(3)	0.002(3)	0.008(3)	-0.002(2)
C13	0.018(3)	0.028(3)	0.019(3)	0.001(2)	0.007(2)	0.004(2)
C14	0.019(3)	0.019(3)	0.022(3)	-0.002(2)	0.006(2)	0.000(2)
C15	0.015(3)	0.028(4)	0.028(4)	0.012(3)	0.008(3)	0.005(3)
C16	0.023(3)	0.024(3)	0.024(3)	0.010(3)	0.006(3)	0.010(3)
C17	0.026(3)	0.014(3)	0.017(3)	-0.001(2)	0.003(2)	0.001(2)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C18	0.022(3)	0.016(3)	0.026(3)	0.004(2)	0.009(2)	0.002(2)
C19	0.015(2)	0.016(3)	0.021(3)	0.005(2)	0.006(2)	0.001(2)
C20	0.039(4)	0.024(3)	0.025(3)	0.013(3)	0.007(3)	-0.004(3)
C21	0.044(4)	0.022(3)	0.026(3)	0.006(3)	0.003(3)	0.013(3)
B1	0.018(3)	0.017(3)	0.015(3)	0.006(2)	0.005(2)	0.004(2)
Mo2	0.0137(2)	0.0121(2)	0.0117(3)	0.0020(2)	0.0037(2)	0.0001(2)
O3	0.027(2)	0.018(2)	0.020(2)	-0.0040(16)	0.0013(17)	-0.0026(17)
O4	0.022(2)	0.0132(18)	0.018(2)	0.0057(15)	0.0050(16)	0.0037(16)
N11	0.016(2)	0.013(2)	0.013(2)	0.0015(17)	0.0034(18)	0.0025(18)
N12	0.018(2)	0.012(2)	0.012(2)	0.0021(17)	0.0059(18)	0.0018(17)
N13	0.016(2)	0.016(2)	0.013(2)	0.0035(18)	0.0079(19)	0.0023(19)
N14	0.014(2)	0.010(2)	0.018(2)	0.0018(17)	0.0050(18)	0.0001(17)
N15	0.016(2)	0.016(2)	0.014(2)	0.009(2)	0.0076(18)	0.001(2)
N16	0.015(2)	0.017(2)	0.016(2)	0.0023(19)	0.0051(19)	0.0038(19)
N17	0.016(2)	0.019(2)	0.016(2)	0.0045(19)	0.0043(18)	0.0028(19)
N18	0.019(2)	0.015(2)	0.019(3)	-0.0018(19)	0.002(2)	0.0026(19)
N19	0.016(2)	0.035(3)	0.022(3)	-0.005(2)	0.008(2)	0.003(2)
N20	0.020(2)	0.015(2)	0.016(2)	0.0064(18)	0.0062(19)	0.0004(19)
C22	0.016(3)	0.019(3)	0.016(3)	0.004(2)	0.004(2)	-0.001(2)
C23	0.024(3)	0.021(3)	0.015(3)	0.003(2)	0.000(2)	-0.005(2)
C24	0.025(3)	0.013(2)	0.012(3)	0.001(2)	0.005(2)	-0.004(2)
C25	0.018(3)	0.022(3)	0.011(3)	0.003(2)	0.005(2)	-0.002(2)
C26	0.017(3)	0.022(3)	0.015(3)	0.008(2)	0.006(2)	-0.002(2)
C27	0.015(2)	0.015(3)	0.022(3)	0.007(2)	0.002(2)	-0.001(2)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C28	0.020(3)	0.016(3)	0.016(3)	0.006(2)	0.002(2)	-0.005(2)
C29	0.016(3)	0.031(3)	0.016(3)	0.009(2)	0.007(2)	-0.002(2)
C30	0.014(3)	0.026(3)	0.009(3)	0.005(2)	0.004(2)	0.004(2)
C31	0.015(3)	0.015(3)	0.016(3)	0.003(2)	0.007(2)	0.000(2)
C32	0.023(3)	0.016(3)	0.018(3)	0.002(2)	0.001(2)	-0.007(2)
C33	0.039(10)	0.015(3)	0.023(8)	0.003(5)	0.007(5)	-0.003(6)
C34	0.026(3)	0.013(3)	0.027(3)	0.006(2)	0.007(2)	0.002(2)
C35	0.020(3)	0.023(3)	0.021(3)	0.002(2)	0.000(2)	0.000(2)
C36	0.026(3)	0.016(3)	0.017(3)	0.005(2)	0.007(3)	0.011(3)
C37	0.025(3)	0.021(3)	0.022(3)	0.002(2)	0.005(2)	0.009(2)
C38	0.015(2)	0.028(3)	0.008(2)	-0.002(2)	0.001(2)	0.005(2)
C39	0.012(2)	0.022(3)	0.018(3)	0.003(2)	0.003(2)	0.002(2)
C40	0.014(2)	0.015(2)	0.020(3)	0.003(2)	0.003(2)	0.000(2)
C41	0.028(3)	0.041(4)	0.054(5)	-0.010(3)	0.026(3)	-0.008(3)
C42	0.019(3)	0.053(4)	0.025(3)	-0.002(3)	0.008(3)	0.017(3)
B2	0.017(3)	0.016(3)	0.013(3)	0.003(2)	0.004(2)	0.001(2)
S1	0.0241(7)	0.0280(8)	0.0173(7)	0.0090(6)	0.0089(6)	0.0022(6)
F1	0.034(2)	0.055(3)	0.062(3)	0.040(2)	0.026(2)	0.018(2)
F2	0.0188(17)	0.0261(18)	0.030(2)	0.0020(15)	0.0004(15)	0.0064(15)
F3	0.034(2)	0.071(3)	0.022(2)	-0.009(2)	-0.0020(17)	0.018(2)
O5	0.030(2)	0.050(3)	0.025(3)	-0.005(2)	0.013(2)	-0.001(2)
O6	0.020(2)	0.035(2)	0.035(3)	0.009(2)	0.0067(19)	0.0060(19)
O7	0.033(3)	0.033(3)	0.065(4)	0.024(3)	0.012(3)	0.002(2)
C43	0.030(3)	0.036(3)	0.011(3)	0.005(3)	0.004(2)	0.008(3)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S2	0.0249(7)	0.0218(7)	0.0181(7)	0.0041(6)	0.0061(6)	0.0015(6)
F4	0.042(2)	0.0227(19)	0.067(3)	0.0078(19)	0.034(2)	0.0111(17)
F5	0.040(3)	0.022(2)	0.096(4)	-0.003(2)	0.044(3)	-0.0020(19)
F6	0.101(4)	0.043(3)	0.038(3)	0.025(2)	0.031(3)	0.023(3)
O8	0.025(2)	0.034(3)	0.052(3)	0.012(2)	0.011(2)	0.001(2)
O9	0.039(3)	0.046(3)	0.023(3)	0.001(2)	0.000(2)	0.008(2)
O10	0.047(3)	0.020(2)	0.022(2)	0.0013(17)	0.013(2)	0.008(2)
C44	0.032(3)	0.022(3)	0.033(4)	-0.006(3)	0.008(3)	0.005(3)
C33A	0.039(10)	0.015(3)	0.023(8)	0.003(5)	0.007(5)	-0.003(6)

Table 6. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for $C_{22}H_{29}BF_3MoN_{10}O_5S$.

	x/a	y/b	z/c	U(eq)
H1	0.5182	0.2121	0.4116	0.021
H2A	0.7371	0.2105	0.5489	0.024
H3	0.7884	-0.0191	0.5155	0.025
H4	0.4473	-0.1499	0.0194	0.02
H5	0.6612	-0.2559	0.0225	0.021
H6	0.7554	-0.2882	0.1962	0.022
H7	0.1521	-0.3030	0.2749	0.028
H8	0.2599	-0.4771	0.3484	0.033
H9	0.5110	-0.4297	0.3849	0.027
H11A	-0.0140	-0.1100	0.2842	0.027
H11B	-0.0173	-0.0444	0.1944	0.027

	x/a	y/b	z/c	U(eq)
H12A	-0.1507	0.1070	0.2430	0.032
H12B	-0.1954	0.0027	0.2939	0.032
H13A	-0.0717	0.2331	0.4057	0.027
H13B	-0.0556	0.1105	0.4520	0.027
H14A	0.1948	0.3302	0.4565	0.033
H14B	0.2973	0.2236	0.4750	0.033
H14C	0.1991	0.2589	0.5423	0.033
H15	0.1689	0.1610	0.1783	0.027
H16	0.1757	0.3381	0.1179	0.028
H18	0.5540	0.2686	0.1044	0.026
H19	0.5395	0.0982	0.1683	0.021
H20A	0.4626	0.3576	-0.0410	0.044
H20B	0.5636	0.4522	0.0612	0.044
H20C	0.4558	0.5099	-0.0186	0.044
H21A	0.2199	0.5147	0.0999	0.048
H21B	0.1935	0.4716	-0.0194	0.048
H21C	0.2996	0.5948	0.0502	0.048
H1A	0.6812	-0.2430	0.3664	0.019
H22	0.8649	0.8575	0.9240	0.021
H23	0.8881	1.0730	1.0457	0.026
H24	0.6548	1.1488	1.0041	0.021
H25	0.4739	0.8089	0.5202	0.021
H26	0.3850	1.0215	0.5075	0.021
H27	0.3576	1.1223	0.6768	0.022

	x/a	y/b	z/c	U(eq)
H28	0.2937	0.5686	0.7965	0.022
H29	0.1287	0.6962	0.8655	0.024
H30	0.2008	0.9281	0.8846	0.02
H32A	0.4944	0.3780	0.7692	0.025
H32B	0.5948	0.3638	0.7019	0.025
H32C	0.5646	0.3786	0.6999	0.025
H32D	0.5075	0.3590	0.7885	0.025
H33A	0.6644	0.1993	0.7599	0.032
H33B	0.5896	0.2344	0.8443	0.032
H34A	0.8009	0.3076	0.9598	0.027
H34B	0.8687	0.3026	0.8721	0.027
H34C	0.7636	0.3015	0.9477	0.027
H34D	0.8848	0.3087	0.8997	0.027
H35A	0.8658	0.6499	0.9827	0.035
H35B	0.9761	0.5532	0.9656	0.035
H35C	0.9056	0.5498	1.0496	0.035
H36	0.7448	0.5192	0.6683	0.023
H37	0.9263	0.5009	0.6115	0.028
H39	0.9430	0.8849	0.6341	0.022
H40	0.7649	0.8921	0.6978	0.021
H41A	1.1530	0.8618	0.6076	0.064
H41B	1.0308	0.8220	0.5024	0.064
H41C	1.1743	0.7659	0.5107	0.064
H42A	1.0551	0.5038	0.4879	0.051

	x/a	y/b	z/c	U(eq)
H42B	1.1343	0.5221	0.6055	0.051
H42C	1.2059	0.5790	0.5384	0.051
H2	0.4070	1.0618	0.8559	0.019
H33C	0.6417	0.1908	0.7894	0.032
H33D	0.7398	0.2533	0.7411	0.032

Compound **12** BF_4: Data collected by Diane A. Dickie

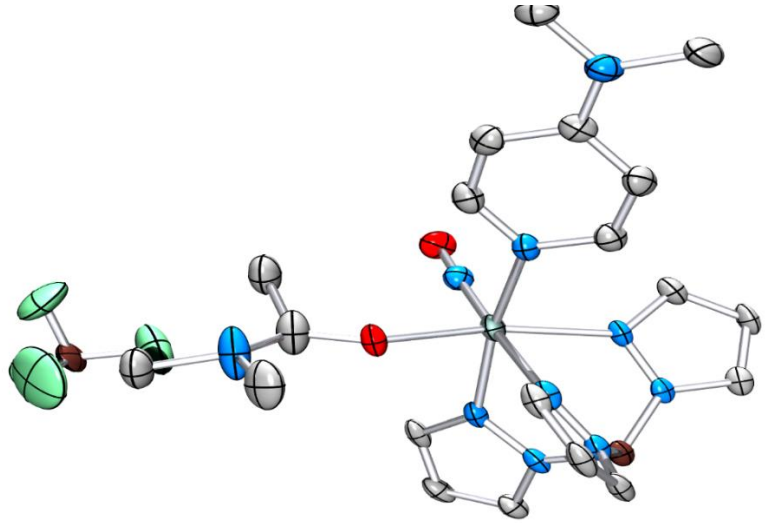


Table 1. Sample and crystal data for $C_{20}H_{29}B_2F_4MoN_{10}O_2$.

Chemical formula	$C_{20}H_{29}B_2F_4MoN_{10}O_2$
Formula weight	635.09 g/mol
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal size	0.075 x 0.114 x 0.588 mm

Crystal habit	green plate	
Crystal system	monoclinic	
Space group	P $2_1/c$	
Unit cell dimensions	a = 7.5837(7) Å	α = 90°
	b = 12.7264(10) Å	β = 90.941(2)°
	c = 29.155(2) Å	γ = 90°
Volume	2813.5(4) $Å^3$	
Z	4	
Density (calculated)	1.499 g/cm^3	
Absorption coefficient	0.530 mm^{-1}	
F(000)	1292	

Table 2. Data collection and structure refinement for $C_{20}H_{29}B_2F_4MoN_{10}O_2$.

Diffractometer	Bruker Kappa APEXII Duo
Radiation source	fine-focus sealed tube (Mo K_α, λ = 0.71073 Å)
Theta range for data collection	1.40 to 26.02°
Index ranges	-8<=h<=9, -15<=k<=15, -35<=l<=33
Reflections collected	34003
Independent reflections	5555 [R(int) = 0.0736]
Coverage of independent reflections	100.0%
Absorption correction	Multi-Scan
Max. and min. transmission	0.9610 and 0.7460
Structure solution technique	direct methods
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)

Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2017/1 (Sheldrick, 2017)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	5555 / 96 / 404	
Goodness-of-fit on F^2	1.142	
Final R indices	4349 data; I>2σ(I)	R1 = 0.0563, wR2 = 0.1174
	all data	R1 = 0.0774, wR2 = 0.1249
Weighting scheme	$w=1/[\sigma^2(F_o^2)+11.7630P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.841 and -0.934 eÅ^{-3}	
R.M.S. deviation from mean	0.098 eÅ^{-3}	

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for $C_{20}H_{29}B_2F_4MoN_{10}O_2$.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
Mo1	0.45595(5)	0.22249(3)	0.65896(2)	0.02310(12)
O1	0.1243(5)	0.2542(3)	0.60366(12)	0.0353(9)
O2	0.6050(5)	0.3536(2)	0.63812(12)	0.0319(8)
N1	0.6922(5)	0.1897(3)	0.70283(14)	0.0233(9)
N2	0.6733(5)	0.1660(3)	0.74791(14)	0.0225(8)
N3	0.3560(5)	0.0853(3)	0.69215(13)	0.0217(8)
N4	0.3880(5)	0.0705(3)	0.73780(13)	0.0194(8)

	x/a	y/b	z/c	U(eq)
N5	0.3609(5)	0.3018(3)	0.71921(14)	0.0226(8)
N6	0.3903(5)	0.2590(3)	0.76166(13)	0.0221(8)
N7	0.2611(5)	0.2428(3)	0.62591(14)	0.0267(9)
N8	0.5862(5)	0.1305(3)	0.60674(14)	0.0255(9)
N9	0.7845(6)	0.9392(3)	0.50285(14)	0.0334(10)
N10	0.7227(7)	0.5045(4)	0.6156(2)	0.0579(16)
C1	0.8670(6)	0.1946(3)	0.69545(19)	0.0283(11)
C2	0.9585(6)	0.1748(4)	0.73592(19)	0.0303(12)
C3	0.8333(6)	0.1564(3)	0.76826(18)	0.0264(11)
C4	0.2634(6)	0.0022(4)	0.67728(18)	0.0271(11)
C5	0.2353(6)	0.9324(3)	0.71307(18)	0.0279(11)
C6	0.3149(6)	0.9783(4)	0.75043(17)	0.0244(10)
C7	0.2653(6)	0.3893(3)	0.72596(18)	0.0268(11)
C8	0.2356(6)	0.4038(4)	0.77158(18)	0.0276(11)
C9	0.3161(6)	0.3203(3)	0.79340(17)	0.0249(10)
C10	0.5858(8)	0.4405(5)	0.6183(2)	0.0506(17)
C11	0.4066(14)	0.4829(9)	0.6078(5)	0.050(2)
C12	0.8937(8)	0.4730(5)	0.6346(3)	0.0565(18)
C13	0.7032(18)	0.6027(10)	0.5859(5)	0.050(2)
C13A	0.725(3)	0.6202(15)	0.6070(7)	0.050(2)
C14	0.6391(6)	0.0303(4)	0.61442(18)	0.0287(11)
C15	0.7066(7)	0.9655(4)	0.58157(18)	0.0328(12)
C16	0.7242(6)	0.0012(4)	0.53653(17)	0.0275(11)
C17	0.6737(7)	0.1069(4)	0.52848(18)	0.0317(12)

	x/a	y/b	z/c	U(eq)
C18	0.6064(6)	0.1643(4)	0.56332(18)	0.0313(11)
C19	0.8002(7)	0.9784(4)	0.45605(17)	0.0352(12)
C20	0.8121(8)	0.8266(4)	0.5108(2)	0.0428(14)
B1	0.4874(7)	0.1524(4)	0.7671(2)	0.0224(11)
F1	0.137(2)	0.6600(7)	0.6186(4)	0.085(4)
F2	0.2392(17)	0.7470(12)	0.5588(3)	0.098(4)
F3	0.3594(14)	0.7733(8)	0.6283(4)	0.085(4)
F4	0.0841(11)	0.8322(7)	0.6135(3)	0.057(3)
B2	0.2048(17)	0.7563(8)	0.6048(4)	0.041(3)
C11A	0.428(2)	0.4505(14)	0.5798(7)	0.050(2)
B2A	0.243(3)	0.7328(16)	0.5975(7)	0.041(3)
F1A	0.234(3)	0.6459(13)	0.6222(5)	0.059(5)
F2A	0.236(4)	0.707(2)	0.5537(7)	0.153(14)
F3A	0.393(3)	0.7813(18)	0.6063(11)	0.131(11)
F4A	0.110(3)	0.796(2)	0.6071(9)	0.136(11)

Table 4. Bond lengths (Å) for $C_{20}H_{29}B_2F_4MoN_{10}O_2$.

Mo1-N7	1.770(4)	Mo1-O2	2.110(3)
Mo1-N3	2.141(4)	Mo1-N5	2.160(4)
Mo1-N8	2.171(4)	Mo1-N1	2.224(4)
O1-N7	1.223(5)	O2-C10	1.255(6)
N1-C1	1.348(6)	N1-N2	1.358(5)
N2-C3	1.347(6)	N2-B1	1.535(6)
N3-C4	1.338(6)	N3-N4	1.362(5)

N4-C6	1.351(6)	N4-B1	1.537(6)
N5-C7	1.345(6)	N5-N6	1.367(5)
N6-C9	1.341(6)	N6-B1	1.551(6)
N8-C18	1.348(6)	N8-C14	1.354(6)
N9-C16	1.345(6)	N9-C19	1.459(6)
N9-C20	1.467(7)	N10-C10	1.323(8)
N10-C12	1.458(8)	N10-C13A	1.494(19)
N10-C13	1.527(13)	C1-C2	1.382(7)
C1-H1	0.95	C2-C3	1.370(7)
C2-H2	0.95	C3-H3	0.95
C4-C5	1.389(7)	C4-H4	0.95
C5-C6	1.368(7)	C5-H5	0.95
C6-H6	0.95	C7-C8	1.365(7)
C7-H7	0.95	C8-C9	1.376(7)
C8-H8	0.95	C9-H9	0.95
C10-C11	1.489(12)	C10-C11A	1.630(18)
C11-H11A	0.98	C11-H11B	0.98
C11-H11C	0.98	C12-H12A	0.98
C12-H12B	0.98	C12-H12C	0.98
C13-H13A	0.98	C13-H13B	0.98
C13-H13C	0.98	C13A-H13D	0.98
C13A-H13E	0.98	C13A-H13F	0.98
C14-C15	1.369(7)	C14-H14	0.95
C15-C16	1.398(7)	C15-H15	0.95
C16-C17	1.418(7)	C17-C18	1.357(7)

C17-H17	0.95	C18-H18	0.95
C19-H19A	0.98	C19-H19B	0.98
C19-H19C	0.98	C20-H20A	0.98
C20-H20B	0.98	C20-H20C	0.98
B1-H1A	1.03(5)	F1-B2	1.391(10)
F2-B2	1.375(11)	F3-B2	1.366(11)
F4-B2	1.358(10)	C11A-H11D	0.98
C11A-H11E	0.98	C11A-H11F	0.98
B2A-F3A	1.313(17)	B2A-F2A	1.318(17)
B2A-F4A	1.322(16)	B2A-F1A	1.323(17)

Table 5. Anisotropic atomic displacement parameters ($Å^2$) for $C_{20}H_{29}B_2F_4MoN_{10}O_2$.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mo1	0.01906(19)	0.01653(19)	0.0337(2)	0.00166(19)	0.00046(15)	0.00161(17)
O1	0.0290(19)	0.037(2)	0.040(2)	-0.0015(16)	-0.0068(16)	0.0082(15)
O2	0.0324(19)	0.0174(16)	0.046(2)	0.0057(15)	-0.0003(17)	-0.0001(14)
N1	0.0146(18)	0.0177(19)	0.038(2)	0.0000(16)	0.0038(17)	-0.0001(14)
N2	0.0179(19)	0.0145(18)	0.035(2)	-0.0004(16)	-0.0018(17)	0.0003(15)
N3	0.0171(19)	0.0134(17)	0.035(2)	-0.0002(16)	0.0012(17)	-0.0012(14)
N4	0.0126(18)	0.0149(18)	0.031(2)	0.0007(16)	-0.0001(16)	0.0032(14)
N5	0.0179(18)	0.0144(18)	0.036(2)	0.0014(16)	-0.0045(17)	0.0001(14)
N6	0.0161(18)	0.0151(18)	0.035(2)	-0.0049(16)	-0.0003(16)	-0.0008(14)
N7	0.027(2)	0.024(2)	0.029(2)	-0.0008(17)	0.0031(18)	0.0044(16)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N8	0.024(2)	0.020(2)	0.032(2)	0.0024(17)	-0.0007(18)	0.0009(16)
N9	0.035(2)	0.034(2)	0.031(2)	-0.0031(19)	-0.001(2)	0.0046(19)
N10	0.033(3)	0.032(3)	0.108(5)	0.026(3)	0.012(3)	0.003(2)
C1	0.016(2)	0.018(2)	0.051(3)	0.000(2)	0.009(2)	-0.0011(17)
C2	0.016(2)	0.016(2)	0.059(4)	-0.002(2)	-0.005(2)	-0.0014(18)
C3	0.020(2)	0.014(2)	0.045(3)	-0.003(2)	-0.009(2)	0.0018(18)
C4	0.020(2)	0.020(2)	0.041(3)	-0.005(2)	-0.001(2)	-0.0001(19)
C5	0.019(2)	0.014(2)	0.050(3)	0.000(2)	0.000(2)	-0.0041(18)
C6	0.015(2)	0.021(2)	0.038(3)	0.003(2)	0.004(2)	0.0006(18)
C7	0.016(2)	0.014(2)	0.050(3)	-0.001(2)	-0.009(2)	-0.0003(18)
C8	0.019(2)	0.020(2)	0.044(3)	-0.011(2)	-0.003(2)	0.0032(19)
C9	0.019(2)	0.021(2)	0.035(3)	-0.006(2)	-0.001(2)	0.0022(18)
C10	0.041(3)	0.034(3)	0.077(5)	0.018(3)	0.004(3)	0.000(3)
C11	0.047(3)	0.033(4)	0.070(7)	0.015(4)	-0.010(4)	-0.001(3)
C12	0.031(3)	0.046(4)	0.093(5)	0.018(4)	0.006(3)	-0.011(3)
C13	0.047(3)	0.033(4)	0.070(7)	0.015(4)	-0.010(4)	-0.001(3)
C13A	0.047(3)	0.033(4)	0.070(7)	0.015(4)	-0.010(4)	-0.001(3)
C14	0.025(3)	0.027(3)	0.034(3)	0.001(2)	-0.002(2)	0.003(2)
C15	0.034(3)	0.028(3)	0.037(3)	0.001(2)	-0.003(2)	0.007(2)
C16	0.017(2)	0.032(3)	0.034(3)	-0.003(2)	-0.002(2)	0.001(2)
C17	0.027(3)	0.033(3)	0.035(3)	0.004(2)	0.000(2)	-0.006(2)
C18	0.026(3)	0.025(3)	0.043(3)	0.001(2)	0.001(2)	-0.001(2)
C19	0.032(3)	0.042(3)	0.032(3)	-0.003(2)	0.003(2)	-0.003(2)
C20	0.059(4)	0.031(3)	0.039(3)	-0.007(3)	-0.003(3)	0.011(3)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
B1	0.017(3)	0.018(3)	0.031(3)	0.000(2)	0.000(2)	0.002(2)
F1	0.093(9)	0.039(4)	0.124(8)	0.007(4)	0.032(7)	-0.017(5)
F2	0.157(9)	0.100(9)	0.039(5)	0.030(4)	0.018(5)	-0.008(6)
F3	0.067(6)	0.077(6)	0.110(8)	-0.049(5)	-0.049(5)	0.037(5)
F4	0.046(4)	0.043(5)	0.080(5)	-0.009(4)	-0.027(3)	0.016(3)
B2	0.059(8)	0.014(6)	0.049(6)	-0.004(4)	-0.007(6)	0.010(6)
C11A	0.047(3)	0.033(4)	0.070(7)	0.015(4)	-0.010(4)	-0.001(3)
B2A	0.059(8)	0.014(6)	0.049(6)	-0.004(4)	-0.007(6)	0.010(6)
F1A	0.065(11)	0.063(9)	0.049(8)	0.018(6)	-0.010(8)	-0.025(8)
F2A	0.27(3)	0.075(16)	0.107(18)	0.039(11)	-0.094(19)	-0.024(15)
F3A	0.111(15)	0.107(14)	0.18(2)	0.017(15)	0.028(15)	-0.077(13)
F4A	0.15(2)	0.089(18)	0.164(19)	-0.051(15)	-0.044(15)	0.053(14)

Table 6. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for $C_{20}H_{29}B_2F_4MoN_{10}O_2$**.**

	x/a	y/b	z/c	U(eq)
H1	0.9193	0.2093	0.6668	0.034
H2	1.0829	0.1742	0.7404	0.036
H3	0.8553	0.1397	0.7996	0.032
H4	0.2227	-0.0077	0.6466	0.032
H5	0.1742	-0.1327	0.7119	0.033
H6	0.3183	-0.0501	0.7805	0.029
H7	0.2242	0.4347	0.7022	0.032
H8	0.1726	0.4598	0.7853	0.033

	x/a	y/b	z/c	U(eq)
H9	0.3187	0.3082	0.8256	0.03
H11A	0.3233	0.4246	0.6039	0.076
H11B	0.4098	0.5240	0.5794	0.076
H11C	0.3689	0.5280	0.6330	0.076
H12A	0.9111	0.5051	0.6649	0.085
H12B	0.9871	0.4965	0.6142	0.085
H12C	0.8979	0.3963	0.6375	0.085
H13A	0.7127	0.5834	0.5535	0.076
H13B	0.7965	0.6529	0.5941	0.076
H13C	0.5878	0.6349	0.5911	0.076
H13D	0.7258	0.6333	0.5739	0.076
H13E	0.8302	0.6511	0.6214	0.076
H13F	0.6191	0.6522	0.6201	0.076
H14	0.6287	0.0031	0.6446	0.034
H15	0.7415	-0.1040	0.5894	0.039
H17	0.6869	0.1374	0.4990	0.038
H18	0.5704	0.2341	0.5565	0.038
H19A	0.6824	-0.0075	0.4432	0.053
H19B	0.8591	-0.0745	0.4373	0.053
H19C	0.8695	0.0433	0.4563	0.053
H20A	0.8973	-0.1832	0.5361	0.064
H20B	0.8575	-0.2060	0.4829	0.064
H20C	0.6998	-0.2064	0.5187	0.064
H11D	0.4792	0.4494	0.5491	0.076

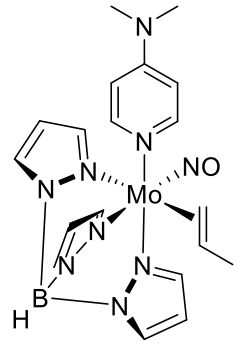
	x/a	y/b	z/c	U(eq)
H11E	0.3649	0.5167	0.5842	0.076
H11F	0.3465	0.3915	0.5830	0.076
H1A	0.491(6)	0.132(4)	0.8012(16)	0.022(12)

Mo$_R$Tp(NO)(DMAP)(I)/[MoTp(NO)(DMAP)(κ^1-DMA)] I (enantioenriched mixture) (**13**/**12**)

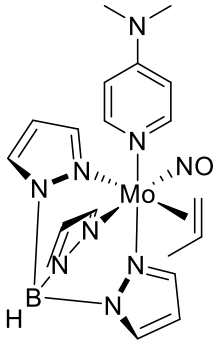
In a 250 mL round bottom flask charged with a stir egg, MoTp(NO)(DMAP)(I) (3.0 g, 0.0050 mol), THF (75mL), (S)-α-pinene (20 mL, 0.13 mol), DMA (0.3 mL), and magnesium powder (6g, untreated, 325 mesh) were combined and allowed to mix, capped, for 2 days. The solution was added to a 30 mL medium porosity fritted disk, ~3/4 full of silica, and eluted with ~100 mL ether. The ether solution was dried *in vacuo* with a nitrogen stream. Once dried, 10 mL of THF was used to dissolve the solid. A solution of iodine (0.33 g, 0.0025 mol) in 20 mL of ether was then added to the orange solution. The now green solution was evaporated *in vacuo* to dryness, then dissolved in minimal THF (3 mL), and added to 150 mL stirring

pentane. The light green solid was then collected on a 30 mL medium porosity fritted disk, washed with hexanes (3x15 mL), desiccated, and collected (1.4 g, ~45 % mass recovery).

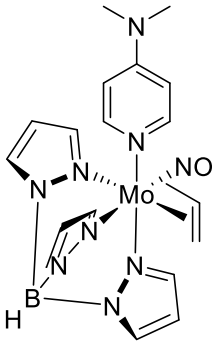
MoTp(NO)(DMAP)(η^2-Propene) (**14**)



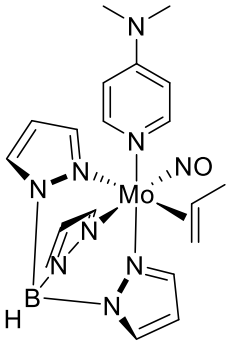
A



B



C



D

Gaussian DFT of:

14A Input

%mem=12GB
%nprocshared=12

#	opt	b3lyp/gen	geom=connectivity	pseudo=read
Title	Card	Required		
0	1			
	Mo	2.09174418	-2.37101084	0
	O	1.04936553	-0.74681203	-2.31810791
	N	4.18557718	-2.51119184	-0.522953
	N	4.94064718	-3.71263884	-0.338903
	N	2.61487818	-3.76050484	1.735527
	N	3.59804818	-4.77828584	1.537245
	N	2.12525318	-4.28578084	-1.117818
	N	3.09380018	-5.30348584	-0.878013
	N	-0.00215282	-3.06195584	0.205494
	N	1.49934318	-1.44795184	-1.317419

C	6.23489618	-3.51395584	-0.816416
C	6.34033018	-2.20874684	-1.299718
C	5.06758618	-1.61893684	-1.108258
C	3.82260418	-5.44797884	2.735934
C	3.00483718	-4.88861184	3.721188
C	2.28043418	-3.85767884	3.07921
C	2.85372018	-6.37692684	-1.730092
C	1.73656218	-6.08102484	-2.516968
C	1.31425518	-4.79004084	-2.119853
C	-0.45134282	-4.04867284	1.086559
B	4.24559318	-5.02193484	0.137413
H	5.00577918	-5.91659884	0.182033
H	6.96804418	-4.32677384	-0.767497
H	7.22274418	-1.73663684	-1.735727
H	4.72809018	-0.60533484	-1.34754
H	4.54791318	-6.26833484	2.78111
H	2.94010118	-5.18310084	4.770408
H	1.54139718	-3.17113584	3.506552
H	3.50299518	-7.25940384	-1.702137
H	1.28667018	-6.71312884	-3.284947
H	0.47963118	-4.18723384	-2.496126
H	0.31971218	-4.47731584	1.741967
C	-1.76985782	-4.49594884	1.165983
H	-2.01723982	-5.27774684	1.889976
C	-0.98644882	-2.54926384	-0.65148
H	-0.60050082	-1.79221584	-1.388381
C	-2.77141082	-3.93729784	0.309652
C	-2.32219382	-2.95149684	-0.624863
H	-3.01778182	-2.49816984	-1.337781
N	-4.13255182	-4.31564684	0.406436
C	-4.50731582	-5.51879484	1.212924
H	-5.60586682	-5.60764284	1.212433
H	-4.07193482	-6.45272184	0.802683
H	-4.16684282	-5.39616384	2.256744
C	-5.09354382	-3.88232784	-0.655591
H	-4.84924382	-4.31620784	-1.646585
H	-6.10437182	-4.20942984	-0.362253
H	-5.09202582	-2.78083884	-0.739214
C	2.80373718	-0.65838684	1.07271
C	1.39701018	-0.96826084	1.445798
H	1.2678818	-1.36279007	2.43198893
H	0.67013824	-0.2707351	1.08522203
C	2.93481311	0.60371149	0.20005491
H	3.96449321	0.76413568	-0.04268565

H	2.37195149	0.47454156	-0.7007236
H	2.55906682	1.44936937	0.73724899
H	3.63932192	-1.25213477	1.37956751

1	10	1		
2	10	1		
3	4	1	13	1
4	11	1	21	1
5	6	1	16	1
6	14	1	21	1
7	8	1	19	1
8	17	1	21	1
9	20	1.5	35	1.5
10				
11	12	1.5	23	1
12	13	1.5	24	1
13	25	1		
14	15	1.5	26	1
15	16	1.5	27	1
16	28	1		
17	18	1.5	29	1
18	19	1.5	30	1
19	31	1		
20	32	1	33	1.5
21	22	1		
22				
23				
24				
25				
26				
27				
28				
29				
30				
31				
32				
33	34	1	37	1.5
34				
35	36	1	38	1.5
36				
37	38	1.5	40	1
38	39	1		
39				
40	41	1	45	1

41 42 1 43 1 44 1
42
43
44
45 46 1 47 1 48 1
46
47
48
49 50 2 53 1 57 1
50 51 1 52 1
51
52
53 54 1 55 1 56 1
54
55
56
57

Mo 0
LANL2DZ
*****
H B C N O 0
6-31G(d)
*****

Mo 0
LANL2DZ

15A Output coordinates

Tag	Symbol	X	Y	Z
1	Mo	-0.62398	0.809586	-0.04509
2	O	-0.23132	3.056062	1.871844
3	N	-2.82787	0.522937	0.368493
4	N	-3.37373	-0.72551	0.364093
5	N	-0.98161	-0.93394	-1.58067
6	N	-1.83019	-1.93962	-1.23439
7	N	-0.57304	-0.94798	1.407904
8	N	-1.41786	-2.00176	1.256431
9	N	1.625039	0.434956	-0.08957
10	N	-0.41529	2.128107	1.122684
11	C	-4.66525	-0.66195	0.767167
12	C	-4.97491	0.65868	1.045169
13	C	-3.78592	1.358591	0.78556

14	C	-1.97248	-2.80035	-2.26504
15	C	-1.19427	-2.35355	-3.32362
16	C	-0.59699	-1.18038	-2.84165
17	C	-1.18628	-2.91748	2.223181
18	C	-0.15685	-2.45439	3.030464
19	C	0.189797	-1.21318	2.475524
20	C	2.159094	-0.74134	-0.4772
21	B	-2.50637	-1.98354	0.155851
22	H	-3.18651	-2.97136	0.23787
23	H	-5.26052	-1.56148	0.828664
24	H	-5.91805	1.059183	1.386214
25	H	-3.57216	2.411268	0.888639
26	H	-2.61575	-3.66334	-2.17053
27	H	-1.08002	-2.80635	-4.29735
28	H	0.083905	-0.50652	-3.34181
29	H	-1.77222	-3.82431	2.268037
30	H	0.271704	-2.93839	3.895628
31	H	0.939004	-0.50034	2.789948
32	H	1.453082	-1.49185	-0.81384
33	C	3.515556	-1.0213	-0.46536
34	H	3.843048	-1.99824	-0.79801
35	C	2.498219	1.370305	0.344943
36	H	2.063441	2.307992	0.672668
37	C	4.43569	-0.04348	-0.01998
38	C	3.867797	1.183876	0.40023
39	H	4.482032	1.994811	0.770815
40	N	5.78784	-0.26889	0.005539
41	C	6.316886	-1.56253	-0.39916
42	H	7.404981	-1.54411	-0.32355
43	H	5.944305	-2.37568	0.239457
44	H	6.054418	-1.79699	-1.43926
45	C	6.688019	0.758167	0.508927
46	H	6.488187	0.998229	1.562518
47	H	7.716156	0.401734	0.431939
48	H	6.607088	1.68465	-0.07442
49	C	-1.39999	2.204599	-1.67635
50	C	0.007989	2.074357	-1.7804
51	H	0.450748	1.456856	-2.56098
52	H	0.642467	2.909368	-1.48156
53	C	-2.04107	3.526639	-1.30844
54	H	-3.06779	3.403319	-0.94757
55	H	-1.46886	4.049747	-0.53436
56	H	-2.09448	4.187258	-2.18793
57	H	-2.00178	1.59131	-2.34902

14B Input

```
%mem=12GB
%nprocshared=12
#                opt    b3lyp/gen        geom=connectivity    pseudo=read

Title            Card   Required

                 0      1
                 Mo      2.09174418          -2.37101084                0
                 O       1.04936553          -0.74681203       -2.31810791
                 N       4.18557718          -2.51119184        -0.522953
                 N       4.94064718          -3.71263884        -0.338903
                 N       2.61487818          -3.76050484         1.735527
                 N       3.59804818          -4.77828584         1.537245
                 N       2.12525318          -4.28578084        -1.117818
                 N       3.09380018          -5.30348584        -0.878013
                 N      -0.00215282          -3.06195584         0.205494
                 N       1.49934318          -1.44795184        -1.317419
                 C       6.23489618          -3.51395584        -0.816416
                 C       6.34033018          -2.20874684        -1.299718
                 C       5.06758618          -1.61893684        -1.108258
                 C       3.82260418          -5.44797884         2.735934
                 C       3.00483718          -4.88861184         3.721188
                 C       2.28043418          -3.85767884          3.07921
                 C       2.85372018          -6.37692684        -1.730092
                 C       1.73656218          -6.08102484        -2.516968
                 C       1.31425518          -4.79004084        -2.119853
                 C      -0.45134282          -4.04867284         1.086559
                 B       4.24559318          -5.02193484         0.137413
                 H       5.00577918          -5.91659884         0.182033
                 H       6.96804418          -4.32677384        -0.767497
                 H       7.22274418          -1.73663684        -1.735727
                 H       4.72809018          -0.60533484         -1.34754
                 H       4.54791318          -6.26833484          2.78111
                 H       2.94010118          -5.18310084         4.770408
                 H       1.54139718          -3.17113584         3.506552
                 H       3.50299518          -7.25940384        -1.702137
                 H       1.28667018          -6.71312884        -3.284947
                 H       0.47963118          -4.18723384        -2.496126
                 H       0.31971218          -4.47731584         1.741967
```

C	-1.76985782	-4.49594884	1.165983
H	-2.01723982	-5.27774684	1.889976
C	-0.98644882	-2.54926384	-0.65148
H	-0.60050082	-1.79221584	-1.388381
C	-2.77141082	-3.93729784	0.309652
C	-2.32219382	-2.95149684	-0.624863
H	-3.01778182	-2.49816984	-1.337781
N	-4.13255182	-4.31564684	0.406436
C	-4.50731582	-5.51879484	1.212924
H	-5.60586682	-5.60764284	1.212433
H	-4.07193482	-6.45272184	0.802683
H	-4.16684282	-5.39616384	2.256744
C	-5.09354382	-3.88232784	-0.655591
H	-4.84924382	-4.31620784	-1.646585
H	-6.10437182	-4.20942984	-0.362253
H	-5.09202582	-2.78083884	-0.739214
C	2.80373718	-0.65838684	1.07271
C	1.39701018	-0.96826084	1.445798
H	1.2678818	-1.36279007	2.43198893
C	3.89220818	-0.83106984	2.173248
H	3.70794518	-1.71584984	2.797893
H	4.89464018	-0.93457184	1.726582
H	3.91807718	0.04956416	2.839107
H	0.67013824	-0.2707351	1.08522203
H	2.89480942	0.21852564	0.46638471

1	10	1	
2	10	1	
3	4	1	13
4	11	1	21
5	6	1	16
6	14	1	21
7	8	1	19
8	17	1	21
9	20	1.5	35
10			
11	12	1.5	23
12	13	1.5	24
13	25	1	
14	15	1.5	26
15	16	1.5	27
16	28	1	
17	18	1.5	29
18	19	1.5	30

19	31	1	
20	32	1	33
21	22	1	
22			
23			
24			
25			
26			
27			
28			
29			
30			
31			
32			
33	34	1	37
34			
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39			
40	41	1	45
41	42	1	43
42			
43			
44			
45	46	1	47
46			
47			
48			
49	50	2	52
50	51	1	56
51			
52	53	1	54
53			
54			
55			
56			
57			

Mo 0
LANL2DZ
*****
H B C N O

6-31G(d)
*****

Mo 0
LANL2DZ

14B Output Coordinates

Tag	Symbol	X	Y	Z
1	Mo	0.604579	-0.86326	0.047655
2	O	0.118503	-2.95811	2.108817
3	N	2.799054	-0.60767	0.450102
4	N	3.367887	0.628763	0.433418
5	N	0.981683	0.836402	-1.52486
6	N	1.851603	1.832013	-1.20343
7	N	0.551257	0.946194	1.432351
8	N	1.430373	1.970706	1.277208
9	N	-1.64369	-0.46904	-0.08022
10	N	0.342342	-2.0968	1.295222
11	C	4.674919	0.535264	0.774687
12	C	4.970754	-0.79573	1.02133
13	C	3.75872	-1.46978	0.804237
14	C	1.967681	2.694467	-2.23614
15	C	1.149928	2.258829	-3.2697
16	C	0.555761	1.091089	-2.7705
17	C	1.210438	2.911315	2.222675
18	C	0.153821	2.494333	3.019829
19	C	-0.22086	1.253715	2.48168
20	C	-2.15969	0.711338	-0.48051
21	B	2.52749	1.898929	0.189341
22	H	3.22816	2.873902	0.24712
23	H	5.291491	1.421442	0.816541
24	H	5.920834	-1.21806	1.31325
25	H	3.530313	-2.52307	0.880472
26	H	2.620847	3.551861	-2.16049
27	H	1.009774	2.715051	-4.23844
28	H	-0.14951	0.423964	-3.24596
29	H	1.822499	3.80103	2.260949
30	H	-0.27501	3.007315	3.867986
31	H	-0.99582	0.569151	2.796639

32	H	-1.44054	1.458243	-0.7958
33	C	-3.51396	1.000871	-0.50512
34	H	-3.82498	1.980832	-0.84464
35	C	-2.53569	-1.39582	0.334269
36	H	-2.11747	-2.33418	0.680509
37	C	-4.45304	0.029753	-0.08539
38	C	-3.90499	-1.19988	0.353404
39	H	-4.53401	-2.0047	0.712335
40	N	-5.80413	0.2639	-0.0989
41	C	-6.31165	1.566816	-0.50153
42	H	-7.40193	1.552599	-0.46729
43	H	-5.9592	2.369161	0.162128
44	H	-6.00989	1.814453	-1.52752
45	C	-6.72328	-0.74892	0.399144
46	H	-6.55657	-0.96934	1.462994
47	H	-7.74717	-0.3907	0.283161
48	H	-6.62848	-1.6865	-0.16349
49	C	1.418359	-2.45337	-1.38648
50	C	0.031013	-2.26964	-1.60977
51	H	-0.2926	-1.74788	-2.51178
52	C	2.460637	-2.06803	-2.41641
53	H	2.147407	-1.20446	-3.01115
54	H	3.425544	-1.82431	-1.95779
55	H	2.632461	-2.90301	-3.11333
56	H	-0.68805	-3.00557	-1.25273
57	H	1.706162	-3.31131	-0.77696

14C Input

```
%mem=12GB                14C
%nprocshared=12
#                opt     freq              b3lyp/gen       geom=connectivity   pseudo=read

Title                    Card    Required

                  0      1
                         Mo        -6.20487812     -5.25876521                0
                         O         -4.67281312     -5.49931221          -2.533437
                         N         -8.06166812     -6.27973121          -0.481357
                         N         -9.35391012     -5.69661821          -0.305642
                         N         -7.41272812     -4.38177821           1.777962
                         N         -8.79961912     -4.08975521           1.575343
```

N	-7.31639712	-3.63928421	-1.063542
N	-8.69131712	-3.34617121	-0.826558
N	-4.80705712	-3.56398521	0.15997
N	-5.39969212	-5.62321121	-1.46755
C	-10.32328112	-6.58116921	-0.774503
C	-9.68863312	-7.73082821	-1.247643
C	-8.30245412	-7.51617721	-1.056517
C	-9.36363412	-3.63414221	2.762068
C	-8.37683312	-3.61864421	3.748689
C	-7.19961812	-4.07990921	3.116947
C	-9.10791212	-2.34370021	-1.697307
C	-8.02404412	-1.96862121	-2.495353
C	-6.94248312	-2.78480421	-2.087229
C	-4.78896712	-2.60478721	1.174538
B	-9.48708312	-4.22694321	0.182813
H	-10.61341312	-3.89800021	0.242683
H	-11.38348612	-6.30898021	-0.726658
H	-10.16207912	-8.61584521	-1.676752
H	-7.45985112	-8.17523921	-1.292283
H	-10.42366412	-3.35860221	2.79611
H	-8.48809312	-3.31662421	4.791686
H	-6.21052512	-4.21823921	3.560234
H	-10.14369312	-1.98690821	-1.671789
H	-8.01471512	-1.20795721	-3.278227
H	-5.91898012	-2.81846421	-2.476038
H	-5.52116512	-2.75667621	1.979335
C	-3.93912312	-1.49776321	1.200586
H	-4.01015112	-0.80080021	2.040666
C	-3.90321112	-3.32703521	-0.887793
H	-3.95408812	-4.08854221	-1.715021
C	-3.00292212	-1.28493021	0.140479
C	-3.02898412	-2.24111821	-0.925277
H	-2.36342112	-2.13589721	-1.787641
N	-2.08231112	-0.20956321	0.160731
C	-2.25790712	0.89156479	1.158388
H	-1.41361112	1.59213679	1.053284
H	-3.20595012	1.44729879	1.008717
H	-2.24504212	0.47931379	2.183293
C	-1.29263412	0.10669279	-1.070403
H	-1.93849012	0.42473679	-1.913996
H	-0.59058712	0.92203379	-0.831408
H	-0.70917312	-0.77786821	-1.38261
C	-4.71143212	-6.28008421	1.21577
C	-5.94151112	-7.08447121	0.9988

H	-5.85386212	-7.99619021	0.393911
H	-6.58764412	-7.24256821	1.873887
C	-4.41359412	-5.83764821	2.680818
H	-5.30086512	-5.96546321	3.315825
H	-3.61616812	-6.45739721	3.122205
H	-4.08060512	-4.78791121	2.754577
H	-3.87253652	-6.64116549	0.65829848

1	10	1	49	1	50
2	10	1			
3	4	1	13	1	
4	11	1	21	1	
5	6	1	16	1	
6	14	1	21	1	
7	8	1	19	1	
8	17	1	21	1	
9	20	1	35	1	
10					
11	12	1.5	23	1	
12	13	1.5	24	1	
13	25	1			
14	15	1.5	26	1	
15	16	1.5	27	1	
16	28	1			
17	18	1.5	29	1	
18	19	1.5	30	1	
19	31	1			
20	32	1	33	1.5	
21	22	1			
22					
23					
24					
25					
26					
27					
28					
29					
30					
31					
32					
33	34	1	37	1.5	
34					
35	36	1	38	1.5	
36					

```
                37              38              1.5             40              1
                38              39              1
                39
                40              41              1               45              1
                41              42              1               43              1   44
                42
                43
                44
                45              46              1               47              1   48
                46
                47
                48
                49              50              1               53              1   57
                50              51              1               52              1
                51
                52
                53              54              1               55              1   56
                54
                55
                56
                57

Mo                      0
LANL2DZ
*****
H                   B       C               N               O                   0
6-31G(d)
*****

Mo                      0
LANL2DZ
```

14C Output coordinates

Tag	Symbol	X	Y	Z
1	Mo	0.659645	0.887518	-0.00533
2	O	0.221895	2.918724	-2.13494
3	N	2.890897	0.739649	-0.30223
4	N	3.514867	-0.46884	-0.33007
5	N	1.084879	-0.86191	1.561
6	N	2.017739	-1.79452	1.218981
7	N	0.726649	-0.90525	-1.40963

8	N	1.665429	-1.87697	-1.272
9	N	-1.57037	0.420174	0.020723
10	N	0.42195	2.089361	-1.28273
11	C	4.829741	-0.3004	-0.6044
12	C	5.074418	1.053826	-0.76443
13	C	3.824751	1.660905	-0.56549
14	C	2.148983	-2.70453	2.207747
15	C	1.277634	-2.37105	3.234035
16	C	0.636243	-1.21183	2.776503
17	C	1.519402	-2.7988	-2.24965
18	C	0.45188	-2.42234	-3.05229
19	C	-0.0077	-1.22531	-2.48242
20	C	-2.06621	-0.75721	0.455443
21	B	2.730089	-1.78207	-0.15541
22	H	3.479065	-2.71995	-0.22489
23	H	5.4873	-1.15554	-0.66464
24	H	6.015272	1.533121	-0.99096
25	H	3.554674	2.705952	-0.60059
26	H	2.849778	-3.52075	2.107293
27	H	1.131604	-2.88577	4.172112
28	H	-0.12666	-0.62162	3.260191
29	H	2.186046	-3.64746	-2.30411
30	H	0.069131	-2.93329	-3.9234
31	H	-0.81809	-0.57992	-2.79051
32	H	-1.33955	-1.45873	0.848308
33	C	-3.40856	-1.0975	0.421176
34	H	-3.70288	-2.06965	0.796144
35	C	-2.47098	1.289188	-0.49118
36	H	-2.06841	2.224722	-0.86263
37	C	-4.35651	-0.18725	-0.10178
38	C	-3.82873	1.039315	-0.57395
39	H	-4.46523	1.800222	-1.00771
40	N	-5.69625	-0.47315	-0.15176
41	C	-6.18121	-1.76562	0.308447
42	H	-7.26674	-1.79816	0.205745
43	H	-5.75807	-2.59435	-0.27639
44	H	-5.93672	-1.93323	1.365636
45	C	-6.62368	0.482978	-0.73868
46	H	-6.40272	0.671354	-1.79855
47	H	-7.63761	0.086571	-0.66933
48	H	-6.59959	1.443672	-0.208
49	C	-0.04414	2.425307	1.552233
50	C	1.366833	2.457149	1.44229
51	H	1.861828	3.263569	0.905286

52	H	1.967172	2.018525	2.239782
53	C	-0.74538	2.008113	2.82886
54	H	-0.08197	1.427678	3.477983
55	H	-1.046	2.897047	3.403797
56	H	-1.65702	1.422352	2.650249
57	H	-0.59667	3.178922	0.988858

14D Input

```
%mem=12GB
%nprocshared=12
#                opt    b3lyp/gen        geom=connectivity     pseudo=read

Title            Card   Required

                0      1
                   Mo        2.09174418          -2.37101084                0
                   O         1.04936553          -0.74681203       -2.31810791
                   N         4.18557718          -2.51119184         -0.522953
                   N         4.94064718          -3.71263884         -0.338903
                   N         2.61487818          -3.76050484          1.735527
                   N         3.59804818          -4.77828584          1.537245
                   N         2.12525318          -4.28578084         -1.117818
                   N         3.09380018          -5.30348584         -0.878013
                   N        -0.00215282          -3.06195584          0.205494
                   N         1.49934318          -1.44795184         -1.317419
                   C         6.23489618          -3.51395584         -0.816416
                   C         6.34033018          -2.20874684         -1.299718
                   C         5.06758618          -1.61893684         -1.108258
                   C         3.82260418          -5.44797884          2.735934
                   C         3.00483718          -4.88861184          3.721188
                   C         2.28043418          -3.85767884           3.07921
                   C         2.85372018          -6.37692684         -1.730092
                   C         1.73656218          -6.08102484         -2.516968
                   C         1.31425518          -4.79004084         -2.119853
                   C        -0.45134282          -4.04867284          1.086559
                   B         4.24559318          -5.02193484          0.137413
                   H         5.00577918          -5.91659884          0.182033
                   H         6.96804418          -4.32677384         -0.767497
                   H         7.22274418          -1.73663684         -1.735727
                   H         4.72809018          -0.60533484          -1.34754
                   H         4.54791318          -6.26833484           2.78111
```

H	2.94010118	-5.18310084	4.770408
H	1.54139718	-3.17113584	3.506552
H	3.50299518	-7.25940384	-1.702137
H	1.28667018	-6.71312884	-3.284947
H	0.47963118	-4.18723384	-2.496126
H	0.31971218	-4.47731584	1.741967
C	-1.76985782	-4.49594884	1.165983
H	-2.01723982	-5.27774684	1.889976
C	-0.98644882	-2.54926384	-0.65148
H	-0.60050082	-1.79221584	-1.388381
C	-2.77141082	-3.93729784	0.309652
C	-2.32219382	-2.95149684	-0.624863
H	-3.01778182	-2.49816984	-1.337781
N	-4.13255182	-4.31564684	0.406436
C	-4.50731582	-5.51879484	1.212924
H	-5.60586682	-5.60764284	1.212433
H	-4.07193482	-6.45272184	0.802683
H	-4.16684282	-5.39616384	2.256744
C	-5.09354382	-3.88232784	-0.655591
H	-4.84924382	-4.31620784	-1.646585
H	-6.10437182	-4.20942984	-0.362253
H	-5.09202582	-2.78083884	-0.739214
C	2.80373718	-0.65838684	1.07271
C	1.39701018	-0.96826084	1.445798
H	1.2678818	-1.36279007	2.43198893
H	3.59839665	-1.29040696	1.41029982
H	3.02064607	0.19646169	0.46683499
C	0.35085804	0.03565471	0.92683819
H	0.39451456	0.07600494	-0.14150911
H	-0.62577203	-0.27701567	1.23233933
H	0.55695998	1.00550033	1.32910857

1	10	1		
2	10	1		
3	4	1	13	1
4	11	1	21	1
5	6	1	16	1
6	14	1	21	1
7	8	1	19	1
8	17	1	21	1
9	20	1.5	35	1.5
10				
11	12	1.5	23	1
12	13	1.5	24	1

13	25	1				
14	15	1.5	26	1		
15	16	1.5	27	1		
16	28	1				
17	18	1.5	29	1		
18	19	1.5	30	1		
19	31	1				
20	32	1	33	1.5		
21	22	1				
22						
23						
24						
25						
26						
27						
28						
29						
30						
31						
32						
33	34	1	37	1.5		
34						
35	36	1	38	1.5		
36						
37	38	1.5	40	1		
38	39	1				
39						
40	41	1	45	1		
41	42	1	43	1	44	1
42						
43						
44						
45	46	1	47	1	48	1
46						
47						
48						
49	50	2	52	1	53	1
50	51	1	54	1		
51						
52						
53						
54	55	1	56	1	57	1
55						
56						

57

Mo 0
LANL2DZ
*****
H B C N O 0
6-31G(d)
*****

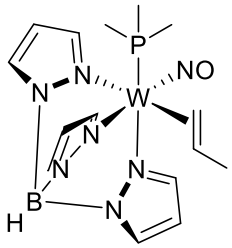
Mo 0
LANL2DZ

14D Output Coordinates

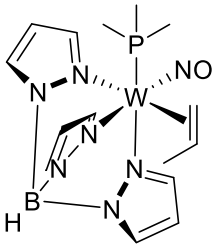
Tag	Symbol	X	Y	Z
1	Mo	0.666694	0.849392	0.0469
2	O	0.214114	3.029209	-1.9331
3	N	2.877115	0.667887	-0.34544
4	N	3.474666	-0.55235	-0.41821
5	N	1.150116	-0.88199	1.570617
6	N	2.024613	-1.85144	1.187353
7	N	0.654063	-0.90541	-1.40965
8	N	1.559838	-1.91161	-1.29571
9	N	-1.56711	0.387963	0.111398
10	N	0.411701	2.137656	-1.14345
11	C	4.782189	-0.40322	-0.7363
12	C	5.048079	0.94924	-0.87812
13	C	3.818656	1.576594	-0.62212
14	C	2.253081	-2.69927	2.213332
15	C	1.507293	-2.28169	3.306637
16	C	0.838121	-1.13747	2.85001
17	C	1.349721	-2.83052	-2.26452
18	C	0.27281	-2.41752	-3.03569
19	C	-0.12454	-1.20259	-2.45702
20	C	-2.07344	-0.70821	0.713805
21	B	2.669221	-1.85291	-0.22242
22	H	3.393144	-2.80668	-0.32916
23	H	5.420519	-1.26918	-0.8363
24	H	5.989977	1.414427	-1.1285
25	H	3.56574	2.626824	-0.62359
26	H	2.928964	-3.53342	2.091449
27	H	1.459212	-2.73422	4.285988

28	H	0.155342	-0.48818	3.380235
29	H	1.982947	-3.70316	-2.33591
30	H	-0.15493	-2.9166	-3.89263
31	H	-0.92243	-0.53131	-2.74138
32	H	-1.35862	-1.33039	1.240012
33	C	-3.41084	-1.06516	0.686606
34	H	-3.71346	-1.96803	1.201985
35	C	-2.45299	1.154196	-0.56442
36	H	-2.04388	2.025212	-1.06369
37	C	-4.34459	-0.26098	-0.00891
38	C	-3.80686	0.879215	-0.65235
39	H	-4.43138	1.555581	-1.22226
40	N	-5.68014	-0.56671	-0.05842
41	C	-6.17257	-1.77923	0.577741
42	H	-7.25366	-1.83953	0.444941
43	H	-5.72408	-2.68301	0.141734
44	H	-5.96449	-1.77998	1.655733
45	C	-6.59038	0.271087	-0.82529
46	H	-6.33465	0.284743	-1.8941
47	H	-7.60485	-0.11714	-0.72437
48	H	-6.58703	1.305997	-0.45945
49	C	1.460059	2.246651	1.608782
50	C	0.058744	2.167024	1.803844
51	H	-0.29463	1.515995	2.60716
52	H	2.134994	1.69444	2.259867
53	H	1.889114	3.155957	1.188986
54	C	-0.85361	3.345973	1.540537
55	H	-0.49152	3.945915	0.698489
56	H	-1.88051	3.034878	1.311907
57	H	-0.90771	4.004482	2.421249

WTp(NO)(PMe_3)(η^2-Propene) (**15**)



A



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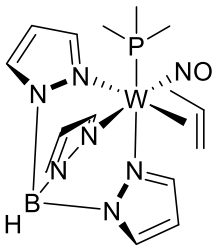
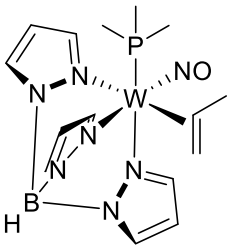


C



D

Gaussian DFT of:

15A Input

%mem=12GB
%nprocshared=12

#	opt	freq	b3lyp/sdd	geom=connectivity
Title	Card	Required		
0	1			
	O	-4.67281312	-5.49931221	-2.533437
	N	-8.06166812	-6.27973121	-0.481357
	N	-9.35391012	-5.69661821	-0.305642
	N	-7.41272812	-4.38177821	1.777962
	N	-8.79961912	-4.08975521	1.575343
	N	-7.31639712	-3.63928421	-1.063542
	N	-8.69131712	-3.34617121	-0.826558
	N	-5.39969212	-5.62321121	-1.46755
	C	-10.32328112	-6.58116921	-0.774503
	C	-9.68863312	-7.73082821	-1.247643
	C	-8.30245412	-7.51617721	-1.056517
	C	-9.36363412	-3.63414221	2.762068
	C	-8.37683312	-3.61864421	3.748689
	C	-7.19961812	-4.07990921	3.116947
	C	-9.10791212	-2.34370021	-1.697307

C	-8.02404412	-1.96862121	-2.495353
C	-6.94248312	-2.78480421	-2.087229
B	-9.48708312	-4.22694321	0.182813
H	-10.61341312	-3.89800021	0.242683
H	-11.38348612	-6.30898021	-0.726658
H	-10.16207912	-8.61584521	-1.676752
H	-7.45985112	-8.17523921	-1.292283
H	-10.42366412	-3.35860221	2.79611
H	-8.48809312	-3.31662421	4.791686
H	-6.21052512	-4.21823921	3.560234
H	-10.14369312	-1.98690821	-1.671789
H	-8.01471512	-1.20795721	-3.278227
H	-5.91898012	-2.81846421	-2.476038
C	-4.71143212	-6.28008421	1.21577
C	-5.94151112	-7.08447121	0.9988
H	-6.58764412	-7.24256821	1.873887
W	-6.20487812	-5.25876521	0
P	-4.80705712	-3.56398521	0.15997
C	-3.63530806	-3.25680242	-1.19835355
H	-3.71992772	-4.03701205	-1.92568596
H	-3.85915169	-2.31617251	-1.65662138
H	-2.63795959	-3.23662629	-0.81132778
C	-4.7834783	-2.31375003	1.48237539
H	-5.02755765	-1.35610031	1.0722141
H	-5.50111816	-2.57404643	2.23213457
H	-3.80789678	-2.27607528	1.92023532
C	-3.1802876	-3.45112369	0.96822938
H	-3.29563389	-3.58995803	2.02289532
H	-2.53438071	-4.20928704	0.57721452
H	-2.75445114	-2.48777332	0.77976353
H	-4.58770787	-5.89394258	2.20596541
H	-3.84572	-6.61855826	0.6857909
C	-5.81853823	-8.36362694	0.15013146
H	-5.80592316	-9.21858817	0.79339048
H	-6.65287776	-8.43103253	-0.51637737
H	-4.91137155	-8.33002378	-0.4162778

1	8	1		
2	3	1	11	1
3	9	1	18	1
4	5	1	14	1
5	12	1	18	1
6	7	1	17	1
7	15	1	18	1

8	32	1							
9	10	1.5	20	1					
10	11	1.5	21	1					
11	22	1							
12	13	1.5	23	1					
13	14	1.5	24	1					
14	25	1							
15	16	1.5	26	1					
16	17	1.5	27	1					
17	28	1							
18	19	1							
19									
20									
21									
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24									
25									
26									
27									
28									
29	30	1	32	1	46	1	47	1	
30	31	1	32	1	48	1			
31									
32									
33	34	1	38	1	42	1			
34	35	1	36	1	37	1			
35									
36									
37									
38	39	1	40	1	41	1			
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41									
42	43	1	44	1	45	1			
43									
44									
45									
46									
47									
48	49	1	50	1	51	1			
49									
50									
51									

15A Output Coordinates

Tag	Symbol	X	Y	Z
1	O	1.183571	2.313206	2.392548
2	N	-1.88572	0.950769	0.231416
3	N	-2.80414	-0.07813	0.029051
4	N	-0.35614	-0.79819	-1.66148
5	N	-1.48533	-1.59389	-1.50325
6	N	-0.36901	-1.09317	1.346152
7	N	-1.4427	-1.9072	1.006985
8	N	0.809372	1.619526	1.406374
9	C	-4.06734	0.386733	0.281384
10	C	-3.97951	1.731069	0.660049
11	C	-2.59719	2.035821	0.619336
12	C	-1.69074	-2.33163	-2.63346
13	C	-0.68239	-2.02203	-3.55694
14	C	0.12353	-1.05992	-2.90558
15	C	-1.6646	-2.80973	2.009375
16	C	-0.72333	-2.58825	3.02482
17	C	0.056582	-1.49833	2.569546
18	B	-2.3271	-1.52844	-0.21054
19	H	-3.26237	-2.27258	-0.29205
20	H	-4.92535	-0.26121	0.183766
21	H	-4.78779	2.392016	0.930588
22	H	-2.09324	2.956698	0.860625
23	H	-2.52597	-3.01145	-2.70817
24	H	-0.55471	-2.42341	-4.54999
25	H	0.995567	-0.54601	-3.27699
26	H	-2.4706	-3.52507	1.944432
27	H	-0.62824	-3.11907	3.959058
28	H	0.861635	-0.97821	3.065543
29	C	1.475002	1.748111	-1.50292
30	C	0.133182	2.308249	-1.42148
31	H	-0.54973	2.023884	-2.22974
32	W	0.30443	0.599266	0.025082
33	P	2.601796	-0.67268	0.079645
34	C	3.671239	-0.20725	1.557521
35	H	3.809551	0.877386	1.570494
36	H	3.165562	-0.49079	2.484815
37	H	4.644229	-0.70947	1.505047
38	C	2.53056	-2.55632	0.20153
39	H	1.950558	-2.8517	1.079263

40	H	2.037609	-2.95358	-0.69184
41	H	3.54163	-2.97377	0.273941
42	C	3.835623	-0.48291	-1.33211
43	H	3.399021	-0.85941	-2.26237
44	H	4.084865	0.572957	-1.46263
45	H	4.747209	-1.04929	-1.10921
46	H	1.764185	1.19427	-2.39818
47	H	2.296932	2.347263	-1.10369
48	C	-0.05963	3.752825	-0.96144
49	H	0.245508	4.454087	-1.75587
50	H	-1.10811	3.979223	-0.72826
51	H	0.543948	3.971457	-0.07154

15B Input

```
%mem=12GB
%nprocshared=12
#                opt    freq              b3lyp/sdd       geom=connectivity

Title             Card  Required

                0     1
                   O         -4.67281312    -5.49931221          -2.533437
                   N         -8.06166812    -6.27973121          -0.481357
                   N         -9.35391012    -5.69661821          -0.305642
                   N         -7.41272812    -4.38177821           1.777962
                   N         -8.79961912    -4.08975521           1.575343
                   N         -7.31639712    -3.63928421          -1.063542
                   N         -8.69131712    -3.34617121          -0.826558
                   N         -5.39969212    -5.62321121           -1.46755
                   C        -10.32328112    -6.58116921          -0.774503
                   C         -9.68863312    -7.73082821          -1.247643
                   C         -8.30245412    -7.51617721          -1.056517
                   C         -9.36363412    -3.63414221           2.762068
                   C         -8.37683312    -3.61864421           3.748689
                   C         -7.19961812    -4.07990921           3.116947
                   C         -9.10791212    -2.34370021          -1.697307
                   C         -8.02404412    -1.96862121          -2.495353
                   C         -6.94248312    -2.78480421          -2.087229
                   B         -9.48708312    -4.22694321           0.182813
                   H        -10.61341312    -3.89800021           0.242683
                   H        -11.38348612    -6.30898021          -0.726658
```

H	-10.16207912	-8.61584521	-1.676752
H	-7.45985112	-8.17523921	-1.292283
H	-10.42366412	-3.35860221	2.79611
H	-8.48809312	-3.31662421	4.791686
H	-6.21052512	-4.21823921	3.560234
H	-10.14369312	-1.98690821	-1.671789
H	-8.01471512	-1.20795721	-3.278227
H	-5.91898012	-2.81846421	-2.476038
C	-4.71143212	-6.28008421	1.21577
C	-5.94151112	-7.08447121	0.9988
W	-6.20487812	-5.25876521	0
P	-4.80705712	-3.56398521	0.15997
C	-3.63530806	-3.25680242	-1.19835355
H	-3.71992772	-4.03701205	-1.92568596
H	-3.85915169	-2.31617251	-1.65662138
H	-2.63795959	-3.23662629	-0.81132778
C	-4.7834783	-2.31375003	1.48237539
H	-5.02755765	-1.35610031	1.0722141
H	-5.50111816	-2.57404643	2.23213457
H	-3.80789678	-2.27607528	1.92023532
C	-3.1802876	-3.45112369	0.96822938
H	-3.29563389	-3.58995803	2.02289532
H	-2.53438071	-4.20928704	0.57721452
H	-2.75445114	-2.48777332	0.77976353
H	-4.58770787	-5.89394258	2.20596541
H	-3.84572	-6.61855826	0.6857909
H	-5.81504786	-7.93142045	0.35725185
C	-6.82080937	-7.26698262	2.24984923
H	-7.85200253	-7.26576492	1.96429858
H	-6.58223173	-8.19767261	2.72080235
H	-6.63913456	-6.4643201	2.93368192

1	8	1		
2	3	1	11	1
3	9	1	18	1
4	5	1	14	1
5	12	1	18	1
6	7	1	17	1
7	15	1	18	1
8	31	1		
9	10	1.5	20	1
10	11	1.5	21	1
11	22	1		
12	13	1.5	23	1

13	14	1.5	24	1					
14	25	1							
15	16	1.5	26	1					
16	17	1.5	27	1					
17	28	1							
18	19	1							
19									
20									
21									
22									
23									
24									
25									
26									
27									
28									
29	30	1	31	1	45	1	46	1	
30	31	1	47	1	48	1			
31									
32	33	1	37	1	41	1			
33	34	1	35	1	36	1			
34									
35									
36									
37	38	1	39	1	40	1			
38									
39									
40									
41	42	1	43	1	44	1			
42									
43									
44									
45									
46									
47									
48	49	1	50	1	51	1			
49									
50									
51									

15B Output Coordinates

Tag	Symbol	X	Y	Z
1	O	-1.33896	0.253863	-3.29598
2	N	1.840026	0.543244	-0.89102
3	N	2.790367	-0.14954	-0.14678
4	N	0.413516	0.342929	1.741087
5	N	1.563021	-0.37536	2.053764
6	N	0.310552	-1.73582	-0.41614
7	N	1.425811	-2.17509	0.288931
8	N	-0.89912	0.339405	-2.11517
9	C	4.033039	0.082306	-0.67227
10	C	3.897686	0.935121	-1.77482
11	C	2.509147	1.195202	-1.87122
12	C	1.818169	-0.27502	3.390859
13	C	0.823653	0.521469	3.976348
14	C	-0.02742	0.882645	2.907307
15	C	1.637511	-3.49983	0.026989
16	C	0.649473	-3.9413	-0.86417
17	C	-0.14787	-2.80084	-1.12065
18	B	2.35312	-1.13353	0.963359
19	H	3.306711	-1.67271	1.448109
20	H	4.911737	-0.36977	-0.2375
21	H	4.680576	1.311252	-2.41439
22	H	1.971349	1.803136	-2.58171
23	H	2.673692	-0.76502	3.83051
24	H	0.732586	0.802491	5.013724
25	H	-0.90532	1.507545	2.923444
26	H	2.469011	-4.02744	0.469588
27	H	0.533094	-4.93041	-1.27836
28	H	-0.98842	-2.68991	-1.78762
29	C	-1.40514	2.352779	0.03289
30	C	-0.08565	2.656308	-0.50226
31	W	-0.32571	0.420962	-0.42223
32	P	-2.69386	-0.39946	0.340325
33	C	-4.02598	0.091744	-0.89396
34	H	-4.16618	1.175874	-0.86166
35	H	-3.69892	-0.17907	-1.90217
36	H	-4.97409	-0.40521	-0.658
37	C	-3.03575	-2.24947	0.532092
38	H	-2.98911	-2.74039	-0.44384
39	H	-2.28508	-2.70219	1.186504
40	H	-4.03434	-2.40197	0.958019
41	C	-3.422	0.228854	1.963507
42	H	-2.84423	-0.16369	2.805931
43	H	-3.38884	1.321566	1.980402

44	H	-4.46286	-0.10119	2.058266
45	H	-1.58243	2.591878	1.085724
46	H	-2.27983	2.536109	-0.59226
47	H	-0.05817	2.973562	-1.5485
48	C	0.956167	3.377773	0.354135
49	H	1.97799	3.194987	-0.00389
50	H	0.787255	4.4666	0.324736
51	H	0.910867	3.066562	1.404867

15C Input

%mem=12GB
%nprocshared=12
opt freq b3lyp/sdd geom=connectivity

Title Card Required

0 1

O	-1.187946	-1.541664	-2.956531
N	1.80737	0.435223	-1.138858
N	2.853638	0.229596	-0.240636
N	0.399351	1.235352	1.28804
N	1.641386	0.912556	1.847309
N	0.625966	-1.656052	0.45708
N	1.806954	-1.529752	1.183558
N	-0.818023	-0.832029	-1.976275
C	4.04811	0.373468	-0.893448
C	3.786385	0.660104	-2.238434
C	2.374798	0.688584	-2.341658
C	1.867725	1.680254	2.950547
C	0.770192	2.52739	3.139092
C	-0.121712	2.205345	2.093166
C	2.279092	-2.772547	1.506098
C	1.396923	-3.732706	0.998174
C	0.387467	-2.988118	0.345169
B	2.549428	-0.167577	1.222744
H	3.556498	-0.283881	1.858501
H	4.9841	0.260798	-0.366896
H	4.504543	0.825123	-3.026331
H	1.753273	0.872579	-3.203467
H	2.781733	1.577086	3.516424
H	0.635719	3.265453	3.914323

H	-1.087038	2.633021	1.877601
H	3.199303	-2.887818	2.059667
H	1.476296	-4.805746	1.076585
H	-0.452636	-3.338779	-0.232353
C	-1.688723	1.889901	-1.225675
C	-0.345763	2.041704	-1.746197
H	-0.146528	1.845447	-2.800224
H	0.284512	2.824624	-1.318078
C	-2.311107	2.9989	-0.361458
H	-1.536241	3.645024	0.069344
H	-2.948948	3.6296	-0.998658
H	-2.944773	2.645417	0.469938
W	-0.313174	0.152574	-0.572461
P	-2.526009	-0.618549	0.567948
C	-3.045015	-2.340175	-0.013945
H	-2.909341	-2.428774	-1.09487
H	-2.431623	-3.090963	0.493747
H	-4.092952	-2.53791	0.23062
C	-2.251823	-0.893401	2.409965
H	-1.531739	-1.715223	2.505809
H	-1.824966	-0.003481	2.878492
H	-3.175051	-1.164648	2.932544
C	-4.213729	0.203882	0.539397
H	-4.189022	1.206016	0.971449
H	-4.518258	0.302705	-0.505865
H	-4.958383	-0.39346	1.077692
H	-2.420445	1.456949	-1.91087

1	8	1.5		
2	3	1	11	1.5
3	9	1.5	18	1
4	5	1	14	1.5
5	12	1.5	18	1
6	7	1	17	1.5
7	15	1.5	18	1
8	37	1		
9	10	1.5	20	1
10	11	1.5	21	1
11	22	1		
12	13	1.5	23	1
13	14	1.5	24	1
14	25	1		
15	16	1.5	26	1
16	17	1.5	27	1

17	28	1					
18	19	1					
19							
20							
21							
22							
23							
24							
25							
26							
27							
28							
29	30	1	33	1	51	1	
30	31	1	32	1			
31							
32							
33	34	1	35	1	36	1	
34							
35							
36							
37							
38	39	1	43	1	47	1	
39	40	1	41	1	42	1	
40							
41							
42							
43	44	1	45	1	46	1	
44							
45							
46							
47	48	1	49	1	50	1	
48							
49							
50							
51							

15C Output Coordinates

Tag	Symbol	X	Y	Z
1	O	1.094386	0.210313	-3.379
2	N	-1.88572	-0.82315	-0.82677
3	N	-2.8617	-0.29024	0.010839

4	N	-0.30684	-0.54327	1.711062
5	N	-1.51924	-0.00494	2.135279
6	N	-0.63381	1.633859	-0.30876
7	N	-1.75013	1.879001	0.481798
8	N	0.740098	-0.08181	-2.20219
9	C	-4.09832	-0.67843	-0.42859
10	C	-3.93526	-1.47214	-1.57045
11	C	-2.53665	-1.5343	-1.77889
12	C	-1.62785	-0.12396	3.490384
13	C	-0.47051	-0.74662	3.977814
14	C	0.321997	-0.98545	2.832377
15	C	-2.14828	3.176568	0.321538
16	C	-1.28272	3.798112	-0.58932
17	C	-0.36195	2.791334	-0.96508
18	B	-2.48223	0.684859	1.144544
19	H	-3.46211	1.063441	1.720636
20	H	-4.99304	-0.36771	0.089528
21	H	-4.70723	-1.93511	-2.16466
22	H	-1.98208	-2.0436	-2.55049
23	H	-2.50284	0.236445	4.009872
24	H	-0.23886	-0.99534	5.001512
25	H	1.29003	-1.45166	2.768242
26	H	-3.01268	3.560711	0.841959
27	H	-1.32275	4.816174	-0.94363
28	H	0.434493	2.831384	-1.69116
29	C	1.627515	-2.28821	-0.39763
30	C	0.303134	-2.60412	-0.9017
31	H	0.159445	-2.81712	-1.96173
32	H	-0.35722	-3.18318	-0.25039
33	C	2.108832	-3.02326	0.858675
34	H	1.268986	-3.26885	1.520522
35	H	2.570973	-3.9806	0.568285
36	H	2.86066	-2.47393	1.440093
37	W	0.281815	-0.41742	-0.50749
38	P	2.489202	0.813551	0.237878
39	C	3.240262	1.830609	-1.163
40	H	3.256835	1.233074	-2.07852
41	H	2.628865	2.71871	-1.34527
42	H	4.255642	2.148163	-0.90016
43	C	2.284695	2.109518	1.596865
44	H	1.50878	2.822128	1.304084
45	H	1.975063	1.618829	2.525033
46	H	3.227334	2.643622	1.76415
47	C	4.02797	-0.08487	0.856403

48	H	3.833458	-0.54613	1.828467
49	H	4.308869	-0.86524	0.144384
50	H	4.852267	0.630268	0.959615
51	H	2.414995	-2.19001	-1.15002

15D Input

%mem=12GB
%nprocshared=12
opt freq b3lyp/sdd geom=connectivity

Title Card Required

0 1

O	-1.175466	0.759404	-2.70738
N	1.552144	2.026264	-0.124655
N	2.920844	1.972113	0.126068
N	1.693651	-0.420181	1.622145
N	3.051171	-0.124625	1.535136
N	2.040599	-0.415014	-1.35972
N	3.357682	-0.209024	-0.966492
N	-0.618769	0.553278	-1.591807
C	3.454565	3.226986	0.004288
C	2.427958	4.115777	-0.334799
C	1.259661	3.31925	-0.404568
C	3.70617	-0.639011	2.615892
C	2.77341	-1.291144	3.434161
C	1.535741	-1.128991	2.772088
C	4.198149	-0.553674	-1.989232
C	3.42418	-0.992026	-3.072419
C	2.082263	-0.873095	-2.637493
B	3.636264	0.617612	0.314501
H	4.814282	0.779703	0.460165
H	4.509279	3.397321	0.159399
H	2.508226	5.177053	-0.509663
H	0.250208	3.610411	-0.646054
H	4.771983	-0.511388	2.730063
H	2.958439	-1.798564	4.367819
H	0.562608	-1.47949	3.07053
H	5.267862	-0.448245	-1.888264
H	3.773645	-1.325453	-4.036938
H	1.167831	-1.046153	-3.183468

C	-1.685041	0.407463	1.240466
C	-0.85718	1.596963	1.185189
H	-1.213999	2.464926	0.627235
H	-0.278757	1.87509	2.0706
W	0.282736	0.193998	-0.091888
P	-0.227145	-2.400648	-0.263163
C	-0.995793	-2.904211	-1.911355
H	-1.847526	-2.258828	-2.137454
H	-0.25521	-2.783903	-2.706635
H	-1.317293	-3.951507	-1.878816
C	1.34105	-3.459117	-0.246865
H	2.02677	-3.122688	-1.027121
H	1.835762	-3.357532	0.72399
H	1.08405	-4.511597	-0.414702
C	-1.258096	-3.420744	0.94764
H	-0.824471	-3.360429	1.950104
H	-2.283303	-3.050545	0.977427
H	-1.256586	-4.468111	0.623364
H	-1.56125385	-0.29387156	2.03903133
C	-2.74227609	0.15377554	0.14982553
H	-3.19760123	-0.80121776	0.30972182
H	-3.49043285	0.91746839	0.19381079
H	-2.2733663	0.1688127	-0.81183838

1	8	1.5		
2	3	1	11	1.5
3	9	1.5	18	1
4	5	1	14	1.5
5	12	1.5	18	1
6	7	1	17	1.5
7	15	1.5	18	1
8	33	1		
9	10	1.5	20	1
10	11	1.5	21	1
11	22	1		
12	13	1.5	23	1
13	14	1.5	24	1
14	25	1		
15	16	1.5	26	1
16	17	1.5	27	1
17	28	1		
18	19	1		
19				
20				

21							
22							
23							
24							
25							
26							
27							
28							
29	30	2	47	1	48	1	
30	31	1	32	1			
31							
32							
33							
34	35	1	39	1	43	1	
35	36	1	37	1	38	1	
36							
37							
38							
39	40	1	41	1	42	1	
40							
41							
42							
43	44	1	45	1	46	1	
44							
45							
46							
47							
48	49	1	50	1	51	1	
49							
50							
51							

15D Output Coordinates

Tag	Symbol	X	Y	Z
1	O	-1.26371	-2.309	2.343695
2	N	1.792279	-1.27433	0.028751
3	N	2.85209	-0.38035	-0.09761
4	N	0.485736	0.824578	-1.59809
5	N	1.722315	1.437792	-1.428
6	N	0.647495	0.871797	1.42043
7	N	1.824357	1.537656	1.101868

8	N	-0.88524	-1.61172	1.361843
9	C	4.034127	-1.06803	-0.0329
10	C	3.7486	-2.42775	0.141232
11	C	2.334953	-2.50653	0.172361
12	C	2.005907	2.207756	-2.51937
13	C	0.94258	2.104421	-3.42754
14	C	0.020805	1.228123	-2.80911
15	C	2.230066	2.283497	2.173795
16	C	1.306763	2.107094	3.213938
17	C	0.342785	1.207087	2.699636
18	B	2.592948	1.141891	-0.18323
19	H	3.62647	1.743396	-0.25428
20	H	4.979857	-0.55323	-0.11126
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22	H	1.698232	-3.36866	0.292712
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26	H	3.138743	2.865078	2.133841
27	H	1.336135	2.545449	4.199124
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30	C	-0.4153	-2.17392	-1.52686
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33	W	-0.32186	-0.5807	0.010931
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35	C	-3.61857	0.508591	1.539498
36	H	-4.0045	-0.4867	1.305481
37	H	-3.1111	0.450837	2.506703
38	H	-4.4456	1.225883	1.598624
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40	H	-1.50929	2.857755	1.647567
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42	H	-2.953	3.388341	0.738327
43	C	-3.50981	1.323945	-1.26936
44	H	-2.94069	1.817153	-2.06363
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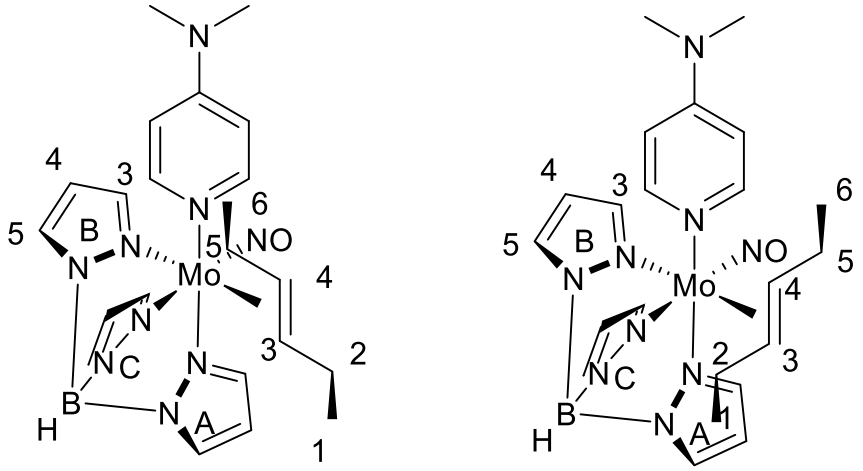
48	C	-2.94223	-2.33384	-1.06195
49	H	-3.79474	-1.69805	-0.78072
50	H	-3.29123	-3.00288	-1.86575
51	H	-2.69622	-2.9542	-0.19205

MoTp(NO)(DMAP)(η^2-trans-3-hexene) (**16**)

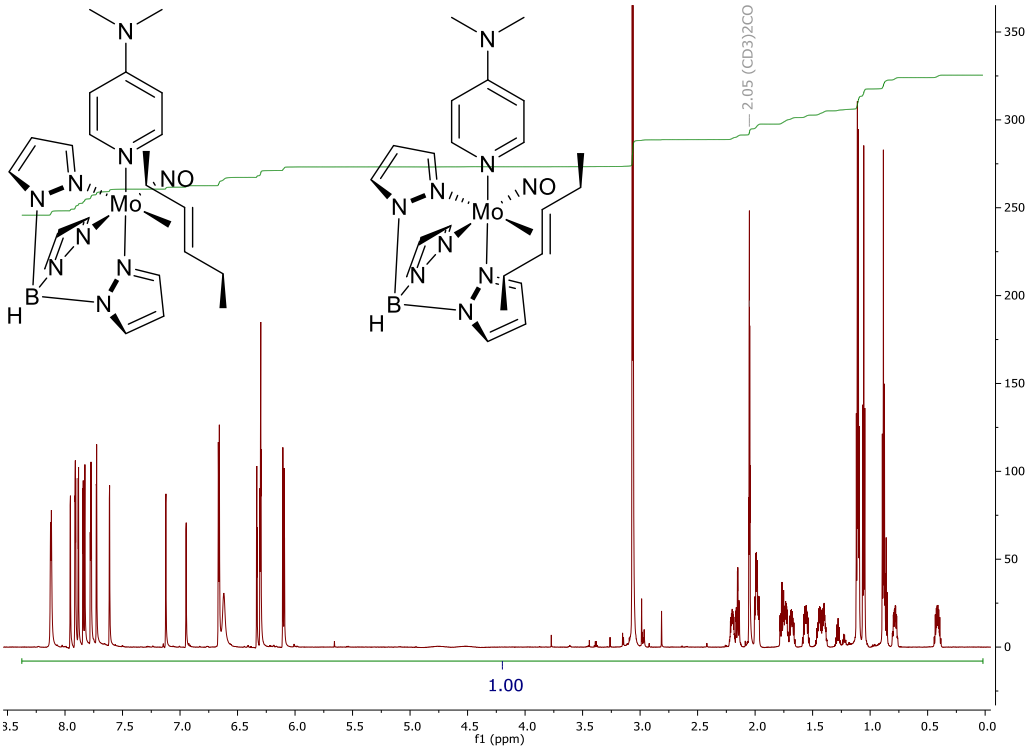


A B

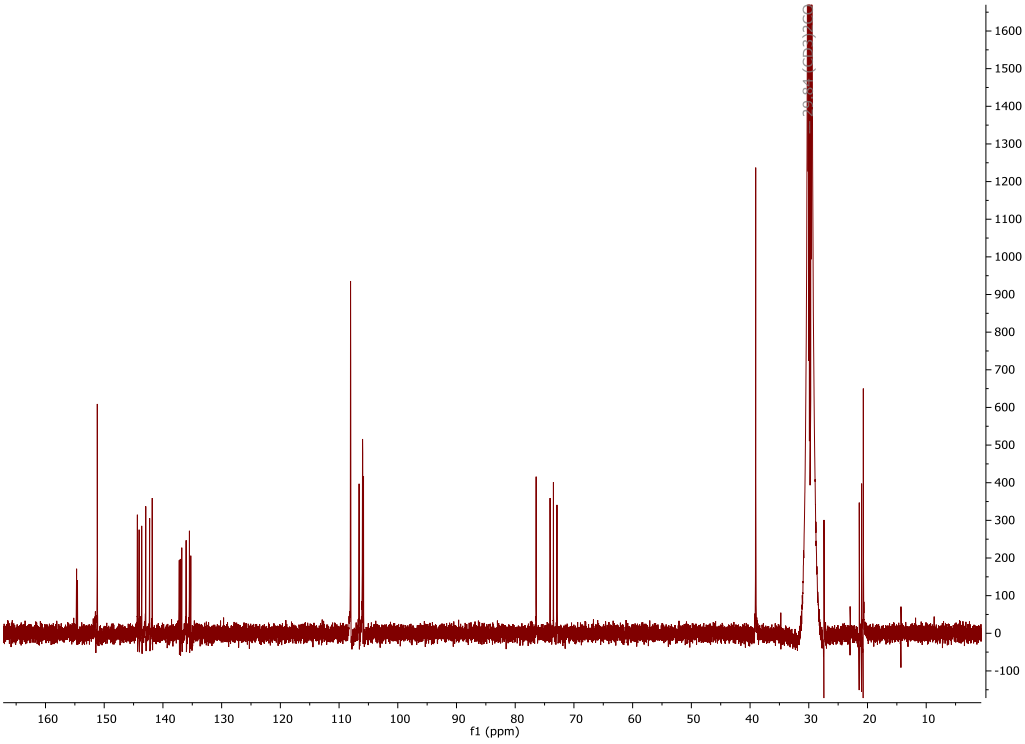
To a 4 dram vial charged with a stir pea, MoTp(NO)(DMAP)(η^2-trifluorotoluene) (1.0 g, 0.0017 mol) was combined with trans-3-hexene (1.6 g, 0.019 mol, 12 eq) and 12 mL of THF. The vial was capped and allowed to mix for four hours (at this point, the mixture of diastereomers is about 1:1). About 10 mL of ether was added to the reaction vial and then the solution was loaded onto a 60 mL medium porosity fritted disk, 3/4 full of silica. The orange band was then eluted with ~200 mL of ether. The filtrate was then dried and dissolved in ~5 mL THF. The THF solution was added to 75 mL stirring cold pentane to precipitate out a yellow solid. The yellow solid was collected on a 30 mL fine porosity fritted disk and washed with pentane (3 x 20 mL). The yellow solid was dried and collected (0.43 g, 0.00079 mol, 48% yield, Diastereomer ratio 1:1.5). IR υ_{NO}: 1557 cm^{-1} υ_{BH}: 2476 cm^{-1}.CV E_{pa}: 120 mV. ^{1}H NMR (d_6-Acetone, δ): **A**: 7.91 (2H, d, TpA3 and Tp3/5), 7.88 (1H, d, Tp3/5), 7.78 (1H, broad, DMAP H2 and H6), 7.75 (1H, d, Tp3/5), 7.62 (1H, d, TpC3), 6.96 (1H, d, Tp3/5), 6.60 (1H, b, DMAP H3 and H5), 6.29 (2H, t, Tp4), 6.08 (1H, t, Tp4), 3.07 (6H, s, DMAP Methyls), 2.20 (1H, m, H 2x proximal to TpA), 2.00 (1H, m, H 4), 1.77 (1H, m, H 3), 1.69 (1H, m, H2y proximal to NO), 1.45 (1H, m, H5x proximal to TpC), 1.40 (1H, m, H5y proximal t NO), 1.13 (3H, t, J = 7.3, H6), 1.10 (3H, t, J = 7.3, H1). ^{1}H NMR (d_6-Acetone, δ): B : 8.13 (2H, m, DMAP H2 and H6), 7.86 (1H, d, TpC5), 7.83 (1H, d, TpA5), 7.82 (1H, d, TpA3), 7.74 (1H, d, TpB5), 7.71 (1H, d, TpC3), 7.13 (1H, d, TpB3), 6.65 (2H, m, DMAP H3 and H5), 6.32 (1H, t, TpA4), 6.29 (1H, t, TpC4), 6.09 (1H, t, TpB4), 3.07 (6H, s, DMAP

Methyl), 2.17 (1H, td, *J* = 2.5, 10.5, H3), 2.01 (1H, td, *J* = 2.5, 10.5, H4), 1.75 (1H, m, H5x proximal to DMAP), 1.57 (1H, m, H5y proximal to NO), 1.07 (3H, t, J = 7.3, H6), 0.89 (3H, t, J = 7.3, H1), 0.81 (1H, m, H2x proximal to Tp A), 0.44 (1H, m, H2y proximal to Tp C). ^{13}C NMR (d_6-Acetone, δ): Isolated **B**: 154.1 (DMAP 4), 150.5 (DMAP 2 and 6), 143.6 (TpA3), 142.1 (TpC3), 141.0 (TpB3), 135.9 (TpC5), 135.2 (TpA5), 134.6 (TpB5), 107.3 (DMAP 3 and 5), 105.7 (TpA4), 105.1 (TpB4), 105.0 (TpC4), 75.8 (C4), 72.9 (C3), 38.2 (DMAP Methyl), 29.3 (C5), 26.6 (C2), 20.1 (C6), 19.7 (C1). ^{13}C NMR (d_6-Acetone, δ): Mixture of diastereomers: (154.7, 154.6) DMAP 4, (151.2, 144.4) DMAP 2 and 6, (144.1, 143.6, 142.9, 142.3, 141.8) Pz3, (137.2, 137.0, 136.8, 136.0, 135.5, 135.3) Pz5, (108.0, 108.0) DMAP 3 and 5, (106.6, 106.0, 106.0, 106.0, 106.0, 105.8) Pz4, (76.4, 74.1, 73.5, 72.9) C3 and C4, (39.0) DMAP methyl, (29.5, 27.4) C2 and C5, (21.4, 21.0, 20.7) C1 and C6. Analysis calculated for Calculated for 4($C_{22}H_{32}BMoN_9O$) • CH_2Cl_2: C, 47.17; H, 5.78; N, 22.25.Found: C, 47.54; H, 5.97; N, 22.07

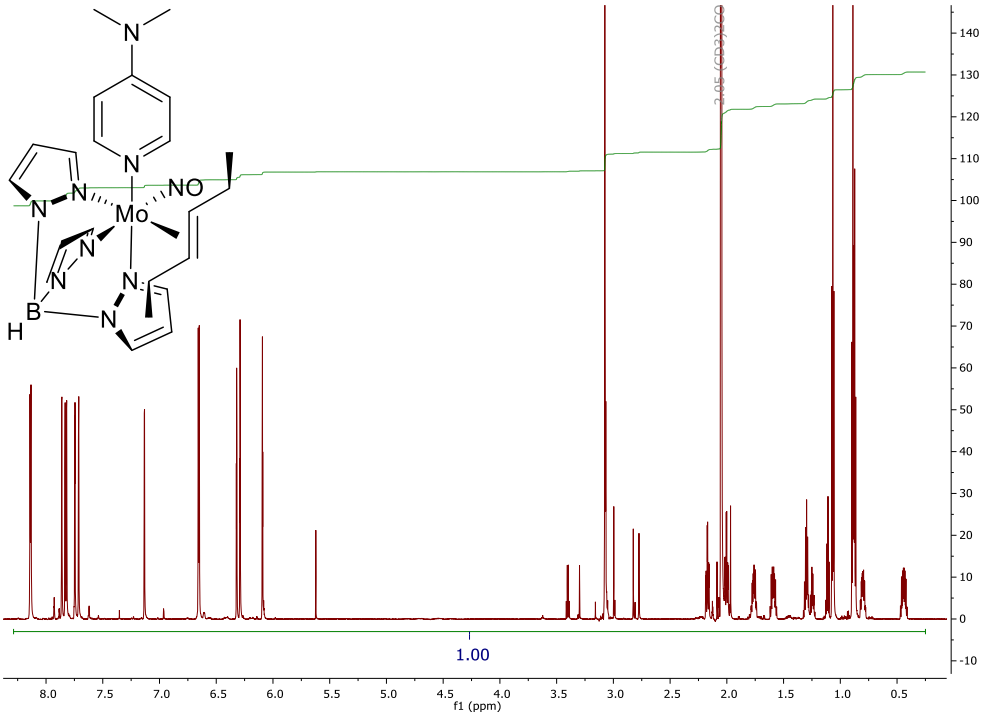
^{1}H NMR (d^6-Acetone) of **16**



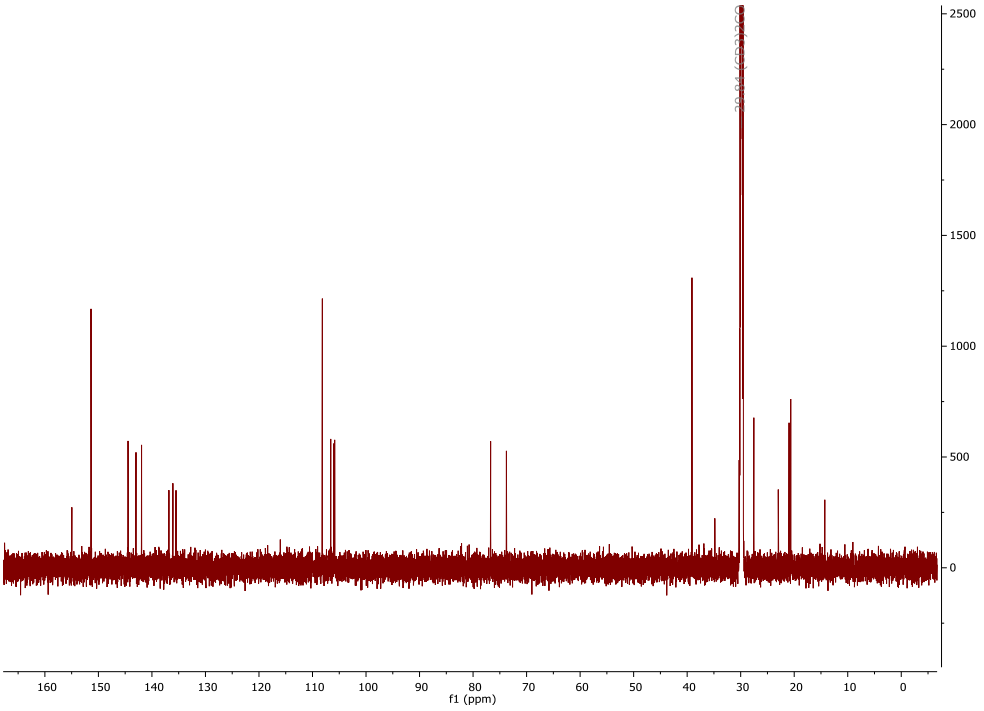
^{13}C NMR (d^6-Acetone) of **16**



^{1}H NMR (d^6-Acetone) of **16**B



^{13}C NMR (d^{6}-Acetone) of **16**B



Gaussian DFT of:

16A Input (Done by Emmit Pert)

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16A⁺ Input (Done by Emmit Pert)

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C	-2.71662849	5.0534839	1.32817839
H	-2.69866149	4.7823939	2.39890839
H	-3.13553249	6.0771909	1.27950639
C	-1.25676249	5.1161769	0.78382639
H	-1.25391449	5.4659269	-0.26000261
H	-0.64531749	5.8120489	1.38019739
H	-0.77948349	4.1257589	0.81110239
H	-3.27653049	4.0052569	-0.52874561

1	2	1	3	1	4	1	5	1	
2	6	1	17	1					
3	8	1	15	1					
4	7	1	13	1					
5									
6	10	1							
7	11	1							
8	9	1							
9	14	1.5	48	1					
10	16	1.5	22	1					
11	12	1.5	21	1					
12	13	1.5	19	1					

13	20	1				
14	15	1.5	49	1		
15	18	1				
16	17	1.5	50	1		
17	43	1				
18						
19						
20						
21						
22						
23	24	1	26	1	27	1
24	25	1				
25						
26	27	1	59	1	66	1
27	51	1	58	1		
28	29	1	30	1		
29	32	1.5	44	1		
30	31	1.5	47	1		
31	33	1.5	46	1		
32	33	1.5	45	1		
33	34	1				
34	35	1	36	1		
35	40	1	41	1	42	1
36	37	1	38	1	39	1
37						
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51	52	1	53	1	54	1
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53						
54	55	1	56	1	57	1
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59 60 1 61 1 62 1
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62 63 1 64 1 65 1
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Mo 0
LANL2DZ
****
N O H C B 0
6-31G*

16A^{+} Output Coordinates (Done by Emmit Pert)

Tag	Symbol	X	Y	Z
1	B	-2.2439	-2.26019	0.913379
2	N	-1.073	-2.71978	-0.01737
3	N	-1.63028	-1.36398	2.02765
4	N	-3.17214	-1.38177	0.016902
5	H	-2.82208	-3.17542	1.366668
6	N	-0.30018	-1.73719	-0.70509
7	N	-2.63207	-0.26798	-0.70392
8	N	-0.84311	-0.22262	1.690099
9	C	-0.4759	0.330797	2.9111
10	C	0.568086	-2.45532	-1.51623
11	C	-3.60776	0.07093	-1.63454
12	C	-4.7362	-0.76683	-1.51355
13	C	-4.43638	-1.66971	-0.4855
14	C	-0.99307	-0.41963	3.988189
15	C	-1.71396	-1.47211	3.410219
16	C	0.369689	-3.84337	-1.36185
17	C	-0.66308	-3.98271	-0.4234
18	H	-2.28056	-2.29389	3.866236
19	H	-5.65373	-0.72257	-2.10551
20	H	-5.0171	-2.50196	-0.06732
21	H	-3.43713	0.899295	-2.33241
22	H	1.27997	-1.92566	-2.16095
23	Mo	-0.6149	0.404909	-0.43359
24	N	-0.51678	0.76441	-2.15316

25	O	-0.4865	0.997949	-3.40179
26	C	-1.46672	2.263741	0.344549
27	C	-0.18719	2.581242	-0.27069
28	N	1.530471	0.233443	-0.19822
29	C	2.419233	0.701273	-1.17984
30	C	2.143725	-0.45805	0.855882
31	C	3.51298	-0.66565	0.969524
32	C	3.796577	0.526707	-1.14153
33	C	4.41007	-0.1705	-0.04103
34	N	5.789149	-0.35787	0.037434
35	C	6.69162	0.178096	-1.03495
36	C	6.392089	-1.08556	1.20277
37	H	6.163615	-0.56315	2.151519
38	H	7.484678	-1.11527	1.065506
39	H	6.009068	-2.12261	1.257288
40	H	6.598865	1.278466	-1.11103
41	H	6.448139	-0.27598	-2.01458
42	H	7.730923	-0.07555	-0.77232
43	H	-1.14296	-4.87883	-0.00939
44	H	1.952115	1.237007	-2.02005
45	H	4.401899	0.930881	-1.9593
46	H	3.892426	-1.21412	1.83755
47	H	1.457177	-0.84172	1.624444
48	H	0.143546	1.234846	2.942499
49	H	-0.85956	-0.21937	5.054078
50	H	0.905981	-4.64657	-1.87302
51	C	1.010263	3.078186	0.583626
52	H	1.087699	2.503197	1.521802
53	H	1.957393	2.941374	0.033963
54	C	0.846766	4.593694	0.927475
55	H	1.708222	4.94157	1.518832
56	H	0.790223	5.195624	0.007813
57	H	-0.07035	4.763619	1.511362
58	H	-0.24124	3.104806	-1.23765
59	C	-2.77121	2.925292	-0.19156
60	H	-2.92719	2.692816	-1.25805
61	H	-2.63121	4.021912	-0.13009
62	C	-4.03491	2.552173	0.636845
63	H	-3.90696	2.860721	1.685495
64	H	-4.91903	3.068046	0.231854
65	H	-4.22383	1.469683	0.615473
66	H	-1.45443	2.2372	1.444176

16B Input (Done by Emmit Pert)

```
%nprocshared=4
#                opt    b3lyp         geom=connectivity

Title

                0      1
                B          1.11203          -1.13266          -1.5062
                N          0.90052          -2.56586          -1.03691
                N          0.16104           -0.8894          -2.62238
                N          0.63422          -0.23519          -0.40098
                H          2.24554          -0.91565          -1.81349
                N           -0.2821          -2.99262           -0.6269
                N           -0.5873           -0.3626           0.08488
                N          -1.13564          -1.07764          -2.45421
                C          -1.70843          -0.80465          -3.65819
                C          -0.15708          -4.26351          -0.19907
                C          -0.70224           0.50902           1.11628
                C           0.47657            1.2206           1.23981
                C           1.30766           0.72075           0.26096
                C          -0.74047          -0.41516          -4.56126
                C           0.44056          -0.47909          -3.86976
                C           1.15808          -4.65578          -0.37759
                C           1.80358          -3.55387          -0.90937
                H           1.42906          -0.25658          -4.25136
                H           0.70476           1.99145           1.96332
                H           2.32968           1.01806           0.06357
                H          -1.57763           0.62453           1.74096
                H          -0.96367           -4.8602           0.20455
                Mo         -2.07109          -1.81585          -0.59035
                N          -1.80338          -2.16798           1.48331
                O           -0.7325           -2.1826           2.01238
                C           -3.1765          -0.29556          -0.81094
                C          -3.88604          -1.90225           0.04776
                C          -4.40412          -1.56258           1.46231
                H           -3.9817          -0.59751           1.81339
                H          -4.11673          -2.36823           2.17103
                C          -5.92607          -1.48859           1.49241
                H          -6.29913           -0.6833           0.83544
                H           -6.3659          -2.45591           1.16811
                H          -6.26584          -1.27441           2.52774
                N          -2.82936          -3.01506          -2.28825
                C          -1.94482          -3.81349          -2.97201
```

C	-4.14113	-3.0208	-2.71212
C	-4.57066	-3.7986	-3.78967
C	-2.33453	-4.60344	-4.05504
C	-3.66817	-4.61323	-4.48983
N	-4.09195	-5.4226	-5.60804
C	-3.13667	-6.25941	-6.32192
C	-5.48236	-5.4168	-6.04295
H	-6.13746	-5.76601	-5.21694
H	-5.65646	-6.08594	-6.91154
H	-5.77779	-4.39077	-6.34855
H	-2.69311	-7.00311	-5.62654
H	-2.33411	-5.62776	-6.75821
H	-3.60743	-6.82205	-7.15519
H	2.85288	-3.47826	-1.16407
H	-0.90536	-3.85066	-2.71665
H	-1.57459	-5.1982	-4.54197
H	-5.616	-3.74839	-4.0602
H	-4.90653	-2.43261	-2.23764
C	-3.97731	0.30107	-1.98021
H	-3.30671	0.98433	-2.54203
C	-5.14644	1.14341	-1.48465
H	-4.39206	-0.44416	-2.66499
H	-5.88144	0.51046	-0.95686
H	-5.65914	1.6122	-2.35124
H	-4.79141	1.94882	-0.80675
H	-2.74506	-0.8983	-3.91507
H	-0.88112	-0.13854	-5.59736
H	-2.92581	0.49083	-0.08136
H	-4.25651	-2.88013	-0.29309
H	1.59238	-5.61723	-0.13952

1	2	1	3	1	4	1	5	1
2	6	1	17	1.5				
3	8	1	15	1.5				
4	7	1	13	1.5				
5								
6	10	1.5						
7	11	1.5						
8	9	1.5						
9	14	2	62	1				
10	16	2	22	1				
11	12	2	21	1				
12	13	2	19	1				
13	20	1						

14	15	2	63	1		
15	18	1				
16	17	2	66	1		
17	50	1				
18						
19						
20						
21						
22						
23	26	1	27	1		
24	25	2				
25						
26	55	1	64	1		
27	28	1	65	1		
28	29	1	30	1	31	1
29						
30						
31	32	1	33	1	34	1
32						
33						
34						
35	36	1.5	37	1.5		
36	39	1.5	51	1		
37	38	1.5	54	1		
38	40	1.5	53	1		
39	40	1.5	52	1		
40	41	1				
41	42	1	43	1		
42	47	1	48	1	49	1
43	44	1	45	1	46	1
44						
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52						
53						
54						
55	56	1	57	1	58	1
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57	59	1	60	1	61	1

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Mo 0
LANL2DZ
****
N O H C B 0
6-31G*

16B Output Coordinates (Done by Emmit Pert)

Tag	Symbol	X	Y	Z
1	B	-2.35275	-2.32664	0.718612
2	N	-1.13463	-2.79644	-0.13579
3	N	-1.80362	-1.45327	1.891837
4	N	-3.22758	-1.4342	-0.21086
5	H	-2.96465	-3.24033	1.132375
6	N	-0.32524	-1.81418	-0.77753
7	N	-2.66441	-0.28869	-0.85526
8	N	-0.99881	-0.29774	1.646972
9	C	-0.71497	0.202122	2.910081
10	C	0.591133	-2.53535	-1.52335
11	C	-3.66358	0.183042	-1.68941
12	C	-4.82603	-0.62033	-1.5989
13	C	-4.52891	-1.62246	-0.6734
14	C	-1.29948	-0.59017	3.925456
15	C	-1.97602	-1.6174	3.262922
16	C	0.387539	-3.92803	-1.37462
17	C	-0.7003	-4.06524	-0.50746
18	H	-2.56758	-2.4561	3.64711
19	H	-5.76313	-0.48154	-2.14128
20	H	-5.12918	-2.45847	-0.29759
21	H	-3.47919	1.076804	-2.29634
22	H	1.335081	-2.00387	-2.1279
23	Mo	-0.63572	0.366024	-0.50444
24	N	-0.17092	0.726267	-2.11724
25	O	0.544658	0.917727	-3.18053

26	C	-1.65169	2.205025	-0.16053
27	C	-0.22574	2.316795	0.234439
28	C	0.708299	3.303254	-0.5157
29	H	0.475176	3.283174	-1.59446
30	H	1.763602	2.990681	-0.40919
31	C	0.582578	4.773373	-0.00104
32	H	-0.44578	5.142349	-0.1325
33	H	0.833469	4.834192	1.069428
34	H	1.263403	5.441689	-0.55231
35	N	1.533542	0.162933	-0.12592
36	C	2.114875	-0.28075	1.063782
37	C	2.441627	0.439029	-1.15791
38	C	3.824828	0.313555	-1.0238
39	C	3.487639	-0.42655	1.264846
40	C	4.405242	-0.11076	0.21334
41	N	5.808608	-0.18014	0.400277
42	C	6.354629	-0.87457	1.608172
43	C	6.711743	-0.0847	-0.78935
44	H	6.569683	-0.92813	-1.49541
45	H	7.754807	-0.08939	-0.43317
46	H	6.529271	0.863212	-1.32617
47	H	6.097362	-1.95328	1.626814
48	H	5.964173	-0.39981	2.525976
49	H	7.451809	-0.77	1.601159
50	H	-1.20735	-4.95687	-0.12166
51	H	1.406644	-0.52417	1.868532
52	H	3.841723	-0.78694	2.235037
53	H	4.45586	0.543081	-1.88792
54	H	1.95125	0.737141	-2.12687
55	C	-2.77417	2.361771	0.902225
56	H	-3.70225	1.879628	0.544502
57	C	-3.09497	3.857129	1.223406
58	H	-2.49008	1.855306	1.839284
59	H	-2.20659	4.366723	1.626234
60	H	-3.90531	3.934034	1.966175
61	H	-3.4108	4.390294	0.313411
62	H	-0.11198	1.111019	3.011874
63	H	-1.23737	-0.42907	5.003371
64	H	-1.91678	2.749627	-1.08069
65	H	-0.05115	2.363187	1.321419
66	H	0.958179	-4.73034	-1.84617

16B⁺ Input (Done by Emmit Pert)

%mem=12GB
%nprocshared=12

#	opt	ub3lyp	geom=connectivity	
Stable	state	0	charge	1
1	2			
	B	1.19249752	1.8954582	0
	N	2.39177452	1.4634152	-0.903668
	N	1.78945852	2.7417812	1.170492
	N	0.30330152	2.8262282	-0.870819
	H	0.59501452	0.9698652	0.404348
	N	3.22959552	2.4696472	-1.465829
	N	0.86322352	3.9945282	-1.469928
	N	2.60612252	3.8890032	0.917969
	C	2.97916652	4.3442612	2.180297
	C	4.15343452	1.7853592	-2.245566
	C	-0.14785148	4.5221752	-2.259089
	C	-1.31510148	3.7303702	-2.179348
	C	-1.00910848	2.6789332	-1.308623
	C	2.43623152	3.5337292	3.196441
	C	1.69683452	2.5394582	2.53955
	C	3.92431052	0.3950062	-2.191403
	C	2.81885452	0.2191642	-1.345572
	H	1.11165552	1.6988022	2.934433
	H	-2.26343748	3.9059412	-2.692994
	H	-1.61382248	1.8329422	-0.958476
	H	0.02650752	5.4408212	-2.832077
	H	4.92253752	2.3384092	-2.798163
	Mo	2.90977252	4.6065862	-1.157069
	N	3.11771552	5.0468542	-2.845265
	O	3.27111252	5.3716342	-4.090628
	C	1.87941752	6.3986502	-0.618452
	C	3.31861352	6.5556862	-0.366043
	C	4.15228552	7.5962482	-1.160841
	H	3.82983352	7.6092762	-2.216774
	H	5.22147352	7.3205472	-1.144176
	C	4.00421352	9.0326012	-0.567776
	H	2.95495952	9.3616832	-0.603894
	H	4.34031452	9.0574652	0.480066
	H	4.61311752	9.7462772	-1.144381
	N	5.06585252	4.4310732	-0.840384

C	5.64929252	3.7497792	0.235612
C	5.98588252	4.9246382	-1.777392
C	7.36575252	4.7893062	-1.674571
C	7.01763252	3.5793292	0.412417
C	7.94729852	4.1080032	-0.54929
N	9.32712152	3.9616442	-0.404749
C	9.89421552	3.2495372	0.787003
C	10.26293052	4.5390342	-1.424837
H	10.08647252	4.0862782	-2.419432
H	11.29601452	4.3196432	-1.111583
H	10.13550552	5.6361962	-1.497753
H	9.53992852	2.2015012	0.82234
H	9.60579252	3.7620072	1.724902
H	10.99256652	3.2517242	0.702404
H	2.29995052	-0.6913358	-1.018808
H	4.94184252	3.3401242	0.970136
H	7.37012552	3.0342692	1.293847
H	7.99548952	5.2115602	-2.464202
H	5.54781052	5.4426912	-2.642946
C	0.81924852	6.4778682	0.51276
H	-0.07565948	5.8968672	0.227613
C	0.39024952	7.9520232	0.793701
H	1.21712952	6.0373682	1.440943
H	1.25212052	8.5546652	1.117434
H	-0.37153148	7.9788472	1.588338
H	-0.03618748	8.4132502	-0.110143
H	3.61784952	5.2294632	2.281045
H	2.56361352	3.6561722	4.274876
H	1.51997852	6.9047762	-1.529884
H	3.61205752	6.5333922	0.693946
H	4.49014852	-0.3865188	-2.704487

1	2	1	3	1	4	1	5	1	
2	6	1	17	1					
3	8	1	15	1					
4	7	1	13	1					
5									
6	10	1							
7	11	1							
8	9	1							
9	14	1.5	62	1					
10	16	1.5	22	1					
11	12	1.5	21	1					
12	13	1.5	19	1					

13	20	1				
14	15	1.5	63	1		
15	18	1				
16	17	1.5	66	1		
17	50	1				
18						
19						
20						
21						
22						
23	24	1	26	1	27	1
24	25	1				
25						
26	27	1	55	1	64	1
27	28	1	65	1		
28	29	1	30	1	31	1
29						
30						
31	32	1	33	1	34	1
32						
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34						
35	36	1	37	1		
36	39	1.5	51	1		
37	38	1.5	54	1		
38	40	1.5	53	1		
39	40	1.5	52	1		
40	41	1				
41	42	1	43	1		
42	47	1	48	1	49	1
43	44	1	45	1	46	1
44						
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46						
47						
48						
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51						
52						
53						
54						
55	56	1	57	1	58	1
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Mo 0
LANL2DZ
****
N O H C B 0
6-31G*

16B^{+} Output Coordinates (Done by Emmit Pert)

Tag	Symbol	X	Y	Z
1	B	-2.27194	-2.4003	0.675036
2	N	-1.05835	-2.81038	-0.21246
3	N	-1.71125	-1.54034	1.853384
4	N	-3.16775	-1.47857	-0.20565
5	H	-2.86341	-3.33356	1.070427
6	N	-0.25401	-1.78705	-0.79229
7	N	-2.63962	-0.27246	-0.76091
8	N	-0.94166	-0.36144	1.60726
9	C	-0.60609	0.116761	2.870658
10	C	0.675781	-2.45388	-1.57655
11	C	-3.67097	0.263232	-1.52243
12	C	-4.81654	-0.55777	-1.46648
13	C	-4.47997	-1.63412	-0.63478
14	C	-1.12846	-0.7119	3.884094
15	C	-1.81759	-1.7381	3.22296
16	C	0.48506	-3.85099	-1.50728
17	C	-0.60617	-4.0485	-0.65076
18	H	-2.37614	-2.59842	3.613794
19	H	-5.77277	-0.38608	-1.96689
20	H	-5.06649	-2.50196	-0.30693
21	H	-3.52055	1.206724	-2.061
22	H	1.422939	-1.88614	-2.14388
23	Mo	-0.60275	0.354769	-0.46363
24	N	-0.46542	0.760625	-2.16776

25	O	-0.45359	0.965589	-3.44802
26	C	-1.64956	2.165503	0.035683
27	C	-0.2106	2.323606	0.27461
28	C	0.622773	3.344808	-0.54606
29	H	0.28631	3.341331	-1.59776
30	H	1.690611	3.063061	-0.53744
31	C	0.489933	4.791614	0.024396
32	H	-0.55811	5.125217	-0.00398
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37	C	2.457303	0.653827	-1.11037
38	C	3.837032	0.516286	-1.01328
39	C	3.501435	-0.59575	1.130617
40	C	4.424909	-0.11707	0.136966
41	N	5.804946	-0.26403	0.275842
42	C	6.379323	-0.92513	1.493428
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45	H	7.768962	0.04709	-0.46589
46	H	6.613591	1.35305	-0.9004
47	H	6.019425	-1.96834	1.579164
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49	H	7.476793	-0.93329	1.39868
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51	H	1.428468	-0.79899	1.716448
52	H	3.859283	-1.10068	2.033559
53	H	4.462032	0.90011	-1.82602
54	H	2.012909	1.136034	-1.99326
55	C	-2.69469	2.256033	1.180445
56	H	-3.59314	1.671701	0.913764
57	C	-3.12264	3.733583	1.446397
58	H	-2.28968	1.828734	2.111058
59	H	-2.25843	4.341028	1.75471
60	H	-3.87778	3.771223	2.246915
61	H	-3.55656	4.183052	0.540184
62	H	-0.00555	1.028093	2.974214
63	H	-1.02058	-0.57906	4.96344
64	H	-2.01858	2.671457	-0.87043
65	H	0.09163	2.316105	1.333588
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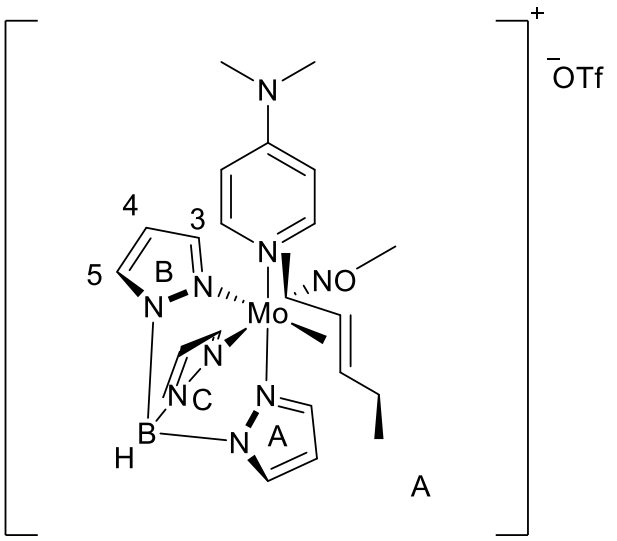
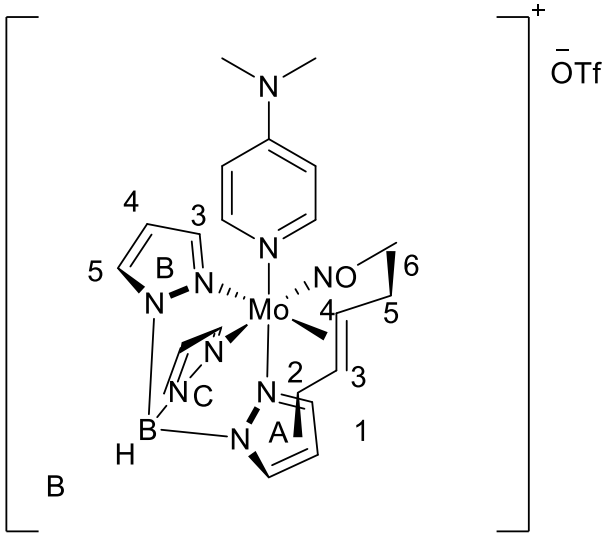
(MoTp(NO-Me)(DMAP)(η²-3-Trans-Hexene))(OTf) (**16•CH_3**)

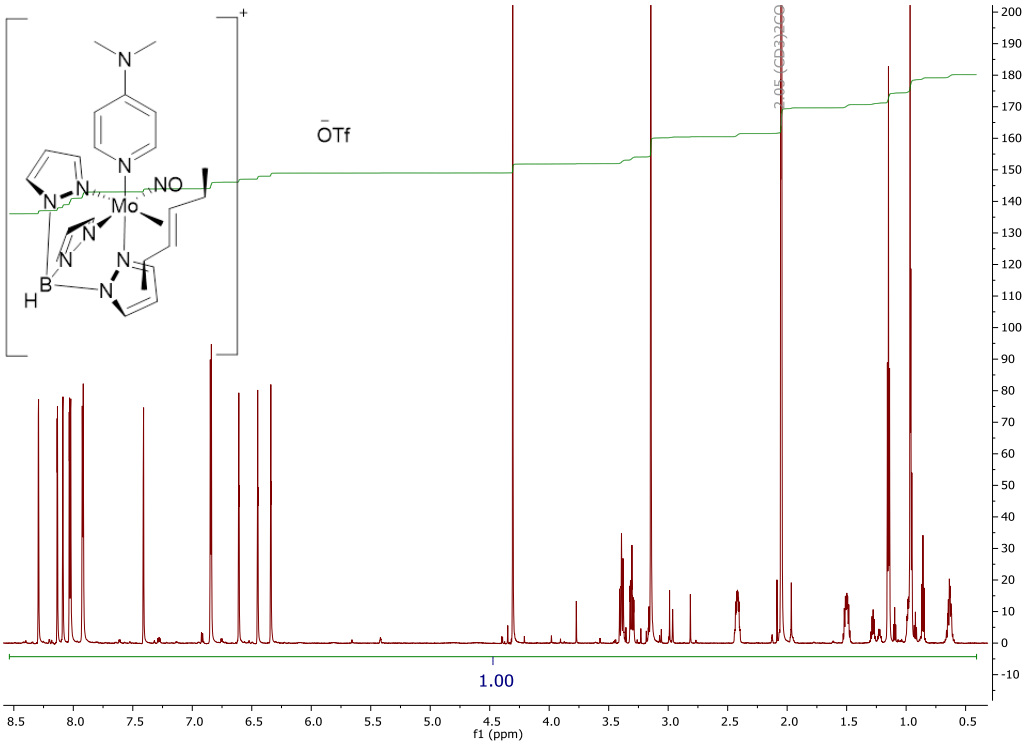




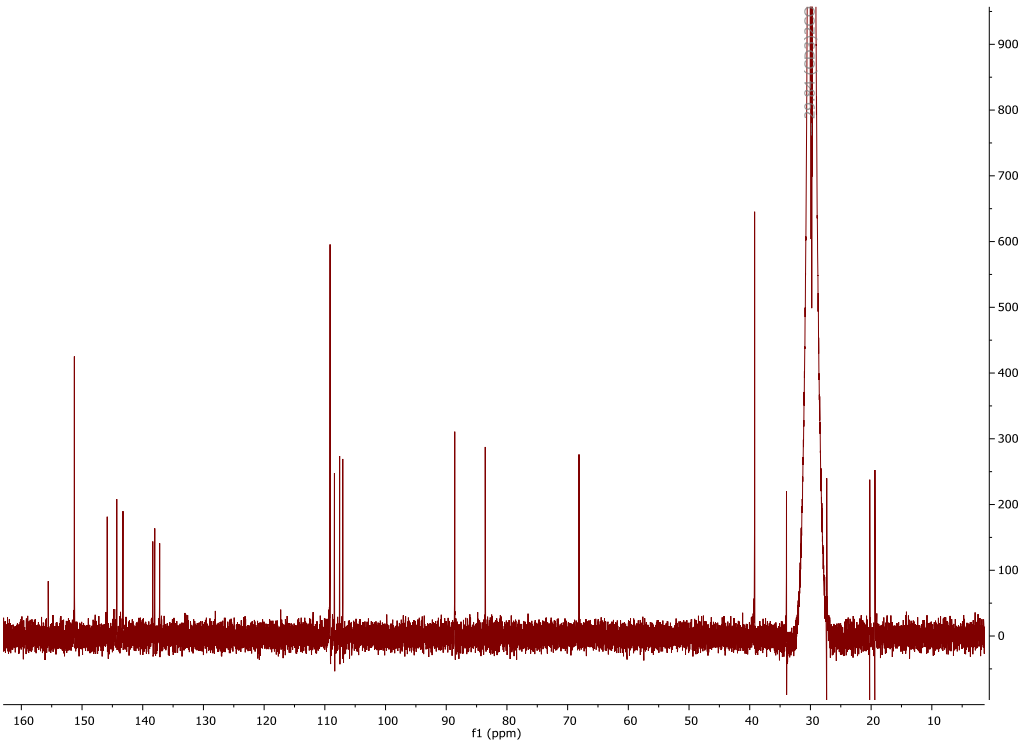
To a 4 dram vial with MoTp(NO)(DMAP)(η²-trans-3-hexene) (0.10g, 0.18 mmol) and DCM (1 mL), an excess of methyl triflate (~10 drops from a 2 mL pasture pipette) was added. The reaction was then mixed with a clean pipette for about 10 seconds before being added to 50 mL stirring ether. The resulting brown oily precipitate was collected on a 15 mL F porosity fritted disk and the brown orange filtrate was concentrated *in vacuo* to ~10 mL. At this point 10 mL of pentane was added and the volume was again reduced to 10 mL. The resulting orange brown solid was then collected on a 15 mL fine porosity fritted disk and washed pentane (3 x 10 mL). The solid was dried and collected (0.032 g, 0.000046mol, 15% mass recovered, ~12% yield of product). IR υ_{NO}: 1540 cm^{-1}, υ_{BH}: 2490 cm^{-1}. CV E_{pa}: E_{pa} 950 mV, E_{pc} -1,390 mV. ^{1}H NMR (d_6-Acetone, δ): 8.29 (1H, d, PzA3), 8.13 (1H, d, PzA5), 8.09 (1H, d, PzC5), 8.03 (1H, d, PzB5), 8.02 (1H, d, PzC3), 7.92 (2H, m, DMAP H2 and H6), 7.41 (1H, d, PzB3), 6.84 (2H, m, DMAP H3 and H5), 6.61 (1H, t, Pz4A), 6.45 (1H, t, PzC4), 6.34 (1H, t PzB4), 4.31 (3H, s, NO-methyl), 3.39 (1H, m, H3), 3.30 (1H, m, H4), 3.15 (6H, s, DMAP Methyls), 2.42 (1H, m H5x proximal to Pz), 1.50 (1H, m, H5y proximal to NO), 1.15 (3H t, H6), 0.98 (1H, m, H2x proximal to NO), 0.97 (3H, t, Hexene 1), 0.64 (1H, m, H2y proximal to Pz). ^{13}C NMR (d_6-Acetone, δ): 155.6 (DMAP 4), 151.3 (DMAP 2 and 6) 145.9 (PzA3), 144.3 (Pz3C), 143.3 (Pz3B), 138.3 (PzC5), 138.0 (Pz5

A or B), 137.2 (Pz5 A or B), 109.1 (DMAP 3 and 5), 108.4 (Pz4A), 107.6 (Pz4B), 107.0 (Pz4C), 88.6 (C3), 83.6 (C4), 68.1 (NO-Methyl), 39.2 (DMAP Methyl), 33.9 (C5), 27.3 (C2), 20.2 (C6), 19.4 (C1).

^{1}H NMR (d^{6}-Acetone) of **16**B • Me



^{13}C NMR (d^{6}-Acetone) of **16**B • Me



Gaussian DFT of:

16A•CH_3 Input (Done by Emmit Pert)

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                   C           -1.43624          -2.507567           3.072283
                   C           0.299973          -3.442607          -2.237742
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                   H           1.192068          -1.372649          -2.494802
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                   C           6.681756             0.66142          -0.993719
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H	6.565514	1.702156	-0.634681
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H	0.330931	2.095604	2.952543
H	1.785207	1.854595	1.947576
C	1.221567	3.939955	2.23696
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16A•CH_3 Output Coordinates (Done by Emmit Pert)

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5	H	-2.72691	-3.59372	0.748677
6	N	-0.31607	-1.61513	-0.9741
7	N	-2.68498	-0.21933	-0.42022
8	N	-0.72025	-0.79763	1.711611
9	C	-0.21227	-0.63181	2.994865
10	C	0.505772	-2.06731	-1.99602
11	C	-3.73929	0.366306	-1.10456
12	C	-4.86009	-0.49236	-1.14875
13	C	-4.47451	-1.65821	-0.48092
14	C	-0.63572	-1.6661	3.854185
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18	H	-1.97015	-3.43322	3.321959
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20	H	-5.01916	-2.58935	-0.28083
21	H	-3.63024	1.37124	-1.52434

22	H	1.192068	-1.37265	-2.4948
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16B•CH_3 Input (Done by Emmit Pert)

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6-31G*

16B•CH_3 Output Coordinates (Done by Emmit Pert)

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15	C	-1.6792	-2.3924	3.00599
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38	C	3.543525	-0.83776	1.050504
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54	C	-2.67773	1.885184	1.719868
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56	C	-3.08039	3.273144	2.310088
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67	H	-2.09205	2.039112	-3.64379
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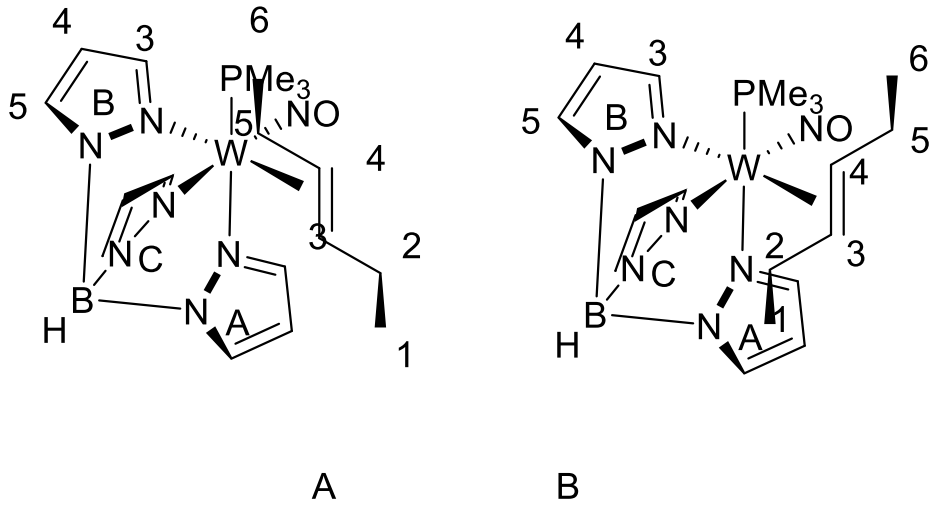
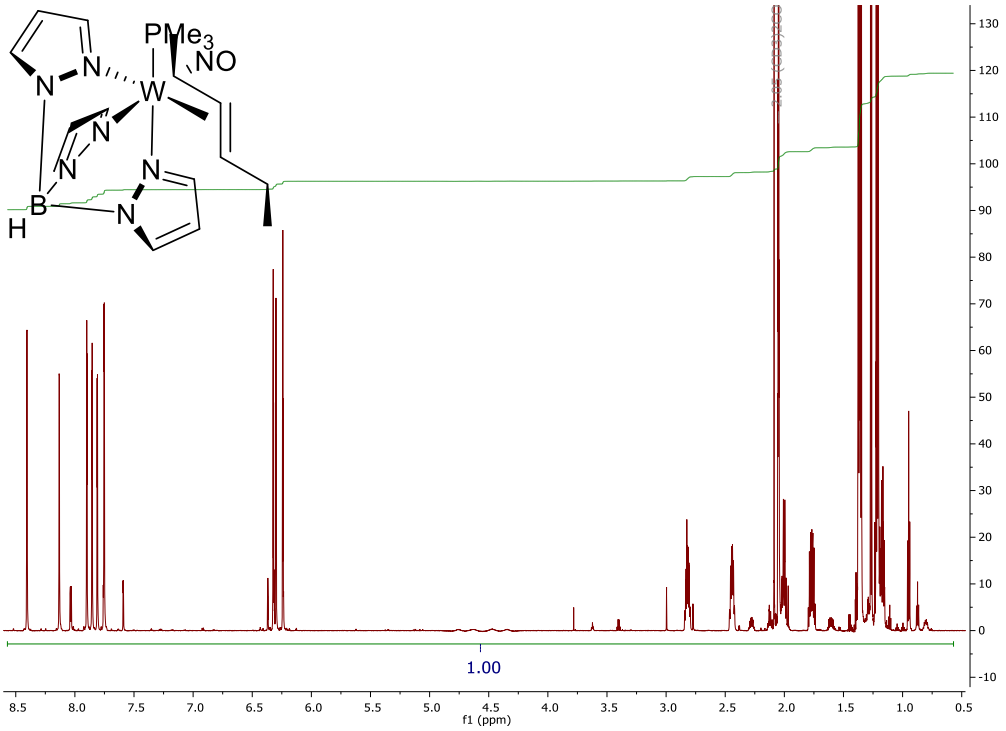
WTp(NO)(PMe$_3$)(η^2-trans-3-hexene) (**17**)



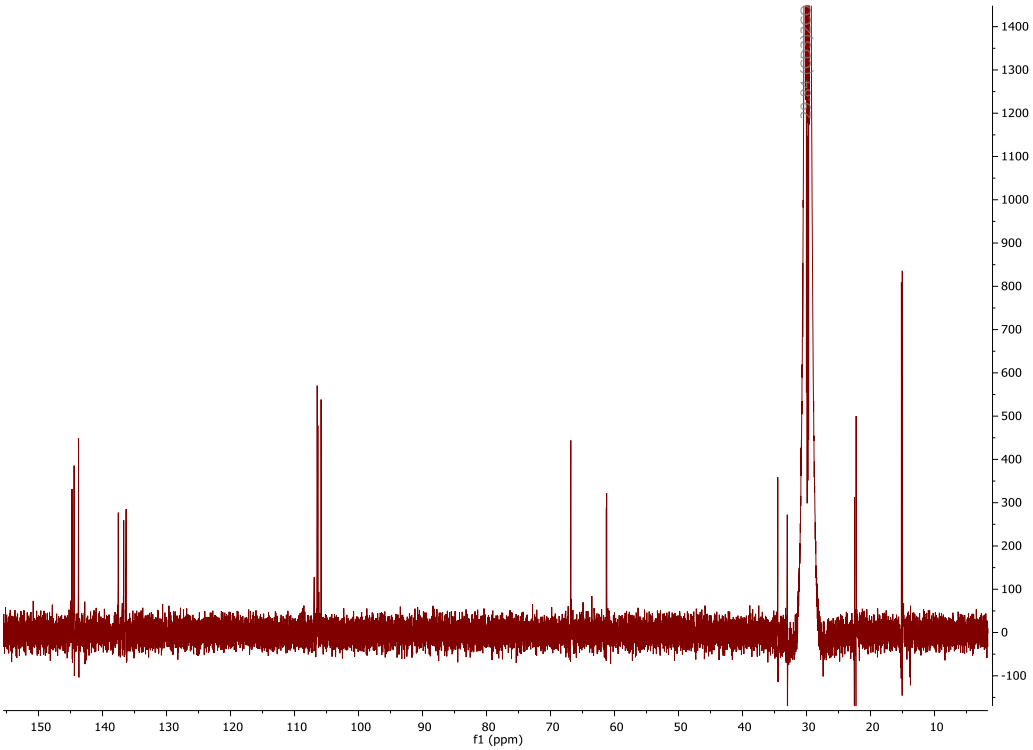
To a 4-dram vial charged with a stir pea, WTp(NO)(PMe$_3$)(η^2-anisole) (0.50 g, 0.82 mmol) was combined with trans-3-hexene (2 mL, 16 mmol) and DME (4 mL, anhydrous). The reaction vial was then capped and allowed to mix for 3 d. At this time, the solution was doubled in volume with ether and added to a 15 mL medium porosity fritted disk filled ~3/4 full with silica and then a yellow band was eluted with ~30 mL ether. The filtrate was evaporated to dryness *in vacuo* and then redissolved in 2 mL of DCM. The DCM solution was added to 100 mL stirring pentane and then concentrated to ~ 50 mL *in vacuo*. At this point a white solid was collected on a 15 mL fine porosity fritted disk and washed with pentane (3x10mL). This solid was dried and collected as mostly isomer **B** by NMR (0.11 g, 0.20 mmol, 25% yield, 1 **A** :10 **B**). The remaining filtrate and pentane from the wash of the first solid were combined and concentrated to ~20 mL *in vacuo*. The resulting precipitate was collected on a separate 15 mL fine porosity fritted disk to yield a solid that was roughly 1:1 **A** to **B** (0.027 g, 0.050 mmol, 5% yield). Again, the filtrate and washes were combined and concentrated to ~3 mL *in vacuo*. The white solid was collected to yield a third solid (~ 8:1 A:B, 0.044g, 0.081 mmol ~10% yield). Alternative Synthesis of **17**: To a 4-dram vial charged with a stir pea,

WTp(NO)(PMe_3)(η^2-benzene) (0.25 g, 0.00041 mol) was combined with trans-3-hexene (1 mL, 16.1 mmol) and DME (3 mL, anhydrous). The vial was capped and allowed to mix 18 h. To the solution, 4 mL of ether was added and the solution was loaded on a 15 mL medium porosity fritted disk, ~3/4 full of silica. A yellow band was eluted with ~20 mL ether. The filtrate was then evaporated to dryness *in vacuo*. The resulting solid was dissolved in 1 mL DCM and added to 75 mL stirring pentane. The pentane solution was concentrated to 10 mL *in vacuo* and the off-white solid was collected on a 15 mL fine porosity fritted disk. The solid was dried and collected (1:1 A:B, 0.065 g, 1.2 mmol, 28% yield). IR : **A**: υ_{NO}: 1540 cm^{-1}, υ_{BH}: 2480 cm^{-1}, **B**: υ_{NO}: 1537 cm^{-1}, υ_{BH}: 2478 cm^{-1}. CV E_{pa}: **A**: E_{pa}: 180 mV, **B**: $E_{1/2}$: 294 mV. ^{1}H NMR (d_6-Acetone, δ): **A**: 8.40 (1H, d, TpA3), 8.13 (1H, d, TpB3), 7.90 (1H, d, TpC5), 7.85 (1H, d, TpB5), 7.81 (1H, d, TpA5), 7.75 (1H, d, TpC3), 6.32 (1H, d, TpB4), 6.30 (1H, d, TpA4), 6.24 (1H, d, TpC4), 2.82 (1H, m, H2x, towards PzC3), 2.44 (1H, m, H5), 2.00 (1H, m, H4), 1.77 (1H, m, H2y towards NO), 1.36 (9 H, d, *J* = 8.0, PMe_3), 1.36 (3H, t, *J* = 7.3, H6), 1.21 (4 H, (t, *J* = 7.3, H1), m H5), 1.17 (1H, m, H3). ^{1}H NMR (d_6-Acetone, δ):**B**: 8.04 (1H, d, PzA3), 8.03 (1H, d, PzB3), 7.90 (1H, d, PzB5), 7.747.86 (1H, d, PzC5), 7.76 (1H, d, PzA5), 7.59 (1H, d, PzC3), 6.37 (1H, t, PzB4), 6.31 (1H, t, PzA4), 6.24 (1H, t, PzC4), 2.28 (1H, m, H5x, syn to PMe_3), 2.12 (1H, m, H4),2.01(1H, m, H3) 1.59 (1H, m, H5y proximal to NO), 1.26 (9H, d, *J* = 8.0, PMe_3), 1.23 (3H, t, *J* = 7.3, H6), 0.95 (3H, t, *J* = 7.3, H1), 0.79 (1H, m, H2x proximal to Tp A), 0.34 (1H, m, H2y proximal to Tp C). ^{13}C NMR (d_6-Acetone, δ): **A**: 144.8 (TpA3), 144.4 (TpAB), 143.7 (TpC3), 137.5 (TpC5), 136.7 (TpA5), 136.3 (TpB5), 106.5 (TpC4), 106.4 (TpA4), 105.8 (TpB4), 66.8 (C3), 61.3 (C4), 34.5 (C2), 33.0 (C5), 22.5 (C1), 22.2 (C6), 15.1 (d, *J* = 26.8, PMe_3). ^{13}C NMR (d_6-Acetone, δ): **B**: 145.0 (PzA/B 3), 144.1 (PzA/B3), 142.8 (PzC3), 136.9 (PzC5), 136.4 (PzB5), 135.8 (PzA5), 107.0 (PzA/B4), 106.9 (PzA/B4), 106.2 (PzC4), 65.0 (C4), 63.5 (C3), 33.3 (C5), 27.4 (C2), 22.4 (C6), 21.7 (C1), 13.9 (d, *J* = 27.3, PMe_3). ^{31}P NMR (THF, δ): **A**: 14.04 (J_{WP}=288 Hz), **B**: 12.40 (J_{WP}=286 Hz). Calculated for $C_{18}H_{32}BN_7OPW$: C, 36.76; H, 5.48; N, 16.67. Found C, 36.22; H, 5.14; N, 16.48.

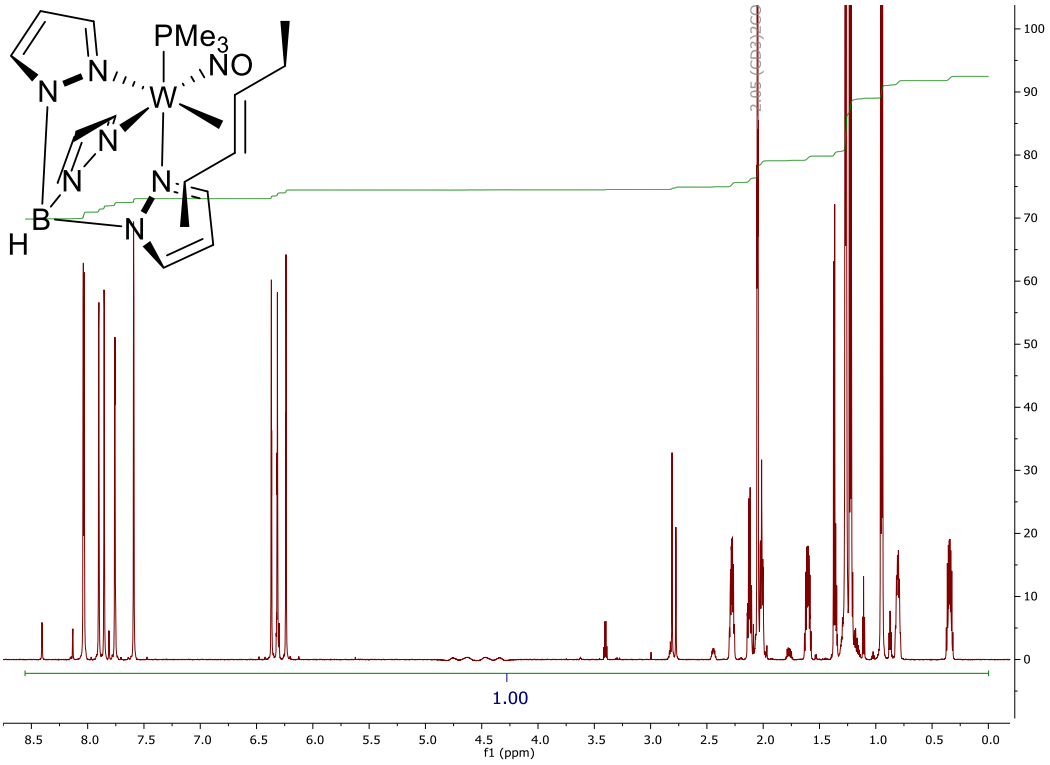
^{1}H NMR (d^{6}-Acetone) of **17**A



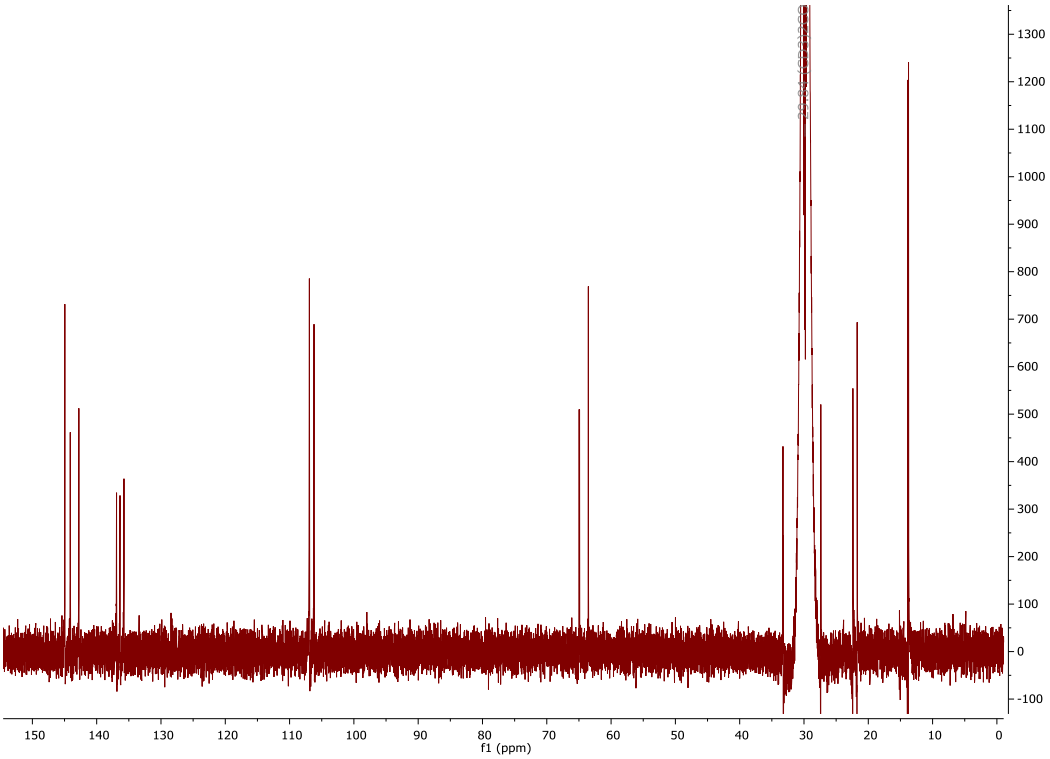
^{13}C NMR (d^{6}-Acetone) of **17**A



^{1}H NMR (d^{6}-Acetone) of **17**B



^{13}C NMR (d^{6}-Acetone) of **17**B



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17A Input (Done by Emmit Pert)

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17A Output Coordinates (Done by Emmit Pert)

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17B Input (Done by Emmit Pert)

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                     N       -6.92372547          0.36559582     8.92837196
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N	-8.13207947	0.85767982	9.33645296
N	-6.20931547	1.47831982	11.62496296
N	-7.52147547	1.84684882	11.57997096
N	-6.12713447	3.02555282	9.11737296
N	-7.42295847	3.23683882	9.49425396
N	-4.14791447	1.17305082	8.15639496
C	-9.12028147	0.21984382	8.67533996
C	-8.55567647	-0.71348718	7.81487696
C	-7.17884747	-0.57668018	8.00132796
C	-8.00530647	1.97860482	12.83092596
C	-6.98840047	1.69117382	13.73315896
C	-5.88715247	1.38773882	12.92931996
C	-7.87579747	4.36930482	8.92115496
C	-6.85826347	4.92287882	8.15140996
C	-5.78892247	4.03825282	8.29277596
B	-8.21113947	2.12016482	10.22931296
H	-9.34883147	2.44818082	10.39660296
H	-10.15339147	0.48076382	8.85484096
H	-9.06852747	-1.38668118	7.14475396
H	-6.36576547	-1.09803818	7.51651496
H	-9.03365447	2.26819882	12.99246096
H	-7.04153247	1.69868382	14.81130696
H	-4.88799647	1.10354882	13.22674196
H	-8.89172247	4.69688182	9.08932896
H	-6.89508447	5.82707082	7.56285796
H	-4.81106247	4.06162982	7.83463696
C	-4.09106347	4.24910882	11.64699196
H	-3.31987647	4.92737882	12.02657996
H	-4.74481547	4.79837282	10.96431396
H	-4.69368147	3.88646582	12.48355196
C	-2.20304647	3.68142582	9.55140596
H	-2.79403747	4.30667982	8.87737996
H	-1.48918747	4.32065782	10.08121596
H	-1.65422547	2.95279882	8.95050896
W	-5.06205047	1.22572882	9.69811396
P	-3.31149347	2.83077282	10.75745296
C	-2.11180947	2.18890382	12.01037396
H	-1.51198547	3.01501682	12.40656696
H	-2.63541847	1.71079382	12.84333696
H	-1.44201447	1.45792182	11.55132796
C	-3.43088447	-0.75764018	10.30469496
C	-4.72391147	-1.22920318	10.34639596
H	-2.98261647	-0.45361318	11.25337996

C	-2.45345647	-1.10706618	9.20162496
H	-1.91087558	-0.21465907	8.87251522
H	-3.08580933	-1.40392263	8.34953387
C	-1.4744038	-2.24759934	9.48736593
H	-1.99986228	-3.15911792	9.79735842
H	-0.90640885	-2.49184054	8.58451971
H	-0.75275679	-1.97394836	10.26094407
C	-5.41059247	-1.70760318	11.61243996
H	-4.8692361	-1.20440552	12.42923158
H	-6.43564081	-1.32824845	11.66758638
C	-5.37110697	-3.21491693	11.87850976
H	-4.3439428	-3.59474562	11.83623477
H	-5.76094386	-3.42954591	12.87856789
H	-5.96684669	-3.77613005	11.15542657
H	-5.09617247	-1.69288918	9.43136996

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5	12	1.5	18	1
6	7	1	17	1.5
7	15	1.5	18	1
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10	11	1.5	21	1
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13	14	1.5	24	1
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49 50 1 51 1 52 1
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53 54 1 55 1 56 1
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56 57 1 58 1 59 1
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W 0
LANL2DZ
*****
H B C N O P 0
6-31G(d)
*****

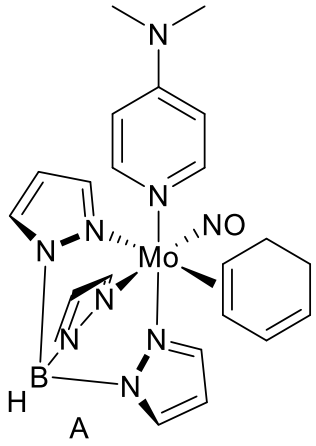
W 0
LANL2DZ

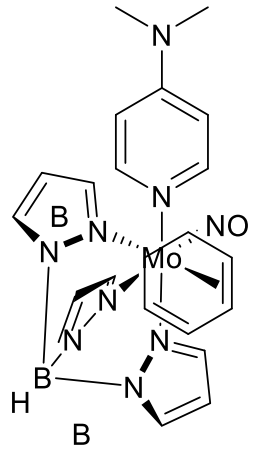
17B Output Coordinates (Done by Emmit Pert)

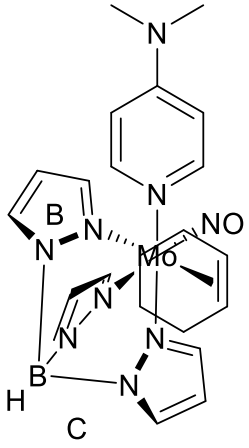
Tag	Symbol	X	Y	Z
1	O	1.093021	0.646779	-3.19408
2	N	-1.27826	-1.48133	-0.90773
3	N	-2.48633	-1.51153	-0.27835
4	N	-0.55793	-0.27517	1.742223
5	N	-1.89834	-0.42423	1.925264
6	N	-1.60527	1.27627	-0.62039
7	N	-2.77319	0.940129	-0.01009
8	N	0.783451	0.388768	-2.05155
9	C	-3.24667	-2.50169	-0.80025
10	C	-2.52002	-3.13755	-1.79449
11	C	-1.29303	-2.45835	-1.8225
12	C	-2.17069	-0.57032	3.239158
13	C	-0.97779	-0.51649	3.946643
14	C	0.000477	-0.33133	2.961818
15	C	-3.7551	1.78016	-0.40678
16	C	-3.21715	2.697886	-1.2975
17	C	-1.86829	2.330194	-1.40598
18	B	-2.87989	-0.41323	0.732151
19	H	-4.00079	-0.58587	1.126523
20	H	-4.24554	-2.67537	-0.42689
21	H	-2.82964	-3.96981	-2.40884
22	H	-0.42432	-2.62435	-2.44258
23	H	-3.18945	-0.70352	3.573138
24	H	-0.83772	-0.60589	5.013514
25	H	1.072892	-0.25813	3.067455
26	H	-4.76243	1.655568	-0.03634
27	H	-3.72689	3.504958	-1.8023
28	H	-1.08333	2.755367	-2.01532
29	C	0.119814	3.420678	1.22375
30	H	0.646196	4.316942	1.570527
31	H	-0.6385	3.709325	0.492827
32	H	-0.39057	2.955389	2.073075
33	C	2.138489	3.212939	-0.81884
34	H	1.42777	3.423268	-1.6234
35	H	2.516659	4.157991	-0.4133
36	H	2.965213	2.645265	-1.25346
37	W	0.281264	0.044446	-0.37886
38	P	1.308597	2.198801	0.486645
39	C	2.581556	2.196429	1.837632
40	H	2.932154	3.216273	2.031285
41	H	2.138533	1.803026	2.757449

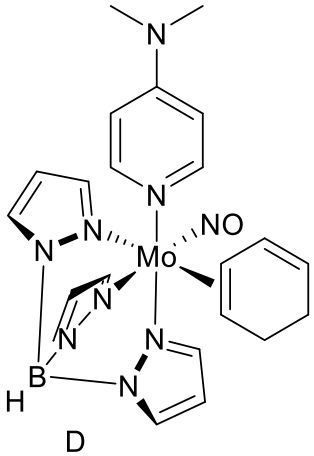
42	H	3.434465	1.570717	1.568355
43	C	2.345556	-0.73209	0.201573
44	C	1.515055	-1.81848	-0.24813
45	H	2.531653	-0.7131	1.281805
46	C	3.570617	-0.32918	-0.61255
47	H	3.875371	0.703864	-0.39257
48	H	3.311122	-0.34218	-1.67788
49	C	4.780897	-1.24681	-0.36851
50	H	4.54705	-2.2831	-0.63681
51	H	5.64787	-0.93075	-0.96266
52	H	5.079876	-1.23891	0.687984
53	C	1.109988	-2.95262	0.685809
54	H	0.922691	-2.56522	1.693825
55	H	0.165258	-3.40168	0.352617
56	C	2.177665	-4.05729	0.768027
57	H	3.126309	-3.66373	1.151837
58	H	1.857037	-4.87289	1.429006
59	H	2.37633	-4.48933	-0.22107
60	H	1.730236	-2.18011	-1.25906

MoTp(NO)(DMAP)(η²-1,3-cyclohexadiene) (18)









Gaussian DFT of:

18A Input

```
%mem=12GB
%nprocshared=12
#                opt    freq              b3lyp/gen       geom=connectivity    pseudo=read

Title            Card   Required

                 0      1
                        Mo      2.09174418      -2.37101084                0
                        O       0.69287118      -0.86437684          -2.156763
                        N       4.18557718      -2.51119184          -0.522953
                        N       4.94064718      -3.71263884          -0.338903
                        N       2.61487818      -3.76050484           1.735527
                        N       3.59804818      -4.77828584           1.537245
                        N       2.12525318      -4.28578084          -1.117818
```

N	3.09380018	-5.30348584	-0.878013
N	-0.00215282	-3.06195584	0.205494
N	1.49934318	-1.44795184	-1.317419
C	6.23489618	-3.51395584	-0.816416
C	6.34033018	-2.20874684	-1.299718
C	5.06758618	-1.61893684	-1.108258
C	3.82260418	-5.44797884	2.735934
C	3.00483718	-4.88861184	3.721188
C	2.28043418	-3.85767884	3.07921
C	2.85372018	-6.37692684	-1.730092
C	1.73656218	-6.08102484	-2.516968
C	1.31425518	-4.79004084	-2.119853
C	-0.45134282	-4.04867284	1.086559
B	4.24559318	-5.02193484	0.137413
H	5.00577918	-5.91659884	0.182033
H	6.96804418	-4.32677384	-0.767497
H	7.22274418	-1.73663684	-1.735727
H	4.72809018	-0.60533484	-1.34754
H	4.54791318	-6.26833484	2.78111
H	2.94010118	-5.18310084	4.770408
H	1.54139718	-3.17113584	3.506552
H	3.50299518	-7.25940384	-1.702137
H	1.28667018	-6.71312884	-3.284947
H	0.47963118	-4.18723384	-2.496126
H	0.31971218	-4.47731584	1.741967
C	-1.76985782	-4.49594884	1.165983
H	-2.01723982	-5.27774684	1.889976
C	-0.98644882	-2.54926384	-0.65148
H	-0.60050082	-1.79221584	-1.388381
C	-2.77141082	-3.93729784	0.309652
C	-2.32219382	-2.95149684	-0.624863
H	-3.01778182	-2.49816984	-1.337781
N	-4.13255182	-4.31564684	0.406436
C	-4.50731582	-5.51879484	1.212924
H	-5.60586682	-5.60764284	1.212433
H	-4.07193482	-6.45272184	0.802683
H	-4.16684282	-5.39616384	2.256744
C	-5.09354382	-3.88232784	-0.655591
H	-4.84924382	-4.31620784	-1.646585
H	-6.10437182	-4.20942984	-0.362253
H	-5.09202582	-2.78083884	-0.739214
C	2.80373718	-0.65838684	1.07271
C	1.39701018	-0.96826084	1.445798
H	1.27150318	-1.37736884	2.459423

C	0.27003418	0.04598716	1.095728
C	2.99096218	0.70639916	0.334476
H	-0.54242926	-0.1142123	1.77332618
C	0.66704018	1.58701016	1.156825
C	2.22287318	1.83301016	1.098174
H	0.28844525	2.00260677	2.06723443
H	3.56015735	0.84827068	-0.56039233
H	2.70325972	2.68307998	1.53579263
H	-0.07353716	-0.16888348	0.1054304
H	0.20891967	2.09188639	0.33212773
H	3.50697923	-0.88167064	1.8476261

1	10	1	49	1	50	1
2	10	1				
3	4	1	13	1		
4	11	1	21	1		
5	6	1	16	1		
6	14	1	21	1		
7	8	1	19	1		
8	17	1	21	1		
9	20	1	35	1		
10						
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12	13	1.5	24	1		
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14	15	1.5	26	1		
15	16	1.5	27	1		
16	28	1				
17	18	1.5	29	1		
18	19	1.5	30	1		
19	31	1				
20	32	1	33	1.5		
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22						
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25						
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31						
32						

33	34	1	37	1.5				
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35	36	1	38	1.5				
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37	38	1.5	40	1				
38	39	1						
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45	46	1	47	1	48	1		
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48								
49	50	1	53	1	62	1		
50	51	1	52	1				
51								
52	54	1	55	1	60	1		
53	56	2	58	1				
54								
55	56	1	57	1	61	1		
56	59	1						
57								
58								
59								
60								
61								
62								

Mo 0
LANL2DZ
*****
H B C N O 0
6-31G(d)
*****

Mo 0
LANL2DZ

18A Output Coordinates

Tag	Symbol	X	Y	Z

1	Mo	0.630898	0.453805	-0.20316
2	O	0.254113	2.044684	-2.69085
3	N	2.81394	0.021413	-0.56141
4	N	3.332132	-1.20777	-0.28707
5	N	1.019024	-0.85726	1.721683
6	N	1.827683	-1.94487	1.605733
7	N	0.487633	-1.60871	-1.15955
8	N	1.319363	-2.61293	-0.777
9	N	-1.63057	0.167688	-0.04596
10	N	0.434738	1.399062	-1.6889
11	C	4.619011	-1.26475	-0.70456
12	C	4.952921	-0.04447	-1.26866
13	C	3.783736	0.724426	-1.15802
14	C	2.02065	-2.50958	2.817001
15	C	1.31844	-1.77651	3.763095
16	C	0.712528	-0.75118	3.023783
17	C	1.030411	-3.73691	-1.46977
18	C	-0.02361	-3.46448	-2.33
19	C	-0.32418	-2.11422	-2.09614
20	C	-2.20269	-0.66714	0.846479
21	B	2.447576	-2.353	0.247208
22	H	3.105514	-3.34851	0.392232
23	H	5.195023	-2.1689	-0.57022
24	H	5.899992	0.248364	-1.69707
25	H	3.589129	1.736598	-1.47911
26	H	2.643338	-3.38692	2.916868
27	H	1.258278	-1.95465	4.826495
28	H	0.081187	0.056221	3.367643
29	H	1.597726	-4.64147	-1.30383
30	H	-0.49735	-4.13932	-3.02753
31	H	-1.07534	-1.4858	-2.55316
32	H	-1.52546	-1.15722	1.536496
33	C	-3.56174	-0.92188	0.915471
34	H	-3.91891	-1.61153	1.669937
35	C	-2.47018	0.763168	-0.92219
36	H	-2.0106	1.418571	-1.65312
37	C	-4.4474	-0.2906	0.010187
38	C	-3.84099	0.572103	-0.93385
39	H	-4.42528	1.0964	-1.67952
40	N	-5.80121	-0.50282	0.042813
41	C	-6.36897	-1.43089	1.00914
42	H	-7.45286	-1.45499	0.888411
43	H	-5.98758	-2.45201	0.869257
44	H	-6.15059	-1.12232	2.040074

45	C	-6.66358	0.147522	-0.93288
46	H	-6.42202	-0.1571	-1.96071
47	H	-7.70034	-0.12682	-0.73323
48	H	-6.58554	1.240913	-0.8727
49	C	1.490573	2.161773	1.047137
50	C	0.073597	2.168419	1.177065
51	H	-0.36264	1.725964	2.073335
52	C	-0.70318	3.361037	0.609206
53	C	2.155743	3.33077	0.439579
54	H	-1.67504	3.44966	1.111096
55	C	0.086194	4.678585	0.74789
56	C	1.521409	4.506422	0.302954
57	H	0.068502	5.025989	1.795176
58	H	3.204044	3.242026	0.159883
59	H	2.044677	5.371176	-0.10178
60	H	-0.91513	3.218418	-0.45649
61	H	-0.40547	5.466148	0.161609
62	H	2.082891	1.632405	1.793588

18B Input

```
%mem=12GB
%nprocshared=12
#                opt    freq              b3lyp/gen       geom=connectivity   pseudo=read

Title             Card  Required

                0     1
                Mo       -5.94450061       -3.961396                0
                O        -7.17514861       -3.283495        -2.623506
                N        -5.38970761       -6.053763        -0.101713
                N        -5.65409861        -6.96707         0.969383
                N        -5.50826861       -4.129851         2.242614
                N        -5.80955561       -5.348356         2.924851
                N        -7.82510561       -4.962761          0.63613
                N        -7.86135861       -5.999292         1.613952
                N        -7.26214561       -2.245812         0.494394
                N        -6.51900761       -3.734941        -1.600509
                C        -5.26028461       -8.247274         0.583045
                C        -4.73864061       -8.187219        -0.709708
                C        -4.83682761       -6.831331         -1.10497
                C        -5.40091161       -5.254426         4.251371
                C        -4.83361761       -3.994133         4.455977
                C        -4.91132261       -3.331121         3.209514
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C	-9.17474861	-6.425985	1.784116
C	-9.99999461	-5.677353	0.939742
C	-9.14191361	-4.79097	0.246161
C	-7.53235161	-1.76716	1.778469
B	-6.51334361	-6.532286	2.193695
H	-6.68888061	-7.430424	2.930491
H	-5.39031061	-9.090862	1.270097
H	-4.33782161	-9.014395	-1.298529
H	-4.54394461	-6.362913	-2.050238
H	-5.55106161	-6.097623	4.935118
H	-4.41255261	-3.602775	5.384041
H	-4.55925961	-2.328118	2.945178
H	-9.40647861	-7.229271	2.492698
H	-11.08287061	-5.763842	0.832044
H	-9.38739561	-4.043705	-0.517293
H	-7.00765361	-2.286797	2.592212
C	-8.40088061	-0.713306	2.063137
H	-8.54569061	-0.41897	3.106652
C	-7.96631261	-1.598829	-0.531722
H	-7.78491261	-2.037232	-1.553375
C	-9.08632161	-0.040212	1.002861
C	-8.84925361	-0.540334	-0.316669
H	-9.36006161	-0.103537	-1.180324
N	-9.92251161	1.077665	1.244253
C	-10.33782861	1.395867	2.646192
H	-10.92831161	2.326363	2.629631
H	-10.95164861	0.589605	3.097049
H	-9.44580861	1.558994	3.277063
C	-10.80147961	1.587514	0.145528
H	-11.56365661	0.843578	-0.163779
H	-11.31375561	2.494838	0.504962
H	-10.18901061	1.855993	-0.733616
C	-3.87005561	-3.680549	-0.496473
C	-4.50344761	-2.399317	-0.066781
C	-2.80848561	-4.318586	0.481793
H	-3.21075461	-4.349611	1.505584
C	-1.47075261	-3.559651	0.507764
H	-4.64973182	-1.68409147	-0.84905548
H	-3.65832672	-3.73590799	-1.54385366
H	-0.70290473	-4.20305265	0.88372137
C	-4.04645563	-1.87880501	1.30865551
H	-4.79121639	-1.22175215	1.70679237
H	-3.90699456	-2.70488112	1.97427467
C	-2.71828487	-1.11502618	1.15307814

H	-2.88885764	-0.06912509	1.30105059			
H	-2.01652712	-1.46823602	1.87949323			
1	10	1	49	1	50	1
2	10	1				
3	4	1	13	1		
4	11	1	21	1		
5	6	1	16	1		
6	14	1	21	1		
7	8	1	19	1		
8	17	1	21	1		
9	20	1	35	1		
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12	13	1.5	24	1		
13	25	1				
14	15	1.5	26	1		
15	16	1.5	27	1		
16	28	1				
17	18	1.5	29	1		
18	19	1.5	30	1		
19	31	1				
20	32	1	33	1.5		
21	22	1				
22						
23						
24						
25						
26						
27						
28						
29						
30						
31						
32						
33	34	1	37	1.5		
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35	36	1	38	1.5		
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37	38	1.5	40	1		
38	39	1				
39						
40	41	1	45	1		
41	42	1	43	1	44	1

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                42
                43
                44
                45              46              1               47              1   48  1
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                47
                48
                49              50              1               51              1   55  1
                50              54              1               57              1
                51              52              1               53              2
                52
                53              56              1               60              1
                54
                55
                56
                57              58              1               59              1   60  1
                58
                59
                60              61              1               62              1
                61
                62

Mo                      0
LANL2DZ
*****
H                   B       C               N               O                   0
6-31G(d)
*****

Mo                      0
LANL2DZ
```

18B Output Coordinates

Tag	Symbol	X	Y	Z
1	Mo	0.581506	0.234083	-0.72778
2	O	0.172548	-0.1463	-3.64845
3	N	2.783798	-0.2431	-0.81657
4	N	3.348584	-1.10741	0.069417
5	N	1.065169	0.272218	1.626348
6	N	1.911414	-0.68523	2.102167
7	N	0.475578	-1.99194	-0.25596
8	N	1.384956	-2.59546	0.550655
9	N	-1.65683	0.099125	-0.34075

10	N	0.349645	0.002996	-2.46554
11	C	4.64675	-1.31191	-0.25364
12	C	4.941739	-0.56585	-1.38339
13	C	3.738196	0.083854	-1.69655
14	C	2.11373	-0.51131	3.4257
15	C	1.380553	0.589134	3.843204
16	C	0.748628	1.042422	2.677429
17	C	1.134257	-3.92182	0.615383
18	C	0.025219	-4.19744	-0.17188
19	C	-0.34699	-2.95144	-0.6984
20	C	-2.16969	-0.205	0.869825
21	B	2.523516	-1.77197	1.190878
22	H	3.230402	-2.49268	1.843819
23	H	5.258878	-1.97147	0.344272
24	H	5.885334	-0.50003	-1.90444
25	H	3.514716	0.761681	-2.50729
26	H	2.763979	-1.18107	3.969831
27	H	1.319915	1.00622	4.837495
28	H	0.099161	1.894026	2.548628
29	H	1.763035	-4.56814	1.210775
30	H	-0.43931	-5.157	-0.34466
31	H	-1.15397	-2.70002	-1.37194
32	H	-1.4488	-0.32936	1.669728
33	C	-3.52209	-0.36236	1.12464
34	H	-3.83099	-0.60533	2.133501
35	C	-2.54978	0.233994	-1.34698
36	H	-2.13376	0.459142	-2.32257
37	C	-4.46184	-0.21233	0.078221
38	C	-3.91662	0.090436	-1.19376
39	H	-4.54707	0.214762	-2.06517
40	N	-5.81008	-0.35381	0.279171
41	C	-6.317	-0.68648	1.602094
42	H	-7.40563	-0.7445	1.564428
43	H	-5.93624	-1.65551	1.953235
44	H	-6.04391	0.077196	2.342521
45	C	-6.73241	-0.21131	-0.8379
46	H	-6.54483	-0.9595	-1.62025
47	H	-7.75332	-0.34706	-0.47841
48	H	-6.66358	0.785336	-1.29363
49	C	1.390886	2.347713	-1.05041
50	C	-0.02598	2.433757	-0.99948
51	C	2.181601	2.96997	0.028697
52	H	3.227103	2.683788	0.13105
53	C	1.645886	3.892342	0.84424

54	H	-0.55961	2.472722	-1.94772
55	H	1.880488	2.310774	-2.02298
56	H	2.253259	4.369928	1.611426
57	C	-0.69274	3.20653	0.141465
58	H	-1.63924	3.632777	-0.21469
59	H	-0.97432	2.538926	0.966012
60	C	0.206849	4.334709	0.691705
61	H	0.166468	5.202093	0.011848
62	H	-0.18994	4.693717	1.651344

18C Input

```
%mem=12GB
%nprocshared=12
#                opt    freq              b3lyp/gen       geom=connectivity   pseudo=read

Title             Card   Required

                0      1
                   Mo       -5.94450061       -3.961396                0
                   O        -7.17514861       -3.283495          -2.623506
                   N        -5.38970761       -6.053763          -0.101713
                   N        -5.65409861        -6.96707           0.969383
                   N        -5.50826861       -4.129851           2.242614
                   N        -5.80955561       -5.348356           2.924851
                   N        -7.82510561       -4.962761            0.63613
                   N        -7.86135861       -5.999292           1.613952
                   N        -7.26214561       -2.245812           0.494394
                   N        -6.51900761       -3.734941          -1.600509
                   C        -5.26028461       -8.247274           0.583045
                   C        -4.73864061       -8.187219          -0.709708
                   C        -4.83682761       -6.831331           -1.10497
                   C        -5.40091161       -5.254426           4.251371
                   C        -4.83361761       -3.994133           4.455977
                   C        -4.91132261       -3.331121           3.209514
                   C        -9.17474861       -6.425985           1.784116
                   C        -9.99999461       -5.677353           0.939742
                   C        -9.14191361        -4.79097           0.246161
                   C        -7.53235161        -1.76716           1.778469
                   B        -6.51334361       -6.532286           2.193695
                   H        -6.68888061       -7.430424           2.930491
                   H        -5.39031061       -9.090862           1.270097
                   H        -4.33782161       -9.014395          -1.298529
                   H        -4.54394461       -6.362913          -2.050238
```

H	-5.55106161	-6.097623	4.935118
H	-4.41255261	-3.602775	5.384041
H	-4.55925961	-2.328118	2.945178
H	-9.40647861	-7.229271	2.492698
H	-11.08287061	-5.763842	0.832044
H	-9.38739561	-4.043705	-0.517293
H	-7.00765361	-2.286797	2.592212
C	-8.40088061	-0.713306	2.063137
H	-8.54569061	-0.41897	3.106652
C	-7.96631261	-1.598829	-0.531722
H	-7.78491261	-2.037232	-1.553375
C	-9.08632161	-0.040212	1.002861
C	-8.84925361	-0.540334	-0.316669
H	-9.36006161	-0.103537	-1.180324
N	-9.92251161	1.077665	1.244253
C	-10.33782861	1.395867	2.646192
H	-10.92831161	2.326363	2.629631
H	-10.95164861	0.589605	3.097049
H	-9.44580861	1.558994	3.277063
C	-10.80147961	1.587514	0.145528
H	-11.56365661	0.843578	-0.163779
H	-11.31375561	2.494838	0.504962
H	-10.18901061	1.855993	-0.733616
C	-3.87005561	-3.680549	-0.496473
C	-4.50344761	-2.399317	-0.066781
C	-2.80848561	-4.318586	0.481793
H	-3.21631488	-4.32805169	1.47097735
C	-1.47075261	-3.559651	0.507764
H	-4.64973182	-1.68409147	-0.84905548
H	-3.65832672	-3.73590799	-1.54385366
H	-0.82228383	-3.9038807	1.28615603
C	-4.04645563	-1.87880501	1.30865551
H	-4.79121639	-1.22175215	1.70679237
C	-2.71828487	-1.11502618	1.15307814
H	-2.88885764	-0.06912509	1.30105059
H	-0.99795651	-3.53475906	-0.45179019
H	-2.62419801	-5.32745018	0.17661905

1	10	1	49	1	50	1
2	10	1				
3	4	1	13	1		
4	11	1	21	1		
5	6	1	16	1		
6	14	1	21	1		

7	8	1	19	1		
8	17	1	21	1		
9	20	1	35	1		
10						
11	12	1.5	23	1		
12	13	1.5	24	1		
13	25	1				
14	15	1.5	26	1		
15	16	1.5	27	1		
16	28	1				
17	18	1.5	29	1		
18	19	1.5	30	1		
19	31	1				
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21	22	1				
22						
23						
24						
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27						
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29						
30						
31						
32						
33	34	1	37	1.5		
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35	36	1	38	1.5		
36						
37	38	1.5	40	1		
38	39	1				
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40	41	1	45	1		
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42						
43						
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45	46	1	47	1	48	1
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47						
48						
49	50	1	51	1	55	1
50	54	1	57	1		

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                    51              52              1               53              1   62  1
                    52
                    53              56              1               59              1   61  1
                    54
                    55
                    56
                    57              58              1               59              2
                    58
                    59              60              1
                    60
                    61
                    62

Mo                  0
LANL2DZ
*****
H                   B       C               N               O                       0
6-31G(d)
*****

Mo                  0
LANL2DZ
```

18C Output Coordinates

Tag	Symbol	X	Y	Z
1	Mo	0.573952	0.237064	-0.72075
2	O	0.087976	-0.04899	-3.6421
3	N	2.763762	-0.28886	-0.7991
4	N	3.301995	-1.16672	0.091368
5	N	1.000211	0.203642	1.618544
6	N	1.818065	-0.77353	2.102628
7	N	0.436269	-2.00079	-0.32195
8	N	1.313741	-2.63877	0.493868
9	N	-1.67637	0.148549	-0.33677
10	N	0.306833	0.065399	-2.46225
11	C	4.602965	-1.38474	-0.21082
12	C	4.926985	-0.63359	-1.32941
13	C	3.737559	0.03362	-1.65838
14	C	1.939776	-0.65266	3.441917
15	C	1.181808	0.432298	3.858122
16	C	0.615824	0.93311	2.67716
17	C	1.045529	-3.96305	0.512259
18	C	-0.04271	-4.20168	-0.31537

19	C	-0.38392	-2.93651	-0.8167
20	C	-2.20241	-0.24737	0.841309
21	B	2.446167	-1.84462	1.181906
22	H	3.129578	-2.58712	1.835257
23	H	5.196439	-2.05666	0.392133
24	H	5.880821	-0.57486	-1.83235
25	H	3.536026	0.725337	-2.46298
26	H	2.556308	-1.34458	3.99761
27	H	1.064054	0.809222	4.863349
28	H	-0.01871	1.793791	2.52609
29	H	1.648622	-4.63451	1.106462
30	H	-0.51321	-5.1499	-0.52964
31	H	-1.16648	-2.65504	-1.50705
32	H	-1.48894	-0.46671	1.626677
33	C	-3.55963	-0.38011	1.082231
34	H	-3.87829	-0.70417	2.064946
35	C	-2.56275	0.402364	-1.32556
36	H	-2.1391	0.693521	-2.28012
37	C	-4.49236	-0.10106	0.055816
38	C	-3.93449	0.293823	-1.18444
39	H	-4.55789	0.514552	-2.04171
40	N	-5.84538	-0.20885	0.246802
41	C	-6.36464	-0.6657	1.52722
42	H	-7.4549	-0.66833	1.491081
43	H	-6.02841	-1.6843	1.766667
44	H	-6.05551	-0.00212	2.345379
45	C	-6.75926	0.04616	-0.85714
46	H	-6.60398	-0.6547	-1.68928
47	H	-7.78559	-0.06742	-0.50536
48	H	-6.64603	1.067236	-1.24381
49	C	1.460779	2.318235	-1.03469
50	C	0.057997	2.467971	-0.85921
51	C	2.391605	2.889542	0.040585
52	H	2.555203	2.16182	0.842263
53	C	1.823104	4.179354	0.670016
54	H	-0.57689	2.527768	-1.74363
55	H	1.847911	2.350415	-2.05176
56	H	2.401614	4.440201	1.566307
57	C	-0.4465	3.223945	0.302232
58	H	-1.50852	3.157247	0.53968
59	C	0.356772	4.035073	1.01277
60	H	-0.04583	4.634901	1.82835
61	H	1.946497	5.027829	-0.02414
62	H	3.378421	3.090239	-0.39327

18D Input

```
%mem=12GB
%nprocshared=12
#                opt    freq              b3lyp/gen       geom=connectivity    pseudo=read

Title             Card   Required

                0      1
                Mo        2.09174418    -2.37101084                   0
                O         0.69287118    -0.86437684            -2.156763
                N         4.18557718    -2.51119184            -0.522953
                N         4.94064718    -3.71263884            -0.338903
                N         2.61487818    -3.76050484             1.735527
                N         3.59804818    -4.77828584             1.537245
                N         2.12525318    -4.28578084            -1.117818
                N         3.09380018    -5.30348584            -0.878013
                N        -0.00215282    -3.06195584             0.205494
                N         1.49934318    -1.44795184            -1.317419
                C         6.23489618    -3.51395584            -0.816416
                C         6.34033018    -2.20874684            -1.299718
                C         5.06758618    -1.61893684            -1.108258
                C         3.82260418    -5.44797884             2.735934
                C         3.00483718    -4.88861184             3.721188
                C         2.28043418    -3.85767884              3.07921
                C         2.85372018    -6.37692684            -1.730092
                C         1.73656218    -6.08102484            -2.516968
                C         1.31425518    -4.79004084            -2.119853
                C        -0.45134282    -4.04867284             1.086559
                B         4.24559318    -5.02193484             0.137413
                H         5.00577918    -5.91659884             0.182033
                H         6.96804418    -4.32677384            -0.767497
                H         7.22274418    -1.73663684            -1.735727
                H         4.72809018    -0.60533484             -1.34754
                H         4.54791318    -6.26833484              2.78111
                H         2.94010118    -5.18310084             4.770408
                H         1.54139718    -3.17113584             3.506552
                H         3.50299518    -7.25940384            -1.702137
                H         1.28667018    -6.71312884            -3.284947
                H         0.47963118    -4.18723384            -2.496126
                H         0.31971218    -4.47731584             1.741967
                C        -1.76985782    -4.49594884             1.165983
                H        -2.01723982    -5.27774684             1.889976
                C        -0.98644882    -2.54926384             -0.65148
```

H	-0.60050082	-1.79221584	-1.388381
C	-2.77141082	-3.93729784	0.309652
C	-2.32219382	-2.95149684	-0.624863
H	-3.01778182	-2.49816984	-1.337781
N	-4.13255182	-4.31564684	0.406436
C	-4.50731582	-5.51879484	1.212924
H	-5.60586682	-5.60764284	1.212433
H	-4.07193482	-6.45272184	0.802683
H	-4.16684282	-5.39616384	2.256744
C	-5.09354382	-3.88232784	-0.655591
H	-4.84924382	-4.31620784	-1.646585
H	-6.10437182	-4.20942984	-0.362253
H	-5.09202582	-2.78083884	-0.739214
C	2.80373718	-0.65838684	1.07271
C	1.39701018	-0.96826084	1.445798
H	1.27150318	-1.37736884	2.459423
C	0.27003418	0.04598716	1.095728
C	2.99096218	0.70639916	0.334476
H	4.06145218	0.97286016	0.291548
H	2.61897018	0.65995116	-0.701098
H	-0.58435482	-0.11039384	1.7762
C	0.66704018	1.58701016	1.156825
C	2.22287318	1.83301016	1.098174
H	0.30904718	1.99179916	2.120562
H	2.42120318	2.81471916	0.633461
H	2.60855518	1.87915516	2.130877
H	3.50697923	-0.88167064	1.8476261

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3	4	1	13	1		
4	11	1	21	1		
5	6	1	16	1		
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15	16	1.5	27	1		
16	28	1				

17	18	1.5	29	1		
18	19	1.5	30	1		
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21	22	1				
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24						
25						
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27						
28						
29						
30						
31						
32						
33	34	1	37	1.5		
34						
35	36	1	38	1.5		
36						
37	38	1.5	40	1		
38	39	1				
39						
40	41	1	45	1		
41	42	1	43	1	44	1
42						
43						
44						
45	46	1	47	1	48	1
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47						
48						
49	50	1	53	1	62	1
50	51	1	52	1		
51						
52	56	1	57	2		
53	54	1	55	1	58	1
54						
55						
56						
57	58	1	59	1		
58	60	1	61	1		
59						
60						

61
62

Mo 0
LANL2DZ
*****
H B C N O 0
6-31G(d)
*****

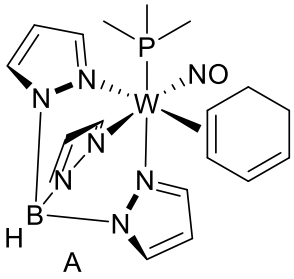
Mo 0
LANL2DZ

18D Output Coordinates

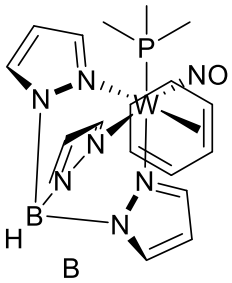
Tag	Symbol	X	Y	Z
1	Mo	2.091744	-2.37101	0
2	O	0.692871	-0.86438	-2.15676
3	N	4.185577	-2.51119	-0.52295
4	N	4.940647	-3.71264	-0.3389
5	N	2.614878	-3.7605	1.735527
6	N	3.598048	-4.77829	1.537245
7	N	2.125253	-4.28578	-1.11782
8	N	3.0938	-5.30349	-0.87801
9	N	-0.00215	-3.06196	0.205494
10	N	1.499343	-1.44795	-1.31742
11	C	6.234896	-3.51396	-0.81642
12	C	6.34033	-2.20875	-1.29972
13	C	5.067586	-1.61894	-1.10826
14	C	3.822604	-5.44798	2.735934
15	C	3.004837	-4.88861	3.721188
16	C	2.280434	-3.85768	3.07921
17	C	2.85372	-6.37693	-1.73009
18	C	1.736562	-6.08102	-2.51697
19	C	1.314255	-4.79004	-2.11985
20	C	-0.45134	-4.04867	1.086559
21	B	4.245593	-5.02193	0.137413
22	H	5.005779	-5.9166	0.182033
23	H	6.968044	-4.32677	-0.7675
24	H	7.222744	-1.73664	-1.73573
25	H	4.72809	-0.60533	-1.34754
26	H	4.547913	-6.26833	2.78111
27	H	2.940101	-5.1831	4.770408
28	H	1.541397	-3.17114	3.506552

29	H	3.502995	-7.2594	-1.70214
30	H	1.28667	-6.71313	-3.28495
31	H	0.479631	-4.18723	-2.49613
32	H	0.319712	-4.47732	1.741967
33	C	-1.76986	-4.49595	1.165983
34	H	-2.01724	-5.27775	1.889976
35	C	-0.98645	-2.54926	-0.65148
36	H	-0.6005	-1.79222	-1.38838
37	C	-2.77141	-3.9373	0.309652
38	C	-2.32219	-2.9515	-0.62486
39	H	-3.01778	-2.49817	-1.33778
40	N	-4.13255	-4.31565	0.406436
41	C	-4.50732	-5.51879	1.212924
42	H	-5.60587	-5.60764	1.212433
43	H	-4.07193	-6.45272	0.802683
44	H	-4.16684	-5.39616	2.256744
45	C	-5.09354	-3.88233	-0.65559
46	H	-4.84924	-4.31621	-1.64659
47	H	-6.10437	-4.20943	-0.36225
48	H	-5.09203	-2.78084	-0.73921
49	C	2.803737	-0.65839	1.07271
50	C	1.39701	-0.96826	1.445798
51	H	1.271503	-1.37737	2.459423
52	C	0.270034	0.045987	1.095728
53	C	2.990962	0.706399	0.334476
54	H	4.061452	0.97286	0.291548
55	H	2.61897	0.659951	-0.7011
56	H	-0.58435	-0.11039	1.7762
57	C	0.66704	1.58701	1.156825
58	C	2.222873	1.83301	1.098174
59	H	0.309047	1.991799	2.120562
60	H	2.421203	2.814719	0.633461
61	H	2.608555	1.879155	2.130877
62	H	3.506979	-0.88167	1.847626

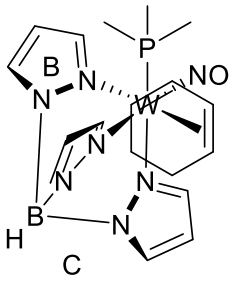
WTp(NO)(PMe$_3$)(η^2-1,3-cyclohexadiene) (**19**)



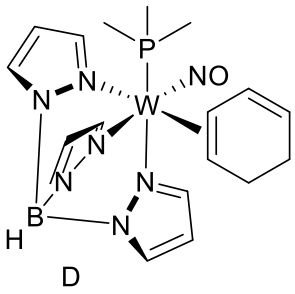
A



B



C



D

Gaussian DFT of:

19A Input

```
%mem=12GB
%nprocshared=12
#                opt    freq              b3lyp/sdd       geom=connectivity

Title            Card   Required

                 0      1
                        O          0.19235075     1.55220907     11.33583384
                        N          3.68505675    -0.09460593     12.96964384
                        N          4.44012675    -1.29605293     13.15369384
                        N          2.11435775    -1.34391893     15.22812384
                        N          3.09752775    -2.36169993     15.02984184
                        N          1.62473275    -1.86919493     12.37477884
                        N          2.59327975    -2.88689993     12.61458384
                        N          0.99882275     0.96863407     12.17517784
                        C          5.73437575    -1.09736993     12.67618084
                        C          5.83980975     0.20783907     12.19287884
                        C          4.56706575     0.79764907     12.38433884
                        C          3.32208375    -3.03139293     16.22853084
```

C	2.50431675	-2.47202593	17.21378484
C	1.77991375	-1.44109293	16.57180684
C	2.35319975	-3.96034093	11.76250484
C	1.23604175	-3.66443893	10.97562884
C	0.81373475	-2.37345493	11.37274384
B	3.74507275	-2.60534893	13.63000984
H	4.50525875	-3.50001293	13.67462984
H	6.46752375	-1.91018793	12.72509984
H	6.72222375	0.67994907	11.75686984
H	4.22756975	1.81125107	12.14505684
H	4.04739275	-3.85174893	16.27370684
H	2.43958075	-2.76651493	18.26300484
H	1.04087675	-0.75454993	16.99914884
H	3.00247475	-4.84281793	11.79045984
H	0.78614975	-4.29654293	10.20764984
H	-0.02088925	-1.77064793	10.99647084
C	2.30321675	1.75819907	14.56530684
C	0.89648975	1.44832507	14.93839484
H	0.77098275	1.03921707	15.95201984
C	-0.23048625	2.46257307	14.58832484
C	2.49044175	3.12298507	13.82707284
C	0.16651975	4.00359607	14.64942184
C	1.72235275	4.24959607	14.59077084
W	1.59122375	0.04557507	13.49259684
P	-0.50267325	-0.64536993	13.69809084
C	-1.08786696	-1.93084063	14.8459207
H	-1.47505053	-2.75772256	14.28801823
H	-0.27341339	-2.26209554	15.45570392
H	-1.85917931	-1.52844722	15.46886275
C	-1.72766337	0.07507953	14.83508326
H	-1.43185407	-0.11562042	15.84554374
H	-1.78608446	1.13124419	14.67382821
H	-2.68523782	-0.36682443	14.65432911
C	-1.78027275	0.02009558	12.58575313
H	-1.34608372	0.7597336	11.94597545
H	-2.18402828	-0.77285953	11.99152786
H	-2.56182215	0.46464774	13.16579961
H	-0.57405759	2.24770243	13.59802724
H	-0.29160076	4.5084723	13.82472457
H	-1.04294969	2.30237361	15.26592302
H	-0.21207518	4.41919268	15.55983127
H	3.05963692	3.26485659	12.93220451
H	2.20273929	5.09966589	15.02838947
H	3.0064588	1.53491527	15.34022294

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2	3	1	11	1					
3	9	1	18	1					
4	5	1	14	1					
5	12	1	18	1					
6	7	1	17	1					
7	15	1	18	1					
8	36	1							
9	10	1.5	20	1					
10	11	1.5	21	1					
11	22	1							
12	13	1.5	23	1					
13	14	1.5	24	1					
14	25	1							
15	16	1.5	26	1					
16	17	1.5	27	1					
17	28	1							
18	19	1							
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22									
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32	34	1	50	1	52	1			
33	35	2	54	1					
34	35	1	51	1	53	1			
35	55	1							
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37	38	1	42	1	46	1			
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41									
42	43	1	44	1	45	1			
43									

44							
45							
46	47	1	48	1	49	1	
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48							
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52							
53							
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55							
56							

19A Output Coordinates

Tag	Symbol	X	Y	Z
1	O	-1.53407	0.463084	-2.95853
2	N	1.144804	1.794063	-0.36299
3	N	2.458043	1.667866	0.08581
4	N	0.793721	-0.2585	1.779609
5	N	2.176196	-0.12529	1.842348
6	N	1.506924	-0.86017	-1.0938
7	N	2.776034	-0.70964	-0.54719
8	N	-1.04837	0.34753	-1.80112
9	C	3.144592	2.818026	-0.19885
10	C	2.277253	3.705997	-0.84594
11	C	1.041252	3.019949	-0.9294
12	C	2.603654	-0.36761	3.115966
13	C	1.488392	-0.66545	3.911817
14	C	0.38314	-0.58137	3.034071
15	C	3.692372	-1.33333	-1.34777
16	C	3.01839	-1.90293	-2.43724
17	C	1.656898	-1.56977	-2.24066
18	B	2.988409	0.30944	0.602313
19	H	4.150901	0.388246	0.880308
20	H	4.18584	2.921455	0.066991
21	H	2.50171	4.696814	-1.20821
22	H	0.110294	3.332822	-1.37326
23	H	3.651089	-0.30827	3.370288
24	H	1.475947	-0.89847	4.96492
25	H	-0.66462	-0.71629	3.250504
26	H	4.744229	-1.31692	-1.105
27	H	3.447048	-2.45671	-3.2577

28	H	0.803929	-1.77302	-2.87031
29	C	-1.48279	1.678013	0.915893
30	C	-2.22399	0.422371	0.979871
31	H	-2.2245	-0.09386	1.943835
32	C	-3.58872	0.37932	0.256161
33	C	-2.1405	2.8587	0.294356
34	C	-4.368	1.711858	0.411382
35	C	-3.47752	2.897964	0.072075
36	W	-0.30065	0.114178	-0.19148
37	P	-1.214	-2.34566	-0.04632
38	C	0.059756	-3.74154	-0.0697
39	H	0.64707	-3.70513	-0.98963
40	H	0.739743	-3.62109	0.779904
41	H	-0.44437	-4.71229	0.002921
42	C	-2.23826	-2.90048	1.437369
43	H	-1.63678	-2.8302	2.348962
44	H	-3.11967	-2.26385	1.538729
45	H	-2.55497	-3.94078	1.299946
46	C	-2.3445	-2.8112	-1.47652
47	H	-3.24171	-2.18797	-1.43731
48	H	-1.83989	-2.61035	-2.42565
49	H	-2.62495	-3.86951	-1.42012
50	H	-3.44556	0.213081	-0.81871
51	H	-5.25338	1.700871	-0.24072
52	H	-4.19994	-0.45396	0.636433
53	H	-4.74114	1.817139	1.445413
54	H	-1.53348	3.739493	0.083507
55	H	-3.94227	3.793594	-0.3402
56	H	-0.86166	1.93685	1.779447

19B Input

```
%mem=12GB
%nprocshared=12
#                opt    freq              b3lyp/sdd       geom=connectivity

Title            Card   Required

                 0      1
                    O       -14.39839499    -3.52029877          1.7008705
                    N       -12.61295399    -6.29056677          4.2226635
                    N       -12.87734499    -7.20387377          5.2937595
                    N       -12.73151499    -4.36665477          6.5669905
                    N       -13.03280199    -5.58515977          7.2492275
```

N	-15.04835199	-5.19956477	4.9605065
N	-15.08460499	-6.23609577	5.9383285
N	-13.74225399	-3.97174477	2.7238675
C	-12.48353099	-8.48407777	4.9074215
C	-11.96188699	-8.42402277	3.6146685
C	-12.06007399	-7.06813477	3.2194065
C	-12.62415799	-5.49122977	8.5757475
C	-12.05686399	-4.23093677	8.7803535
C	-12.13456899	-3.56792477	7.5338905
C	-16.39799499	-6.66278877	6.1084925
C	-17.22324099	-5.91415677	5.2641185
C	-16.36515999	-5.02777377	4.5705375
B	-13.73658999	-6.76908977	6.5180715
H	-13.91212699	-7.66722777	7.2548675
H	-12.61355699	-9.32766577	5.5944735
H	-11.56106799	-9.25119877	3.0258475
H	-11.76719099	-6.59971677	2.2741385
H	-12.77430799	-6.33442677	9.2594945
H	-11.63579899	-3.83957877	9.7084175
H	-11.78250599	-2.56492177	7.2695545
H	-16.62972499	-7.46607477	6.8170745
H	-18.30611699	-6.00064577	5.1564205
H	-16.61064199	-4.28050877	3.8070835
C	-11.09330199	-3.91735277	3.8279035
C	-11.72669399	-2.63612077	4.2575955
C	-10.03173199	-4.55538977	4.8061695
P	-14.48539199	-2.48261577	4.8187705
C	-13.65476556	-0.86418324	4.8747694
H	-12.9305149	-0.86205479	5.6623965
H	-13.16621937	-0.68150574	3.94050416
H	-14.37922734	-0.09749352	5.05432998
C	-14.83747199	-1.85892942	6.4919277
H	-15.88083421	-1.96982786	6.70168183
H	-14.26874509	-2.415678	7.20710652
H	-14.56982863	-0.82460978	6.55066367
C	-15.39909699	-1.64311094	3.48731459
H	-15.13823137	-2.07930913	2.54573068
H	-16.45060833	-1.75288547	3.65215832
H	-15.14562923	-0.60358334	3.48127609
W	-13.16774699	-4.19819977	4.3243765
H	-11.8729782	-1.92089524	3.47532102
H	-10.8815731	-3.97271176	2.78052284
C	-8.73510237	-3.72536228	4.76867297
C	-11.26970201	-2.11560878	5.63303201

C	-10.00998332	-1.24674865	5.46043166
H	-10.18867197	-5.42943591	5.40308925
H	-7.71769978	-3.98179158	4.55882544
H	-9.65378879	-0.82560034	6.37730655
H	-11.04652575	-2.94444261	6.27188007
H	-12.05061681	-1.52880899	6.06976772
H	-10.0754544	-0.55863941	4.643658

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35									
36									

37	38	1	39	1	40	1
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41	42	1	43	1	44	1
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45						
46						
47						
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51						
52						
53						
54						
55						
56						

19B Output Coordinates

Tag	Symbol	X	Y	Z
1	O	-1.65201	0.508947	-2.89057
2	N	1.143504	1.806495	-0.33579
3	N	2.469805	1.662143	0.066073
4	N	0.83527	-0.27326	1.770943
5	N	2.221572	-0.15574	1.794573
6	N	1.492596	-0.83893	-1.13964
7	N	2.772919	-0.70293	-0.61776
8	N	-1.09207	0.349046	-1.77315
9	C	3.144024	2.830199	-0.1666
10	C	2.254608	3.751954	-0.73155
11	C	1.019392	3.06625	-0.81816
12	C	2.685284	-0.4269	3.049543
13	C	1.592325	-0.72938	3.873419
14	C	0.462102	-0.6177	3.031891
15	C	3.670882	-1.3124	-1.44945
16	C	2.972361	-1.8582	-2.53561
17	C	1.616269	-1.52577	-2.30352
18	B	3.008843	0.294372	0.543268
19	H	4.176809	0.367138	0.799767
20	H	4.191744	2.922738	0.076782

21	H	2.464256	4.764583	-1.03811
22	H	0.073155	3.410402	-1.20073
23	H	3.740632	-0.38248	3.272193
24	H	1.609236	-0.98279	4.921728
25	H	-0.57802	-0.75101	3.281788
26	H	4.727656	-1.30298	-1.22866
27	H	3.381851	-2.39694	-3.37565
28	H	0.749408	-1.71474	-2.91842
29	C	-1.4926	1.700893	0.856061
30	C	-2.17828	0.431374	1.071134
31	H	-2.03786	-0.04817	2.04407
32	C	-3.56979	0.289185	0.553799
33	C	-2.23549	2.790783	0.052317
34	H	-1.82377	3.780704	0.294322
35	H	-2.10533	2.63471	-1.02652
36	C	-4.31954	1.367939	0.222193
37	C	-3.76158	2.778311	0.33242
38	H	-4.27473	3.44744	-0.37305
39	H	-3.96383	3.172875	1.3435
40	W	-0.30195	0.11008	-0.18548
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19C Input

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19C Output Coordinates

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38	H	3.481304	3.391951	1.077437
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54	C	3.611281	-2.30861	0.534027
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19D Input

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                   C         1.77991375    -1.44109293          16.57180684
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6	N	-1.49907	1.478811	0.112634

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11	C	-1.92455	-1.73808	-2.15718
12	C	-1.42747	-1.45381	3.303628
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19	H	-3.67903	-0.71456	1.808731
20	H	-4.53742	-2.22928	-0.20382
21	H	-3.73308	-2.91841	-2.75359
22	H	-1.25414	-1.74866	-3.00159
23	H	-2.34548	-1.64674	3.837817
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25	H	1.731053	-1.25146	2.438711
26	H	-4.43531	1.834694	1.50919
27	H	-3.59092	4.053356	0.099112
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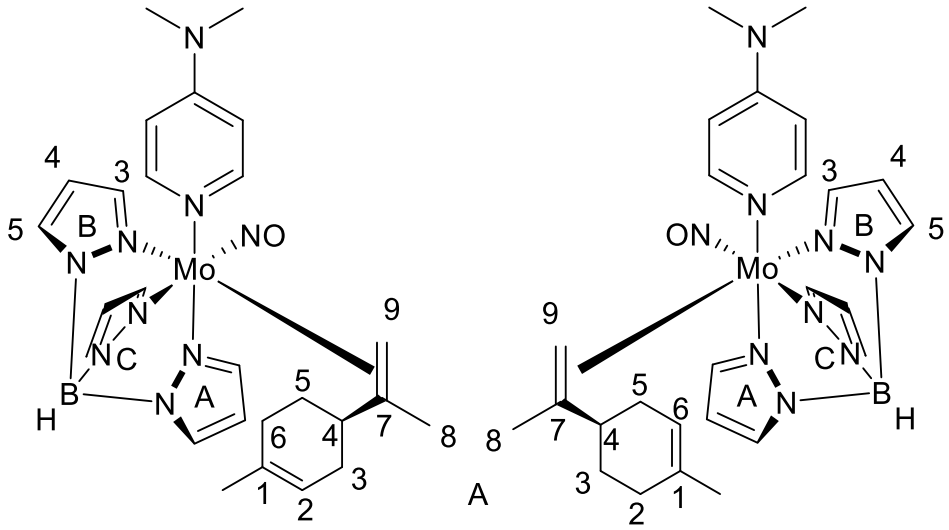
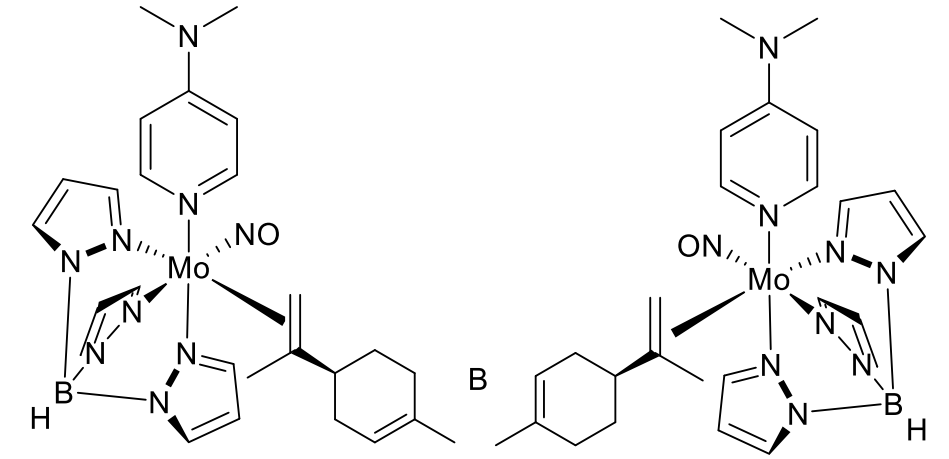
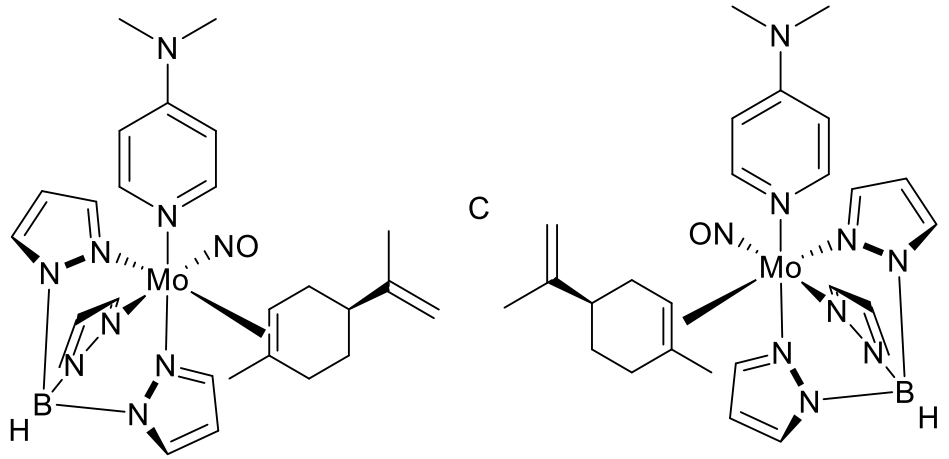
55	H	4.278514	-0.89596	-0.09837
56	H	4.004479	-3.18172	-0.89621

MoTp(NO)(DMAP)(η²-*R*-limonene) (21)



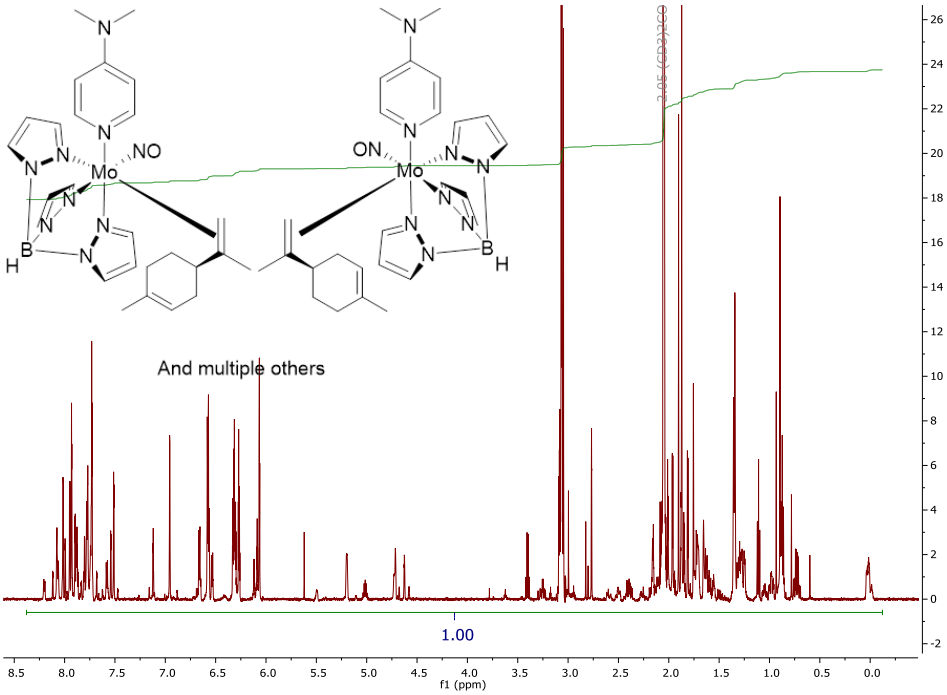




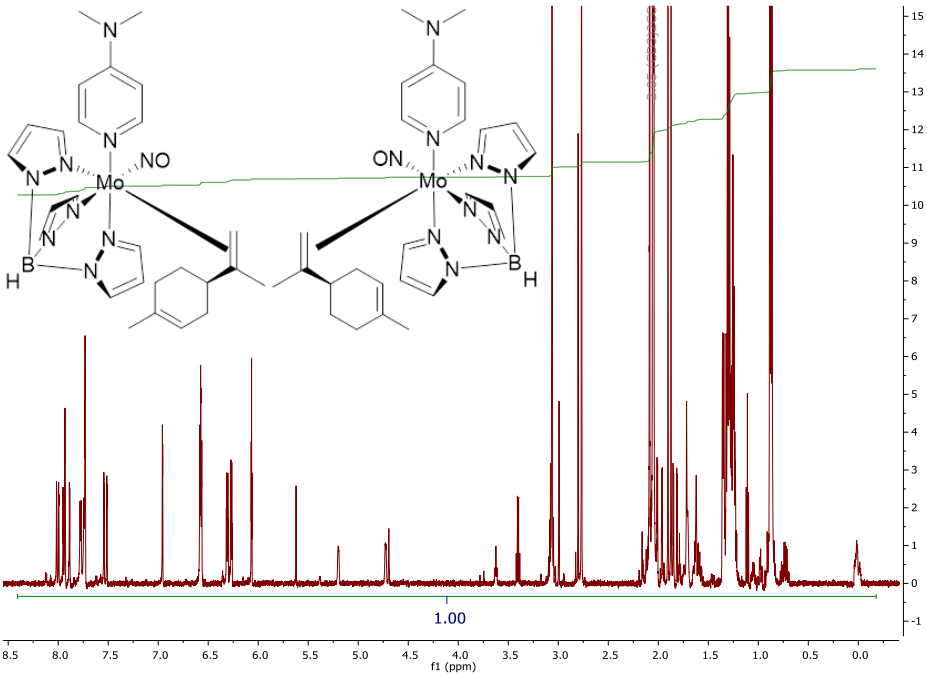
And others

In a 250 mL round bottom charged with a stir egg, of sodium dispersion in paraffin wax (~35% Na^0 by weight, 3 g, 0.050 mol) and ~250 mL of hexanes were combined. The mixture was capped and allowed to mix vigorously for 18 h. The hexanes were then decanted and the remaining Na^0 was crushed with a spatula to yield smaller grains. The sodium was then combined with 50 mL of THF, *R*-limonene (3 mL, 0.019 mol), and then of MoTp(NO)(DMAP)(I) (3.0 g, 5.1 mmol). The flask was recapped and allowed to mix for 2 h. At this time, 200 mL of ether was added to the dark solution and allowed to mix for about 30 seconds. The solution was then added to a 150 mL medium porosity fritted disk about 3/4 full of silica, and the orange band was then eluted with 400 mL of ether. The orange ether solution was then concentrated *in vacuo* to about 10 mL and then added to 300 mL stirring hexanes. The hexanes solution was concentrated *in vacuo* to 150 mL and the orange solid was collected on a 60 mL fine porosity fritted disk and washed with hexanes (3 x 30 mL). Desiccating the solid yielded a fluffy orange solid (0.64 g, 1.1 mmol, 20% yield). IR υ_{NO}: 1555 cm^{-1}, υ_{BH}: 2475 cm^{-1}. CV E_{pa}: -90mV. Anal. Calculated for 2 ($C_{26}H_{36}BMoN9O$) • Et_2O: C, 53.01; H, 6.51; N, 19.87. Found: C, 53.59; H, 6.46; N, 20.09.

^{1}H NMR (d^6-Acetone) of **21**



^{1}H NMR (d^6-Acetone) of **21**A



Compound **21** P-1 Fit: Data collected by Diane A. Dickie

Table 1. Sample and crystal data for $C_{57}H_{84}B_2Mo_2N_{18}O_2$.

Chemical formula	$C_{57}H_{84}B_2Mo_2N_{18}O_2$	
Formula weight	1266.92 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.060 x 0.106 x 0.285 mm	
Crystal habit	yellow rod	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 8.8194(6) Å	α = 85.461(2)°
	b = 9.6136(7) Å	β = 78.641(2)°
	c = 20.2847(16) Å	γ = 66.511(2)°
Volume	1546.5(2) $Å^3$	
Z	1	
Density (calculated)	1.360 g/cm^3	
Absorption coefficient	0.462 mm^{-1}	
F(000)	662	

Table 2. Data collection and structure refinement for $C_{57}H_{84}B_2Mo_2N_{18}O_2$.

Diffractometer	Bruker Kappa APEXII Duo
Radiation source	fine-focus sealed tube (Mo K_α, λ = 0.71073 Å)
Theta range for data collection	2.05 to 26.41°

Index ranges	-11<=h<=11, -12<=k<=12, -25<=l<=25	
Reflections collected	29888	
Independent reflections	6336 [R(int) = 0.0420]	
Coverage of independent reflections	99.9%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.9730 and 0.8800	
Structure solution technique	direct methods	
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2017/1 (Sheldrick, 2017)	
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	6336 / 28 / 413	
Goodness-of-fit on F^2	1.116	
Δ/σ_{max}	0.001	
Final R indices	5564 data; I>2σ(I)	R1 = 0.0303, wR2 = 0.0590
	all data	R1 = 0.0391, wR2 = 0.0610
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0010P)^2+1.7537P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.340 and -0.413 eÅ^{-3}	
R.M.S. deviation from mean	0.065 eÅ^{-3}	

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for $C_{57}H_{84}B_2Mo_2N_{18}O_2$.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
Mo1	0.31400(2)	0.83290(2)	0.18594(2)	0.01135(5)
O1	0.1886(2)	0.8173(2)	0.06174(8)	0.0241(4)
N1	0.4291(2)	0.8343(2)	0.27662(9)	0.0152(4)
N2	0.4246(2)	0.9683(2)	0.29737(9)	0.0157(4)
N3	0.4490(2)	0.9839(2)	0.14598(9)	0.0139(4)
N4	0.4526(2)	0.0914(2)	0.18524(9)	0.0146(4)
N5	0.1246(2)	0.0584(2)	0.22048(9)	0.0149(4)
N6	0.1671(2)	0.1527(2)	0.25355(9)	0.0163(4)
N7	0.2361(2)	0.8306(2)	0.11308(9)	0.0153(4)
N8	0.5621(2)	0.6566(2)	0.14234(9)	0.0136(4)
N9	0.0371(2)	0.3339(2)	0.06062(10)	0.0186(4)
C1	0.5121(3)	0.7274(3)	0.31760(11)	0.0189(5)
C2	0.5614(3)	0.7900(3)	0.36469(12)	0.0221(5)
C3	0.5045(3)	0.9425(3)	0.34986(11)	0.0214(5)
C4	0.5453(3)	0.9876(3)	0.08672(11)	0.0157(5)
C5	0.6120(3)	0.0967(3)	0.08676(12)	0.0197(5)
C6	0.5501(3)	0.1594(3)	0.15001(12)	0.0184(5)
C7	0.9650(3)	0.1359(3)	0.21332(12)	0.0192(5)
C8	0.9022(3)	0.2787(3)	0.24215(12)	0.0236(5)
C9	0.0331(3)	0.2857(3)	0.26664(12)	0.0216(5)
C10	0.2744(3)	0.6264(3)	0.22298(12)	0.0185(5)
C11	0.1252(3)	0.7488(3)	0.25177(11)	0.0159(5)

	x/a	y/b	z/c	U(eq)
C12	0.9662(3)	0.7834(3)	0.22366(12)	0.0218(5)
C13	0.0939(3)	0.7633(3)	0.32863(11)	0.0162(5)
C14	0.0308(3)	0.6407(3)	0.36167(12)	0.0224(5)
C16	0.9363(3)	0.7876(3)	0.46966(12)	0.0264(6)
C18	0.9730(3)	0.9176(3)	0.35822(12)	0.0278(6)
C19	0.8809(4)	0.7967(4)	0.54491(13)	0.0401(7)
C20	0.7073(3)	0.6613(2)	0.15212(11)	0.0143(5)
C21	0.8640(3)	0.5608(3)	0.12517(11)	0.0162(5)
C22	0.8835(3)	0.4403(2)	0.08450(11)	0.0143(5)
C23	0.7327(3)	0.4391(3)	0.07133(11)	0.0154(5)
C24	0.5811(3)	0.5457(3)	0.10059(11)	0.0149(5)
C25	0.1871(3)	0.3443(3)	0.07556(13)	0.0237(5)
C26	0.0570(3)	0.1946(3)	0.02980(12)	0.0224(5)
B1	0.3515(3)	0.1162(3)	0.25775(13)	0.0173(6)
C15	0.9606(14)	0.6720(13)	0.4370(6)	0.023(2)
C17	0.9850(15)	0.9143(7)	0.4354(3)	0.031(2)
C15A	0.0222(15)	0.6304(13)	0.4369(7)	0.023(2)
C17A	0.8993(14)	0.9124(7)	0.4312(3)	0.0240(19)
C27	0.467(4)	0.669(3)	0.5908(10)	0.027(2)
C28	0.571(2)	0.5445(16)	0.5410(7)	0.027(2)
C29	0.4877(17)	0.5061(19)	0.4949(7)	0.027(2)
C30	0.607(2)	0.3935(19)	0.4416(7)	0.027(2)
C31	0.526(3)	0.341(3)	0.3949(8)	0.027(2)
C27A	0.453(4)	0.700(3)	0.5908(14)	0.047(3)

	x/a	y/b	z/c	U(eq)
C28A	0.387(3)	0.623(2)	0.5487(10)	0.047(3)
C29A	0.4877(17)	0.5061(19)	0.4949(7)	0.047(3)
C30A	0.444(2)	0.428(2)	0.4504(11)	0.047(3)
C31A	0.5869(19)	0.317(3)	0.4057(14)	0.047(3)

Table 4. Bond lengths (Å) for $C_{57}H_{84}B_2Mo_2N_{18}O_2$.

Mo1-N7	1.7536(18)	Mo1-C10	2.200(2)
Mo1-N5	2.2078(19)	Mo1-N8	2.2271(18)
Mo1-N3	2.2344(18)	Mo1-N1	2.2724(18)
Mo1-C11	2.288(2)	O1-N7	1.230(2)
N1-C1	1.337(3)	N1-N2	1.370(3)
N2-C3	1.344(3)	N2-B1	1.541(3)
N3-C4	1.335(3)	N3-N4	1.367(2)
N4-C6	1.346(3)	N4-B1	1.544(3)
N5-C7	1.336(3)	N5-N6	1.370(3)
N6-C9	1.352(3)	N6-B1	1.540(3)
N8-C24	1.352(3)	N8-C20	1.352(3)
N9-C22	1.353(3)	N9-C26	1.455(3)
N9-C25	1.457(3)	C1-C2	1.388(3)
C1-H1	0.95	C2-C3	1.376(3)
C2-H2	0.95	C3-H3	0.95
C4-C5	1.392(3)	C4-H4	0.95
C5-C6	1.375(3)	C5-H5	0.95
C6-H6	0.95	C7-C8	1.388(3)

C7-H7	0.95	C8-C9	1.370(3)
C8-H8	0.95	C9-H9	0.95
C10-C11	1.424(3)	C10-H10A	0.99
C10-H10B	0.99	C11-C12	1.522(3)
C11-C13	1.536(3)	C12-H12A	0.98
C12-H12B	0.98	C12-H12C	0.98
C13-C18	1.525(3)	C13-C14	1.548(3)
C13-H13	1.0	C14-C15A	1.510(13)
C14-C15	1.537(12)	C14-H14A	0.99
C14-H14B	0.99	C14-H14C	0.99
C14-H14D	0.99	C16-C15	1.261(13)
C16-C17A	1.339(7)	C16-C19	1.506(3)
C16-C17	1.523(9)	C16-C15A	1.533(12)
C18-C17A	1.501(6)	C18-C17	1.587(7)
C18-H18A	0.99	C18-H18B	0.99
C18-H18C	0.99	C18-H18D	0.99
C19-H19A	0.98	C19-H19B	0.98
C19-H19C	0.98	C20-C21	1.365(3)
C20-H20	0.95	C21-C22	1.410(3)
C21-H21	0.95	C22-C23	1.412(3)
C23-C24	1.371(3)	C23-H23	0.95
C24-H24	0.95	C25-H25A	0.98
C25-H25B	0.98	C25-H25C	0.98
C26-H26A	0.98	C26-H26B	0.98
C26-H26C	0.98	B1-H1A	1.09(2)

C15-H15	0.95	C17-H17A	0.99
C17-H17B	0.99	C15A-H15A	0.99
C15A-H15B	0.99	C17A-H17C	0.95
C27-C28	1.497(13)	C27-H27A	0.98
C27-H27B	0.98	C27-H27C	0.98
C28-C29	1.449(11)	C28-H28A	0.99
C28-H28B	0.99	C29-C30	1.508(11)
C29-H29A	0.99	C29-H29B	0.99
C30-C31	1.515(13)	C30-H30A	0.99
C30-H30B	0.99	C31-H31A	0.98
C31-H31B	0.98	C31-H31C	0.98
C27A-C28A	1.506(14)	C27A-H27D	0.98
C27A-H27E	0.98	C27A-H27F	0.98
C28A-C29A	1.504(12)	C28A-H28C	0.99
C28A-H28D	0.99	C29A-C30A	1.412(11)
C29A-H29C	0.99	C29A-H29D	0.99
C30A-C31A	1.477(14)	C30A-H30C	0.99
C30A-H30D	0.99	C31A-H31D	0.98
C31A-H31E	0.98	C31A-H31F	0.98

Table 5. Anisotropic atomic displacement parameters (Å^2) for $C_{57}H_{84}B_2Mo_2N_{18}O_2$.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mo1	0.01053(9)	0.01089(10)	0.01238(9)	-0.00195(7)	-0.00124(7)	-0.00396(7)
O1	0.0288(9)	0.0315(10)	0.0154(9)	-0.0030(7)	-0.0077(7)	-0.0131(8)
N1	0.0160(9)	0.0149(10)	0.0151(10)	-0.0019(8)	-0.0019(8)	-0.0066(8)
N2	0.0161(9)	0.0179(11)	0.0147(10)	-0.0041(8)	-0.0017(8)	-0.0080(8)
N3	0.0145(9)	0.0116(10)	0.0147(10)	-0.0016(8)	-0.0015(7)	-0.0045(8)
N4	0.0162(9)	0.0116(10)	0.0177(10)	-0.0020(8)	-0.0035(8)	-0.0065(8)
N5	0.0162(9)	0.0147(10)	0.0139(10)	-0.0009(8)	-0.0012(8)	-0.0066(8)
N6	0.0188(10)	0.0131(10)	0.0152(10)	-0.0040(8)	-0.0003(8)	-0.0050(8)
N7	0.0147(9)	0.0144(10)	0.0156(10)	-0.0015(8)	-0.0014(8)	-0.0050(8)
N8	0.0136(9)	0.0122(10)	0.0156(10)	-0.0005(8)	-0.0028(7)	-0.0053(8)
N9	0.0139(9)	0.0159(10)	0.0229(11)	-0.0063(8)	-0.0033(8)	-0.0014(8)
C1	0.0163(11)	0.0180(13)	0.0193(12)	0.0030(10)	-0.0025(9)	-0.0043(10)
C2	0.0195(12)	0.0297(15)	0.0164(12)	0.0026(10)	-0.0062(10)	-0.0080(11)
C3	0.0220(12)	0.0307(15)	0.0149(12)	-0.0052(10)	-0.0030(10)	-0.0132(11)
C4	0.0129(11)	0.0143(12)	0.0154(11)	-0.0005(9)	0.0000(9)	-0.0017(9)
C5	0.0160(11)	0.0199(13)	0.0221(12)	0.0019(10)	-0.0001(10)	-0.0078(10)
C6	0.0161(11)	0.0157(12)	0.0259(13)	0.0010(10)	-0.0044(10)	-0.0087(10)
C7	0.0147(11)	0.0202(13)	0.0200(12)	0.0019(10)	-0.0030(9)	-0.0045(10)
C8	0.0185(12)	0.0183(13)	0.0235(13)	0.0009(10)	0.0010(10)	0.0013(10)
C9	0.0259(13)	0.0134(12)	0.0186(12)	-0.0032(10)	0.0026(10)	-0.0031(10)
C10	0.0213(12)	0.0163(12)	0.0181(12)	-0.0003(10)	-0.0008(10)	-0.0088(10)
C11	0.0168(11)	0.0178(12)	0.0157(11)	-0.0007(9)	-0.0014(9)	-0.0101(10)
C12	0.0218(12)	0.0309(15)	0.0184(12)	-0.0024(11)	-0.0026(10)	-0.0164(11)
C13	0.0169(11)	0.0189(12)	0.0146(11)	-0.0011(9)	-0.0016(9)	-0.0094(10)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C14	0.0274(13)	0.0227(14)	0.0195(13)	-0.0003(10)	-0.0015(10)	-0.0137(11)
C16	0.0292(14)	0.0291(15)	0.0200(13)	-0.0007(11)	0.0014(11)	-0.0129(12)
C18	0.0392(15)	0.0199(14)	0.0177(13)	-0.0023(10)	0.0039(11)	-0.0085(12)
C19	0.0503(19)	0.0461(19)	0.0199(14)	-0.0018(13)	0.0072(13)	-0.0207(16)
C20	0.0171(11)	0.0115(11)	0.0156(11)	-0.0010(9)	-0.0043(9)	-0.0060(9)
C21	0.0155(11)	0.0150(12)	0.0195(12)	0.0008(9)	-0.0054(9)	-0.0065(10)
C22	0.0158(11)	0.0111(11)	0.0138(11)	0.0021(9)	-0.0023(9)	-0.0036(9)
C23	0.0189(11)	0.0116(11)	0.0158(11)	-0.0016(9)	-0.0028(9)	-0.0058(10)
C24	0.0156(11)	0.0150(12)	0.0155(11)	0.0001(9)	-0.0041(9)	-0.0069(9)
C25	0.0137(11)	0.0237(14)	0.0297(14)	-0.0063(11)	-0.0034(10)	-0.0021(10)
C26	0.0190(12)	0.0157(13)	0.0269(14)	-0.0077(10)	-0.0011(10)	-0.0012(10)
B1	0.0206(14)	0.0169(14)	0.0162(13)	-0.0041(11)	-0.0022(11)	-0.0091(11)
C15	0.029(5)	0.022(6)	0.016(3)	0.005(4)	-0.001(4)	-0.012(4)
C17	0.041(5)	0.028(3)	0.020(3)	-0.004(2)	0.002(3)	-0.012(3)
C15A	0.028(5)	0.012(5)	0.024(3)	0.001(4)	0.002(5)	-0.005(4)
C17A	0.024(4)	0.027(3)	0.021(3)	-0.008(2)	0.004(3)	-0.012(3)
C27	0.045(4)	0.016(3)	0.016(4)	0.003(3)	-0.004(3)	-0.010(3)
C28	0.045(4)	0.016(3)	0.016(4)	0.003(3)	-0.004(3)	-0.010(3)
C29	0.045(4)	0.016(3)	0.016(4)	0.003(3)	-0.004(3)	-0.010(3)
C30	0.045(4)	0.016(3)	0.016(4)	0.003(3)	-0.004(3)	-0.010(3)
C31	0.045(4)	0.016(3)	0.016(4)	0.003(3)	-0.004(3)	-0.010(3)
C27A	0.036(5)	0.038(5)	0.069(7)	0.004(5)	-0.010(5)	-0.017(4)
C28A	0.036(5)	0.038(5)	0.069(7)	0.004(5)	-0.010(5)	-0.017(4)
C29A	0.036(5)	0.038(5)	0.069(7)	0.004(5)	-0.010(5)	-0.017(4)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C30A	0.036(5)	0.038(5)	0.069(7)	0.004(5)	-0.010(5)	-0.017(4)
C31A	0.036(5)	0.038(5)	0.069(7)	0.004(5)	-0.010(5)	-0.017(4)

Table 6. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for $C_{57}H_{84}B_2Mo_2N_{18}O_2$.

	x/a	y/b	z/c	U(eq)
H1	0.5343	0.6227	0.3149	0.023
H2	0.6212	0.7389	0.3995	0.027
H3	0.5193	1.0171	0.3729	0.026
H4	0.5656	0.9243	0.0496	0.019
H5	0.6841	1.1221	0.0511	0.024
H6	0.5726	1.2379	0.1662	0.022
H7	-0.0970	1.0985	0.1915	0.023
H8	-0.2078	1.3551	0.2444	0.028
H9	0.0301	1.3701	0.2891	0.026
H10A	0.2619	0.5655	0.1888	0.022
H10B	0.3466	0.5635	0.2548	0.022
H12A	-0.1152	0.8856	0.2374	0.033
H12B	-0.0824	0.7093	0.2410	0.033
H12C	-0.0062	0.7777	0.1745	0.033
H13	0.2048	0.7408	0.3418	0.019
H14A	-0.0581	0.6389	0.3390	0.027
H14B	0.1249	0.5399	0.3558	0.027
H14C	-0.0824	0.6639	0.3518	0.027

	x/a	y/b	z/c	U(eq)
H14D	0.1070	0.5410	0.3414	0.027
H18A	-0.1432	0.9371	0.3533	0.033
H18B	0.0045	0.9989	0.3345	0.033
H18C	0.0335	0.9864	0.3527	0.033
H18D	-0.1197	0.9609	0.3324	0.033
H19A	-0.1699	0.7229	0.5598	0.06
H19B	-0.2019	0.8990	0.5575	0.06
H19C	-0.0216	0.7740	0.5664	0.06
H20	0.6997	0.7400	0.1797	0.017
H21	0.9605	0.5721	0.1339	0.019
H23	0.7362	0.3647	0.0423	0.019
H24	0.4822	0.5411	0.0908	0.018
H25A	1.1840	0.4465	0.0647	0.036
H25B	1.2872	0.2697	0.0486	0.036
H25C	1.1910	0.3238	0.1234	0.036
H26A	0.9640	0.1651	0.0506	0.034
H26B	1.1638	0.1138	0.0365	0.034
H26C	1.0565	0.2111	-0.0185	0.034
H1A	0.361(3)	1.209(3)	0.2811(12)	0.019(6)
H15	-0.0679	0.5953	0.4620	0.027
H17A	0.1011	0.8962	0.4400	0.037
H17B	-0.0918	1.0129	0.4566	0.037
H15A	0.1374	0.5804	0.4468	0.028
H15B	-0.0410	0.5672	0.4563	0.028

	x/a	y/b	z/c	U(eq)
H17C	-0.1797	1.0050	0.4518	0.029
H27A	0.5362	0.6763	0.6215	0.04
H27B	0.3729	0.6461	0.6166	0.04
H27C	0.4226	0.7651	0.5669	0.04
H28A	0.6610	0.5729	0.5140	0.032
H28B	0.6266	0.4517	0.5665	0.032
H29A	0.4211	0.5999	0.4726	0.032
H29B	0.4085	0.4636	0.5208	0.032
H30A	0.6795	0.3034	0.4642	0.032
H30B	0.6808	0.4396	0.4141	0.032
H31A	0.4577	0.2893	0.4210	0.04
H31B	0.6140	0.2700	0.3617	0.04
H31C	0.4548	0.4283	0.3716	0.04
H27D	0.5297	0.7394	0.5615	0.07
H27E	0.5138	0.6270	0.6226	0.07
H27F	0.3592	0.7842	0.6157	0.07
H28C	0.3219	0.5754	0.5811	0.056
H28D	0.3032	0.7058	0.5267	0.056
H29C	0.5559	0.5541	0.4648	0.056
H29D	0.5681	0.4241	0.5184	0.056
H30C	0.3711	0.5035	0.4222	0.056
H30D	0.3778	0.3744	0.4774	0.056
H31D	0.6706	0.3597	0.3880	0.07
H31E	0.5463	0.2924	0.3682	0.07

	x/a	y/b	z/c	U(eq)
H31F	0.6383	0.2240	0.4310	0.07

Compound **21** P1 Fit: Data collected by Diane A. Dickie

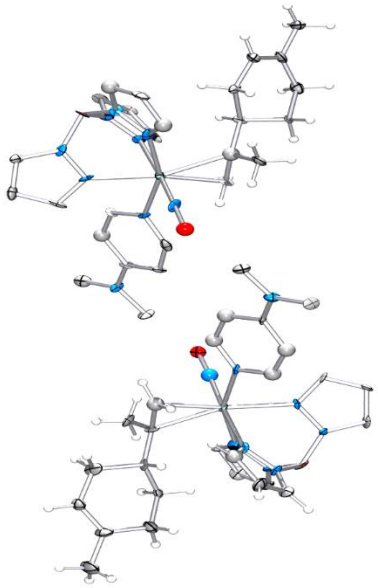


Table 1. Sample and crystal data for $C_{57}H_{84}B_2Mo_2N_{18}O_2$.

Chemical formula	$C_{57}H_{84}B_2Mo_2N_{18}O_2$
Formula weight	1266.92 g/mol
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal size	0.040 x 0.076 x 0.202 mm
Crystal habit	yellow plate

Crystal system	triclinic	
Space group	P 1	
Unit cell dimensions	a = 8.8141(7) Å	α = 85.485(2)°
	b = 9.6056(8) Å	β = 78.635(2)°
	c = 20.2594(16) Å	γ = 66.512(2)°
Volume	1542.3(2) $Å^3$	
Z	1	
Density (calculated)	1.364 g/cm^3	
Absorption coefficient	0.463 mm^{-1}	
F(000)	662	

Table 2. Data collection and structure refinement for $C_{57}H_{84}B_2Mo_2N_{18}O_2$.

Diffractometer	Bruker Kappa APEXII Duo
Radiation source	fine-focus sealed tube (Mo K_α, λ = 0.71073 Å)
Theta range for data collection	2.05 to 28.34°
Index ranges	-11<=h<=11, -12<=k<=12, -27<=l<=26
Reflections collected	57234
Independent reflections	15322 [R(int) = 0.0691]
Coverage of independent reflections	99.7%
Absorption correction	Multi-Scan
Max. and min. transmission	0.9820 and 0.9120
Structure solution technique	direct methods
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)
Refinement method	Full-matrix least-squares on F^2

Refinement program	SHELXL-2018/3 (Sheldrick, 2018)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	15322 / 3 / 464	
Goodness-of-fit on F^2	1.030	
Final R indices	11916 data; I>2σ(I)	R1 = 0.0465, wR2 = 0.0804
	all data	R1 = 0.0740, wR2 = 0.0877
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0197P)^2+2.0132P]$ where $P=(F_o^2+2F_c^2)/3$	
Absolute structure parameter	0.10(4)	
Largest diff. peak and hole	0.597 and -0.877 eÅ^{-3}	
R.M.S. deviation from mean	0.088 eÅ^{-3}	

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for $C_{57}H_{84}B_2Mo_2N_{18}O_2$.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
Mo1	0.68734(6)	0.16390(5)	0.28259(3)	0.0118(2)
Mo2	0.31580(5)	0.82986(5)	0.65450(3)	0.0123(3)
O1	0.8133(12)	0.1780(12)	0.4069(5)	0.025(3)
O2	0.1909(11)	0.8121(12)	0.5303(6)	0.024(3)
N1	0.5737(14)	0.1606(13)	0.1911(7)	0.0147(2)
N2	0.5803(12)	0.0226(9)	0.1718(6)	0.0147(2)
N3	0.5523(14)	0.0142(13)	0.3228(7)	0.0147(2)

	x/a	y/b	z/c	U(eq)
N4	0.5445(11)	0.9076(12)	0.2842(6)	0.0147(2)
N5	0.8741(12)	0.9399(12)	0.2489(6)	0.0147(2)
N6	0.8309(12)	0.8429(11)	0.2147(6)	0.0147(2)
N7	0.7679(14)	0.1651(13)	0.3562(7)	0.0151(5)
N8	0.4385(13)	0.3411(12)	0.3253(7)	0.0139(5)
N9	0.9653(13)	0.6634(13)	0.4071(7)	0.016(3)
N10	0.4312(14)	0.8300(13)	0.7442(7)	0.0147(2)
N11	0.4293(12)	0.9591(9)	0.7666(6)	0.0147(2)
N12	0.4503(14)	0.9821(13)	0.6150(7)	0.0147(2)
N13	0.4485(11)	0.0900(12)	0.6552(6)	0.0147(2)
N14	0.1239(12)	0.0572(12)	0.6903(6)	0.0147(2)
N15	0.1651(12)	0.1478(12)	0.7220(6)	0.0147(2)
N16	0.2405(14)	0.8261(13)	0.5823(7)	0.0151(5)
N17	0.5634(13)	0.6550(12)	0.6101(7)	0.0139(5)
N18	0.0400(14)	0.3308(13)	0.5282(7)	0.020(3)
C1	0.4862(14)	0.2655(14)	0.1501(7)	0.0178(3)
C2	0.4447(12)	0.1950(8)	0.1028(5)	0.0178(3)
C3	0.5053(11)	0.0441(9)	0.1197(5)	0.0178(3)
C4	0.4559(16)	0.0077(16)	0.3825(8)	0.0178(3)
C5	0.3923(14)	0.9005(14)	0.3840(6)	0.0178(3)
C6	0.4487(14)	0.8389(14)	0.3213(5)	0.0178(3)
C7	0.0364(16)	0.8615(15)	0.2567(7)	0.0178(3)
C8	0.0905(11)	0.7123(10)	0.2253(5)	0.0178(3)
C9	0.9571(10)	0.7108(11)	0.2000(5)	0.0178(3)

	x/a	y/b	z/c	U(eq)
C10	0.7338(16)	0.3684(14)	0.2455(8)	0.0179(8)
C11	0.8798(17)	0.2486(15)	0.2173(8)	0.0147(7)
C12	0.0375(16)	0.2067(16)	0.2451(8)	0.0217(9)
C13	0.9047(17)	0.2376(15)	0.1402(8)	0.0155(7)
C14	0.9807(17)	0.3499(16)	0.1053(8)	0.027(3)
C15	0.0431(9)	0.3280(10)	0.0321(5)	0.0204(18)
C16	0.0611(18)	0.2048(16)	0.9965(8)	0.026(3)
C17	0.0157(10)	0.0814(8)	0.0337(4)	0.0279(16)
C18	0.0118(15)	0.0798(14)	0.1098(7)	0.018(2)
C19	0.1137(18)	0.1902(17)	0.9232(8)	0.036(3)
C20	0.4207(16)	0.4539(14)	0.3676(7)	0.0140(3)
C21	0.2704(14)	0.5614(13)	0.3959(7)	0.0140(3)
C22	0.1211(14)	0.5595(12)	0.3852(6)	0.0140(3)
C23	0.1368(15)	0.4406(12)	0.3448(7)	0.0140(3)
C24	0.2924(15)	0.3378(14)	0.3159(8)	0.0140(3)
C25	0.8134(15)	0.6604(12)	0.3938(7)	0.0216(6)
C26	0.9425(16)	0.8039(15)	0.4372(8)	0.0216(6)
C27	0.5116(14)	0.7204(14)	0.7855(7)	0.0178(3)
C28	0.5678(11)	0.7754(8)	0.8324(5)	0.0178(3)
C29	0.5144(11)	0.9291(9)	0.8197(5)	0.0178(3)
C30	0.5460(16)	0.9832(16)	0.5562(8)	0.0178(3)
C31	0.6162(14)	0.0940(14)	0.5579(6)	0.0178(3)
C32	0.5492(14)	0.1578(14)	0.6215(5)	0.0178(3)
C33	0.9669(16)	0.1327(15)	0.6831(7)	0.0178(3)

	x/a	y/b	z/c	U(eq)
C34	0.8952(11)	0.2702(10)	0.7096(5)	0.0178(3)
C35	0.0232(10)	0.2826(11)	0.7335(5)	0.0178(3)
C36	0.2819(16)	0.6203(15)	0.6918(8)	0.0179(8)
C37	0.1307(17)	0.7468(16)	0.7211(8)	0.0147(7)
C38	0.9713(16)	0.7740(16)	0.6923(8)	0.0217(9)
C39	0.0934(17)	0.7636(15)	0.7971(8)	0.0155(7)
C40	0.9571(15)	0.9149(15)	0.8265(8)	0.022(3)
C41	0.9020(9)	0.9084(8)	0.9003(4)	0.0262(16)
C42	0.9346(18)	0.7813(17)	0.9360(8)	0.023(3)
C43	0.0255(9)	0.6304(10)	0.9059(5)	0.0221(19)
C44	0.0411(15)	0.6323(15)	0.8296(7)	0.015(3)
C45	0.876(2)	0.7852(17)	0.0130(7)	0.034(3)
C46	0.7071(15)	0.6607(14)	0.6202(8)	0.0140(3)
C47	0.8661(15)	0.5611(12)	0.5950(7)	0.0140(3)
C48	0.8874(14)	0.4410(12)	0.5542(6)	0.0140(3)
C49	0.7365(14)	0.4386(13)	0.5387(7)	0.0140(3)
C50	0.5823(16)	0.5453(14)	0.5685(7)	0.0140(3)
C51	0.1873(15)	0.3485(12)	0.5448(7)	0.0216(6)
C52	0.0569(16)	0.1931(15)	0.4968(8)	0.0216(6)
C53	0.533(2)	0.3252(18)	0.8697(9)	0.045(4)
C54	0.6130(10)	0.3831(8)	0.9142(4)	0.0412(19)
C55	0.489(2)	0.506(2)	0.9645(12)	0.036(3)
C56	0.5675(10)	0.5520(9)	0.0128(4)	0.0418(19)
C57	0.439(2)	0.678(2)	0.0609(10)	0.065(5)

	x/a	y/b	z/c	U(eq)
B1	0.649(2)	0.8828(19)	0.2125(10)	0.0170(9)
B2	0.352(2)	0.1155(19)	0.7283(10)	0.0170(9)

Table 4. Bond lengths (Å) for $C_{57}H_{84}B_2Mo_2N_{18}O_2$.

Mo1-N7	1.776(13)	Mo1-N5	2.184(10)
Mo1-C10	2.209(13)	Mo1-N3	2.224(12)
Mo1-N8	2.228(11)	Mo1-N1	2.282(12)
Mo1-C11	2.310(15)	Mo2-N16	1.730(13)
Mo2-C36	2.205(13)	Mo2-N17	2.221(11)
Mo2-N14	2.231(10)	Mo2-N12	2.237(12)
Mo2-N10	2.251(12)	Mo2-C37	2.263(15)
O1-N7	1.205(15)	O2-N16	1.252(15)
N1-C1	1.341(17)	N1-N2	1.387(14)
N2-C3	1.313(14)	N2-B1	1.492(19)
N3-C4	1.347(19)	N3-N4	1.367(14)
N4-C6	1.353(16)	N4-B1	1.54(2)
N5-C7	1.360(15)	N5-N6	1.407(14)
N6-C9	1.320(13)	N6-B1	1.498(18)
N8-C24	1.351(16)	N8-C20	1.375(16)
N9-C22	1.347(15)	N9-C25	1.428(15)
N9-C26	1.449(16)	N10-C27	1.345(17)
N10-N11	1.347(14)	N11-C29	1.378(14)
N11-B2	1.591(19)	N12-C30	1.320(19)
N12-N13	1.361(14)	N13-C32	1.352(16)

N13-B2	1.54(2)	N14-C33	1.313(15)
N14-N15	1.317(14)	N15-C35	1.392(13)
N15-B2	1.580(18)	N17-C50	1.339(16)
N17-C46	1.345(16)	N18-C48	1.372(15)
N18-C52	1.454(17)	N18-C51	1.478(16)
C1-C2	1.397(14)	C1-H1	0.95
C2-C3	1.372(11)	C2-H2	0.95
C3-H3	0.95	C4-C5	1.351(18)
C4-H4	0.95	C5-C6	1.357(15)
C5-H5	0.95	C6-H6	0.95
C7-C8	1.471(16)	C7-H7	0.95
C8-C9	1.377(10)	C8-H8	0.95
C9-H9	0.95	C10-C11	1.393(18)
C10-H10A	0.95	C10-H10B	0.95
C11-C12	1.496(18)	C11-C13	1.54(2)
C12-H12A	0.98	C12-H12B	0.98
C12-H12C	0.98	C13-C18	1.531(18)
C13-C14	1.54(2)	C13-H13	1.0
C14-C15	1.477(19)	C14-H14A	0.99
C14-H14B	0.99	C15-C16	1.374(17)
C15-H15	0.95	C16-C19	1.47(2)
C16-C17	1.501(17)	C17-C18	1.534(16)
C17-H17A	0.99	C17-H17B	0.99
C18-H18A	0.99	C18-H18B	0.99
C19-H19A	0.98	C19-H19B	0.98

C19-H19C	0.98	C20-C21	1.362(17)
C20-H20	0.95	C21-C22	1.382(15)
C21-H21	0.95	C22-C23	1.405(13)
C23-C24	1.376(17)	C23-H23	0.95
C24-H24	0.95	C25-H25A	0.98
C25-H25B	0.98	C25-H25C	0.98
C26-H26A	0.98	C26-H26B	0.98
C26-H26C	0.98	C27-C28	1.379(14)
C27-H27	0.95	C28-C29	1.379(11)
C28-H28	0.95	C29-H29	0.95
C30-C31	1.434(18)	C30-H30	0.95
C31-C32	1.387(15)	C31-H31	0.95
C32-H32	0.95	C33-C34	1.321(16)
C33-H33	0.95	C34-C35	1.361(10)
C34-H34	0.95	C35-H35	0.95
C36-C37	1.454(19)	C36-H36A	0.95
C36-H36B	0.95	C37-C39	1.52(2)
C37-C38	1.545(18)	C38-H38A	0.98
C38-H38B	0.98	C38-H38C	0.98
C39-C40	1.540(18)	C39-C44	1.565(19)
C39-H39	1.0	C40-C41	1.484(16)
C40-H40A	0.99	C40-H40B	0.99
C41-C42	1.327(17)	C41-H41	0.95
C42-C43	1.462(18)	C42-C45	1.54(2)
C43-C44	1.524(18)	C43-H43A	0.99

C43-H43B	0.99	C44-H44A	0.99
C44-H44B	0.99	C45-H45A	0.98
C45-H45B	0.98	C45-H45C	0.98
C46-C47	1.366(16)	C46-H46	0.95
C47-C48	1.402(13)	C47-H47	0.95
C48-C49	1.434(15)	C49-C50	1.387(17)
C49-H49	0.95	C50-H50	0.95
C51-H51A	0.98	C51-H51B	0.98
C51-H51C	0.98	C52-H52A	0.98
C52-H52B	0.98	C52-H52C	0.98
C53-C54	1.501(18)	C53-H53A	0.98
C53-H53B	0.98	C53-H53C	0.98
C54-C55	1.53(2)	C54-H54A	0.99
C54-H54B	0.99	C55-C56	1.49(2)
C55-H55A	0.99	C55-H55B	0.99
C56-C57	1.537(19)	C56-H56A	0.99
C56-H56B	0.99	C57-H57A	0.98
C57-H57B	0.98	C57-H57C	0.98
B1-H1A	1.20(9)	B2-H2A	0.98(10)

Table 5. Anisotropic atomic displacement parameters (Å^2) for $C_{57}H_{84}B_2Mo_2N_{18}O_2$.

The anisotropic atomic displacement factor exponent takes the form: -
$2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mo1	0.0145(5)	0.0055(5)	0.0152(7)	-0.0007(5)	-0.0023(5)	-0.0037(4)
Mo2	0.0089(5)	0.0150(5)	0.0128(7)	-0.0023(5)	-0.0019(4)	-0.0042(4)
O1	0.042(6)	0.030(6)	0.009(6)	0.000(5)	-0.006(5)	-0.021(5)
O2	0.016(5)	0.032(6)	0.027(7)	-0.007(5)	-0.012(4)	-0.008(4)
N1	0.0160(5)	0.0122(5)	0.0160(5)	-0.0019(4)	-0.0027(4)	-0.0052(4)
N2	0.0160(5)	0.0122(5)	0.0160(5)	-0.0019(4)	-0.0027(4)	-0.0052(4)
N3	0.0160(5)	0.0122(5)	0.0160(5)	-0.0019(4)	-0.0027(4)	-0.0052(4)
N4	0.0160(5)	0.0122(5)	0.0160(5)	-0.0019(4)	-0.0027(4)	-0.0052(4)
N5	0.0160(5)	0.0122(5)	0.0160(5)	-0.0019(4)	-0.0027(4)	-0.0052(4)
N6	0.0160(5)	0.0122(5)	0.0160(5)	-0.0019(4)	-0.0027(4)	-0.0052(4)
N7	0.0135(13)	0.0142(12)	0.0162(14)	-0.0027(10)	-0.0001(10)	-0.0048(10)
N8	0.0137(12)	0.0122(12)	0.0158(13)	-0.0015(10)	-0.0024(10)	-0.0050(10)
N9	0.009(5)	0.014(6)	0.026(8)	-0.005(5)	-0.006(5)	-0.004(4)
N10	0.0160(5)	0.0122(5)	0.0160(5)	-0.0019(4)	-0.0027(4)	-0.0052(4)
N11	0.0160(5)	0.0122(5)	0.0160(5)	-0.0019(4)	-0.0027(4)	-0.0052(4)
N12	0.0160(5)	0.0122(5)	0.0160(5)	-0.0019(4)	-0.0027(4)	-0.0052(4)
N13	0.0160(5)	0.0122(5)	0.0160(5)	-0.0019(4)	-0.0027(4)	-0.0052(4)
N14	0.0160(5)	0.0122(5)	0.0160(5)	-0.0019(4)	-0.0027(4)	-0.0052(4)
N15	0.0160(5)	0.0122(5)	0.0160(5)	-0.0019(4)	-0.0027(4)	-0.0052(4)
N16	0.0135(13)	0.0142(12)	0.0162(14)	-0.0027(10)	-0.0001(10)	-0.0048(10)
N17	0.0137(12)	0.0122(12)	0.0158(13)	-0.0015(10)	-0.0024(10)	-0.0050(10)
N18	0.014(6)	0.018(6)	0.020(8)	-0.007(6)	-0.001(5)	0.002(5)
C1	0.0163(6)	0.0170(6)	0.0187(6)	0.0002(5)	-0.0027(4)	-0.0053(5)
C2	0.0163(6)	0.0170(6)	0.0187(6)	0.0002(5)	-0.0027(4)	-0.0053(5)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C3	0.0163(6)	0.0170(6)	0.0187(6)	0.0002(5)	-0.0027(4)	-0.0053(5)
C4	0.0163(6)	0.0170(6)	0.0187(6)	0.0002(5)	-0.0027(4)	-0.0053(5)
C5	0.0163(6)	0.0170(6)	0.0187(6)	0.0002(5)	-0.0027(4)	-0.0053(5)
C6	0.0163(6)	0.0170(6)	0.0187(6)	0.0002(5)	-0.0027(4)	-0.0053(5)
C7	0.0163(6)	0.0170(6)	0.0187(6)	0.0002(5)	-0.0027(4)	-0.0053(5)
C8	0.0163(6)	0.0170(6)	0.0187(6)	0.0002(5)	-0.0027(4)	-0.0053(5)
C9	0.0163(6)	0.0170(6)	0.0187(6)	0.0002(5)	-0.0027(4)	-0.0053(5)
C10	0.019(2)	0.0160(16)	0.0195(16)	0.0001(12)	-0.0007(14)	-0.0087(14)
C11	0.0156(16)	0.0152(14)	0.0160(15)	0.0001(12)	-0.0017(12)	-0.0095(12)
C12	0.0231(17)	0.028(2)	0.0194(17)	-0.0020(16)	-0.0030(13)	-0.0151(17)
C13	0.0164(15)	0.0152(17)	0.0158(15)	-0.0001(13)	-0.0022(12)	-0.0074(13)
C14	0.039(7)	0.016(6)	0.028(8)	0.005(5)	-0.011(6)	-0.012(5)
C15	0.021(4)	0.025(5)	0.018(4)	0.006(3)	-0.005(4)	-0.012(4)
C16	0.030(7)	0.019(6)	0.025(7)	-0.006(5)	-0.003(5)	-0.005(5)
C17	0.035(4)	0.025(4)	0.022(4)	0.001(3)	0.004(3)	-0.015(4)
C18	0.020(5)	0.019(5)	0.015(5)	0.003(3)	0.002(3)	-0.010(4)
C19	0.040(6)	0.033(6)	0.034(8)	0.009(5)	0.000(5)	-0.018(5)
C20	0.0157(6)	0.0109(7)	0.0166(7)	-0.0005(5)	-0.0044(5)	-0.0057(5)
C21	0.0157(6)	0.0109(7)	0.0166(7)	-0.0005(5)	-0.0044(5)	-0.0057(5)
C22	0.0157(6)	0.0109(7)	0.0166(7)	-0.0005(5)	-0.0044(5)	-0.0057(5)
C23	0.0157(6)	0.0109(7)	0.0166(7)	-0.0005(5)	-0.0044(5)	-0.0057(5)
C24	0.0157(6)	0.0109(7)	0.0166(7)	-0.0005(5)	-0.0044(5)	-0.0057(5)
C25	0.0167(11)	0.0176(13)	0.0265(14)	-0.0079(11)	-0.0032(9)	-0.0014(10)
C26	0.0167(11)	0.0176(13)	0.0265(14)	-0.0079(11)	-0.0032(9)	-0.0014(10)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C27	0.0163(6)	0.0170(6)	0.0187(6)	0.0002(5)	-0.0027(4)	-0.0053(5)
C28	0.0163(6)	0.0170(6)	0.0187(6)	0.0002(5)	-0.0027(4)	-0.0053(5)
C29	0.0163(6)	0.0170(6)	0.0187(6)	0.0002(5)	-0.0027(4)	-0.0053(5)
C30	0.0163(6)	0.0170(6)	0.0187(6)	0.0002(5)	-0.0027(4)	-0.0053(5)
C31	0.0163(6)	0.0170(6)	0.0187(6)	0.0002(5)	-0.0027(4)	-0.0053(5)
C32	0.0163(6)	0.0170(6)	0.0187(6)	0.0002(5)	-0.0027(4)	-0.0053(5)
C33	0.0163(6)	0.0170(6)	0.0187(6)	0.0002(5)	-0.0027(4)	-0.0053(5)
C34	0.0163(6)	0.0170(6)	0.0187(6)	0.0002(5)	-0.0027(4)	-0.0053(5)
C35	0.0163(6)	0.0170(6)	0.0187(6)	0.0002(5)	-0.0027(4)	-0.0053(5)
C36	0.019(2)	0.0160(16)	0.0195(16)	0.0001(12)	-0.0007(14)	-0.0087(14)
C37	0.0156(16)	0.0152(14)	0.0160(15)	0.0001(12)	-0.0017(12)	-0.0095(12)
C38	0.0231(17)	0.028(2)	0.0194(17)	-0.0020(16)	-0.0030(13)	-0.0151(17)
C39	0.0164(15)	0.0152(17)	0.0158(15)	-0.0001(13)	-0.0022(12)	-0.0074(13)
C40	0.022(5)	0.018(5)	0.022(5)	-0.008(4)	0.002(4)	-0.006(4)
C41	0.026(4)	0.027(4)	0.025(4)	-0.009(3)	0.010(3)	-0.015(3)
C42	0.028(6)	0.038(7)	0.009(6)	0.002(5)	0.002(5)	-0.023(6)
C43	0.016(4)	0.025(5)	0.024(4)	0.004(3)	-0.001(4)	-0.008(4)
C44	0.008(4)	0.021(6)	0.016(6)	-0.006(4)	0.007(4)	-0.008(4)
C45	0.062(8)	0.035(6)	0.013(6)	-0.010(4)	0.013(5)	-0.034(6)
C46	0.0157(6)	0.0109(7)	0.0166(7)	-0.0005(5)	-0.0044(5)	-0.0057(5)
C47	0.0157(6)	0.0109(7)	0.0166(7)	-0.0005(5)	-0.0044(5)	-0.0057(5)
C48	0.0157(6)	0.0109(7)	0.0166(7)	-0.0005(5)	-0.0044(5)	-0.0057(5)
C49	0.0157(6)	0.0109(7)	0.0166(7)	-0.0005(5)	-0.0044(5)	-0.0057(5)
C50	0.0157(6)	0.0109(7)	0.0166(7)	-0.0005(5)	-0.0044(5)	-0.0057(5)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C51	0.0167(11)	0.0176(13)	0.0265(14)	-0.0079(11)	-0.0032(9)	-0.0014(10)
C52	0.0167(11)	0.0176(13)	0.0265(14)	-0.0079(11)	-0.0032(9)	-0.0014(10)
C53	0.054(7)	0.035(7)	0.051(9)	-0.002(6)	-0.003(6)	-0.025(5)
C54	0.042(5)	0.030(4)	0.047(5)	-0.001(4)	-0.008(4)	-0.010(3)
C55	0.038(6)	0.023(4)	0.044(6)	0.007(4)	-0.001(4)	-0.012(4)
C56	0.049(5)	0.047(5)	0.038(5)	0.007(4)	-0.017(4)	-0.025(4)
C57	0.078(11)	0.061(10)	0.055(10)	-0.019(8)	-0.009(8)	-0.023(8)
B1	0.0197(17)	0.0159(18)	0.016(2)	-0.0047(15)	-0.0019(15)	-0.0075(14)
B2	0.0197(17)	0.0159(18)	0.016(2)	-0.0047(15)	-0.0019(15)	-0.0075(14)

Table 6. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for $C_{57}H_{84}B_2Mo_2N_{18}O_2$.

	x/a	y/b	z/c	U(eq)
H1	0.4570	0.3716	0.1529	0.021
H2	0.3871	0.2414	0.0668	0.021
H3	0.4947	-0.0336	0.0970	0.021
H4	0.4349	0.0716	0.4196	0.021
H5	0.3234	-0.1260	0.4207	0.021
H6	0.4248	-0.2398	0.3060	0.021
H7	1.1017	-0.1039	0.2781	0.021
H8	1.1980	-0.3683	0.2228	0.021
H9	0.9562	-0.3704	0.1764	0.021
H10A	0.7345	0.4233	0.2823	0.022
H10B	0.6336	0.3951	0.2279	0.022

	x/a	y/b	z/c	U(eq)
H12A	1.0102	0.2101	0.2944	0.033
H12B	1.0900	0.2787	0.2287	0.033
H12C	1.1156	0.1040	0.2304	0.033
H13	0.7906	0.2694	0.1284	0.019
H14A	0.8940	0.4542	0.1132	0.032
H14B	1.0750	0.3418	0.1272	0.032
H15	1.0731	0.4049	0.0079	0.025
H17A	1.0979	-0.0179	0.0147	0.033
H17B	0.9036	0.0934	0.0261	0.033
H18A	0.9649	0.0062	0.1318	0.022
H18B	1.1279	0.0468	0.1184	0.022
H19A	1.0249	0.1815	-0.0966	0.054
H19B	1.2173	0.0993	-0.0877	0.054
H19C	1.1340	0.2800	-0.0951	0.054
H20	0.5200	0.4571	0.3777	0.017
H21	0.2681	0.6383	0.4233	0.017
H23	0.0384	0.4309	0.3373	0.017
H24	0.2974	0.2607	0.2879	0.017
H25A	-0.1907	0.6790	0.3458	0.032
H25B	-0.2834	0.7394	0.4204	0.032
H25C	-0.1900	0.5609	0.4062	0.032
H26A	-0.0859	0.7971	0.4863	0.032
H26B	-0.1487	0.8883	0.4207	0.032
H26C	0.0469	0.8212	0.4251	0.032

	x/a	y/b	z/c	U(eq)
H27	0.5277	0.6170	0.7826	0.021
H28	0.6295	0.7197	0.8660	0.021
H29	0.5329	1.0010	0.8432	0.021
H30	0.5653	0.9207	0.5188	0.021
H31	0.6915	1.1183	0.5232	0.021
H32	0.5705	1.2362	0.6387	0.021
H33	-0.0907	1.0916	0.6606	0.021
H34	-0.2171	1.3421	0.7115	0.021
H35	0.0167	1.3700	0.7549	0.021
H36A	0.3528	0.5522	0.7200	0.022
H36B	0.3097	0.6058	0.6444	0.022
H38A	-0.1126	0.8764	0.7042	0.033
H38B	-0.0751	0.6992	0.7112	0.033
H38C	0.0005	0.7636	0.6432	0.033
H39	0.2003	0.7505	0.8117	0.019
H40A	0.0014	0.9956	0.8163	0.026
H40B	-0.1415	0.9425	0.8042	0.026
H41	-0.1611	1.0017	0.9237	0.031
H43A	-0.0337	0.5641	0.9256	0.026
H43B	0.1395	0.5863	0.9173	0.026
H44A	-0.0680	0.6457	0.8180	0.018
H44B	0.1262	0.5339	0.8108	0.018
H45A	-0.0261	0.7482	1.0352	0.052
H45B	-0.1876	0.7203	1.0254	0.052

	x/a	y/b	z/c	U(eq)
H45C	-0.1965	0.8897	1.0274	0.052
H46	0.6971	0.7411	0.6474	0.017
H47	0.9611	0.5731	0.6049	0.017
H49	0.7420	0.3652	0.5086	0.017
H50	0.4836	0.5401	0.5588	0.017
H51A	1.1784	0.4527	0.5350	0.032
H51B	1.2904	0.2775	0.5178	0.032
H51C	1.1906	0.3270	0.5927	0.032
H52A	0.9767	0.1536	0.5231	0.032
H52B	1.1717	0.1169	0.4952	0.032
H52C	1.0338	0.2159	0.4509	0.032
H53A	0.6214	0.2487	0.8388	0.068
H53B	0.4659	0.4096	0.8437	0.068
H53C	0.4609	0.2796	0.8975	0.068
H54A	0.6897	0.4246	0.8854	0.049
H54B	0.6821	0.2964	0.9396	0.049
H55A	0.4275	0.5967	0.9391	0.044
H55B	0.4049	0.4683	0.9904	0.044
H56A	0.6531	0.5877	0.9872	0.05
H56B	0.6256	0.4624	1.0395	0.05
H57A	0.3931	0.7721	1.0355	0.098
H57B	0.4941	0.6953	1.0952	0.098
H57C	0.3472	0.6479	1.0829	0.098
H1A	0.643(12)	-0.224(9)	0.187(6)	0.02

	x/a	y/b	z/c	U(eq)
H2A	0.369(13)	1.193(9)	0.751(6)	0.02

Gaussian DFT of:

(*R*,*R*)-**21A Input**

%mem=12GB
%nprocshared=12
opt freq b3lyp/gen geom=connectivity pseudo=read

Title Card Required

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N	1.14796215	-4.2258145	2.182073
N	0.63646415	-3.1419865	2.960184
N	2.66062915	-2.0839395	0.90413
N	2.05577815	-1.3246135	1.94848
N	3.71321415	-4.6177495	0.463104
N	2.31924415	-3.5799875	-1.569086
C	-1.23487585	-0.6921995	0.741968
C	-1.51711185	-0.8453715	-0.61579
C	-0.68663085	-1.8992615	-1.069617
C	0.29083115	-3.6022575	4.227292
C	0.56165515	-4.9712225	4.295508
C	1.08274215	-5.3236285	3.028721
C	2.90670215	-0.2859125	2.31359
C	4.06319615	-0.3600145	1.531439
C	3.88066715	-1.4715965	0.674686
C	4.19150215	-4.9348795	1.735955
B	0.60302415	-1.6864985	2.399334
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H	-2.23155185	-0.2719555	-1.209446
H	-0.59946685	-2.3330225	-2.071732
H	-0.11831585	-2.9102735	4.972133
H	0.40075715	-5.6336265	5.148186

H	1.40968115	-6.3058745	2.670388
H	2.61191415	0.4181695	3.099964
H	4.92646115	0.3071305	1.568793
H	4.54762815	-1.8670235	-0.1001
H	3.47332315	-4.7897505	2.555478
C	5.47847515	-5.4042665	2.001107
H	5.75622515	-5.6211705	3.036632
C	4.64654215	-4.7706435	-0.571529
H	4.26778215	-4.4333395	-1.576332
C	6.40926815	-5.5911555	0.930915
C	5.94813915	-5.2323975	-0.375642
H	6.61096915	-5.3088875	-1.243061
N	7.70059515	-6.1329415	1.149488
C	8.22351815	-6.2425175	2.547316
H	9.20717715	-6.7383895	2.511038
H	8.33891115	-5.2522135	3.033259
H	7.54238215	-6.8613845	3.158282
C	8.71607215	-6.0733785	0.051655
H	8.98987415	-5.0318565	-0.213583
H	9.62084615	-6.6054655	0.388049
H	8.32693615	-6.5794875	-0.849672
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C	-3.52336085	-5.2572715	0.94564
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C	-2.56457285	-7.5861605	1.06603
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C	-3.65671385	-6.5322835	1.343059
H	-4.32739085	-4.5371165	1.158202
H	-3.04154385	-8.5328875	0.751373
H	-2.02476685	-7.8039175	2.008021
H	1.98847515	-6.3705665	-1.174081
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H	0.64386715	-5.0231425	-2.793594
H	-0.66780085	-6.1867705	-2.489695
H	-0.99123485	-4.4459065	-2.399704
C	-4.89189485	-7.0284355	2.11188

H	-5.60443285	-6.2086415	2.286903			
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H	-4.60006585	-7.4516605	3.088624			

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Mo 0
LANL2DZ
*****
H B C N O 0
6-31G(d)
*****

Mo 0
LANL2DZ

(*R*,*R*)-**21A Output Coordinates**

Tag	Symbol	X	Y	Z
1	Mo	0.118033	0.306246	-0.75713
2	O	0.967804	0.71692	-3.58135
3	N	-1.61539	1.736258	-0.86552
4	N	-1.92532	2.525965	0.201889
5	N	-0.47008	0.098752	1.505725
6	N	-0.96141	1.19308	2.147512
7	N	1.04977	2.216531	0.070914
8	N	0.399216	2.968483	0.997249
9	N	2.19482	-0.52875	-0.27784
10	N	0.599576	0.571723	-2.44124
11	C	-2.90838	3.393084	-0.1434
12	C	-3.24941	3.168607	-1.46628
13	C	-2.40246	2.125935	-1.87422
14	C	-1.25975	0.882741	3.427533
15	C	-0.95597	-0.45471	3.64016
16	C	-0.46443	-0.8971	2.404254
17	C	1.145119	4.049385	1.316628
18	C	2.321442	4.004405	0.581626
19	C	2.208776	2.835126	-0.18593
20	C	2.741152	-0.47949	0.95474
21	B	-1.02685	2.57519	1.455454
22	H	-1.44925	3.390005	2.23142
23	H	-3.28128	4.106747	0.576914
24	H	-3.99793	3.681141	-2.05213
25	H	-2.32307	1.640301	-2.83488
26	H	-1.66377	1.633485	4.09123
27	H	-1.07937	-1.02395	4.549465
28	H	-0.11496	-1.87947	2.118808
29	H	0.783198	4.769653	2.036327
30	H	3.134202	4.715538	0.593262
31	H	2.893689	2.413881	-0.90831
32	H	2.110826	-0.06933	1.734872
33	C	4.022047	-0.91107	1.256652
34	H	4.365259	-0.82828	2.280211
35	C	2.987005	-1.01796	-1.25756
36	H	2.556501	-1.03266	-2.25229
37	C	4.850628	-1.43706	0.2377
38	C	4.280509	-1.46597	-1.05804
39	H	4.834696	-1.83198	-1.91311
40	N	6.121878	-1.88597	0.486688

41	C	6.681675	-1.77738	1.825519
42	H	7.685991	-2.20327	1.829285
43	H	6.75223	-0.73226	2.158799
44	H	6.078555	-2.32992	2.557585
45	C	6.952629	-2.36403	-0.6089
46	H	7.147968	-1.57755	-1.35146
47	H	7.910912	-2.7004	-0.21062
48	H	6.485171	-3.21285	-1.12419
49	C	-1.45751	-1.35663	-1.38123
50	C	-0.17848	-1.89163	-1.06785
51	H	-0.05206	-2.44352	-0.13441
52	C	-2.60137	-1.69909	-0.4076
53	C	-3.80246	-0.73421	-0.3983
54	C	-3.12549	-3.13698	-0.65003
55	H	-2.18689	-1.69272	0.606888
56	C	-4.9789	-1.2672	0.383794
57	H	-4.1259	-0.51032	-1.42658
58	H	-3.49815	0.228596	0.025782
59	C	-4.07584	-3.58093	0.470626
60	H	-3.66344	-3.17686	-1.60652
61	H	-2.28327	-3.83527	-0.72916
62	C	-5.11759	-2.53262	0.801108
63	H	-5.75994	-0.5451	0.627539
64	H	-4.57663	-4.51952	0.187786
65	H	-3.50145	-3.82235	1.380769
66	H	0.471454	-2.25205	-1.86577
67	C	-1.85649	-1.28339	-2.84976
68	H	-0.99028	-1.10298	-3.49129
69	H	-2.31917	-2.2276	-3.17566
70	H	-2.58842	-0.49411	-3.05356
71	C	-6.29792	-2.99062	1.619209
72	H	-6.98779	-2.16763	1.834796
73	H	-6.86136	-3.78071	1.10188
74	H	-5.97448	-3.42019	2.578861

(*R*,*R*)-**21B Input**

```
%mem=12GB
%nprocshared=12
#                opt    freq              b3lyp/gen       geom=connectivity   pseudo=read

Title             Card   Required

                0      1
```

Mo	-3.13887745	-0.78982215	-0.01033934
O	-3.26225345	-2.77804615	-2.22107334
N	-4.48979845	0.79974885	-0.56918934
N	-4.22055145	2.17657885	-0.27823134
N	-2.45454745	0.51448685	1.73514166
N	-2.49586745	1.93545485	1.59548866
N	-1.81218845	0.62004785	-1.09879734
N	-1.79045845	2.01851885	-0.81797434
N	-1.17319545	-1.80691015	0.11236066
N	-3.40959745	-1.83603215	-1.34361234
C	-5.18463745	2.96663385	-0.90784034
C	-6.07586145	2.13695985	-1.58772434
C	-5.61536245	0.81415585	-1.37277434
C	-2.13183045	2.53325385	2.79830866
C	-1.85679345	1.52965585	3.73033466
C	-2.06455845	0.30666385	3.05087366
C	-0.85654745	2.63759585	-1.64304434
C	-0.26080745	1.66575985	-2.45267634
C	-0.87014445	0.43904885	-2.09665334
C	-0.09556045	-1.39850115	0.90110266
B	-2.80570745	2.60141385	0.22169366
H	-2.71572445	3.77049885	0.29610466
H	-5.14364645	4.05765185	-0.81474434
H	-6.94727745	2.44094585	-2.17077234
H	-6.01234945	-0.13087515	-1.75843134
H	-2.09908645	3.62536385	2.88316866
H	-1.54813945	1.66064285	4.76922166
H	-1.96403545	-0.71467215	3.43356566
H	-0.69864145	3.72036285	-1.58195734
H	0.51055955	1.82232485	-3.20910734
H	-0.69600145	-0.56494915	-2.50071434
H	-0.27221445	-0.49667615	1.50423566
C	1.13576855	-2.05249915	0.95529566
H	1.91739155	-1.64873215	1.60532566
C	-0.92623345	-2.93545315	-0.68201334
H	-1.77511145	-3.19551915	-1.37422334
C	1.36069255	-3.22615815	0.16891566
C	0.28126055	-3.63385315	-0.67773234
H	0.38671055	-4.49777215	-1.34116134
N	2.57026255	-3.96096315	0.25131666
C	3.75219955	-3.35331615	0.93923366
H	4.56570355	-4.09687815	0.95126266
H	4.11203155	-2.43648815	0.42919266
H	3.49353355	-3.10140215	1.98315466

C	2.85435355	-5.02073215	-0.76666634
H	2.95327755	-4.60652215	-1.79075234
H	3.79727355	-5.52084115	-0.49150234
H	2.04533255	-5.77265415	-0.76364934
C	-4.81114545	-1.53947015	1.15595066
C	-3.54547045	-2.27692115	1.41684266
H	-3.09303945	-2.15692315	2.40977966
H	-3.48456645	-3.31932215	1.08034066
C	-5.97085645	-2.38326415	0.47921166
C	-6.26333745	-3.72146015	1.25530966
C	-7.33814145	-1.62031815	0.36562766
H	-5.65015645	-2.66478915	-0.54169434
C	-7.29356545	-4.62038815	0.49087166
H	-6.65828045	-3.48279215	2.25766366
H	-5.33019545	-4.29093115	1.39376766
C	-8.38255645	-2.44359815	-0.46054434
H	-7.74401745	-1.45131815	1.37617366
H	-7.20250045	-0.63244215	-0.09947034
C	-8.56260045	-3.85469215	0.10607166
H	-9.35270345	-1.91418615	-0.46934434
H	-8.03842145	-2.49569415	-1.51518934
C	-9.84227545	-4.63062115	-0.20311534
H	-9.97970045	-5.46302215	0.50633166
H	-10.72582645	-3.97409215	-0.14407634
H	-9.82392045	-5.06635115	-1.22151134
C	-5.34978745	-0.66481715	2.32916266
H	-5.97249045	0.16825685	1.96640066
H	-5.96928945	-1.26507015	3.01827066
H	-4.52804945	-0.23436515	2.91599066
H	-7.12909484	-5.65288741	0.26328718

1	10	1	49	1	50	1
2	10	1				
3	4	1	13	1		
4	11	1	21	1		
5	6	1	16	1		
6	14	1	21	1		
7	8	1	19	1		
8	17	1	21	1		
9	20	1	35	1		
10						
11	12	1.5	23	1		
12	13	1.5	24	1		
13	25	1				

14	15	1.5	26	1		
15	16	1.5	27	1		
16	28	1				
17	18	1.5	29	1		
18	19	1.5	30	1		
19	31	1				
20	32	1	33	1.5		
21	22	1				
22						
23						
24						
25						
26						
27						
28						
29						
30						
31						
32						
33	34	1	37	1.5		
34						
35	36	1	38	1.5		
36						
37	38	1.5	40	1		
38	39	1				
39						
40	41	1	45	1		
41	42	1	43	1	44	1
42						
43						
44						
45	46	1	47	1	48	1
46						
47						
48						
49	50	1	53	1	70	1
50	51	1	52	1		
51						
52						
53	54	1	55	1	56	1
54	57	1	58	1	59	1
55	60	1	61	1	62	1
56						
57	63	1	74	1		

```
                    58
                    59
                    60              63              1               64              1   65  1
                    61
                    62
                    63              66              1
                    64
                    65
                    66              67              1               68              1   69  1
                    67
                    68
                    69
                    70              71              1               72              1   73  1
                    71
                    72
                    73
                    74

Mo                   0
LANL2DZ
*****
H                 B     C               N               O                       0
6-31G(d)
*****

Mo                   0
LANL2DZ
```

(*R*,*R*)-**21B Output Coordinates**

Tag	Symbol	X	Y	Z
1	Mo	-0.11465	0.266966	-0.15187
2	O	-0.93968	-1.3956	-2.4798
3	N	-1.50751	1.995014	-0.57171
4	N	-1.11733	3.276711	-0.31398
5	N	0.640779	1.608942	1.645379
6	N	0.665816	2.957885	1.475748
7	N	1.241054	1.71102	-1.278
8	N	1.278644	3.033141	-0.96392
9	N	1.819111	-0.9465	-0.0205
10	N	-0.62206	-0.69144	-1.55163
11	C	-2.0289	4.142194	-0.8209
12	C	-3.03861	3.415417	-1.42728
13	C	-2.65596	2.076179	-1.25255

14	C	1.092507	3.560769	2.606083
15	C	1.359995	2.582204	3.552956
16	C	1.061368	1.379158	2.898662
17	C	2.155581	3.670898	-1.77063
18	C	2.712934	2.741096	-2.63725
19	C	2.102257	1.527573	-2.28639
20	C	2.958003	-0.45935	0.51412
21	B	0.326953	3.606817	0.116206
22	H	0.468953	4.797696	0.196387
23	H	-1.88249	5.20752	-0.71672
24	H	-3.9205	3.79288	-1.92318
25	H	-3.13696	1.174776	-1.59742
26	H	1.175453	4.637011	2.652854
27	H	1.71291	2.719272	4.56431
28	H	1.125424	0.367299	3.272442
29	H	2.313761	4.735362	-1.67226
30	H	3.444502	2.917035	-3.41203
31	H	2.232623	0.540628	-2.70743
32	H	2.891871	0.534162	0.941576
33	C	4.161609	-1.14419	0.53921
34	H	5.018323	-0.66274	0.993754
35	C	1.903203	-2.17741	-0.5728
36	H	0.994011	-2.55775	-1.02452
37	C	4.252552	-2.43743	-0.02697
38	C	3.059599	-2.93603	-0.60406
39	H	3.023002	-3.90823	-1.07918
40	N	5.418204	-3.15936	-0.02033
41	C	6.630339	-2.57707	0.535558
42	H	7.440377	-3.30468	0.468725
43	H	6.938347	-1.67196	-0.00687
44	H	6.499872	-2.31402	1.593346
45	C	5.470768	-4.46275	-0.66624
46	H	5.267162	-4.39649	-1.74429
47	H	6.467022	-4.88726	-0.53454
48	H	4.746594	-5.15851	-0.22333
49	C	-1.88186	-0.65925	1.17394
50	C	-0.62545	-1.29065	1.366215
51	H	-0.06452	-1.10106	2.281553
52	H	-0.46087	-2.29327	0.972427
53	C	-2.97704	-1.49119	0.466991
54	C	-3.27582	-2.79043	1.262092
55	C	-4.3235	-0.77425	0.252706
56	H	-2.60719	-1.80357	-0.51668
57	C	-4.45872	-3.55503	0.719356

58	H	-3.44428	-2.54608	2.324101
59	H	-2.39258	-3.44207	1.252298
60	C	-5.26666	-1.62126	-0.61373
61	H	-4.80169	-0.60188	1.226621
62	H	-4.18802	0.210875	-0.19848
63	C	-5.35461	-3.05803	-0.14394
64	H	-6.27313	-1.17567	-0.61607
65	H	-4.93569	-1.60179	-1.66517
66	C	-6.48876	-3.88147	-0.698
67	H	-6.46526	-4.91072	-0.32409
68	H	-7.46426	-3.44602	-0.43726
69	H	-6.45089	-3.92004	-1.79641
70	C	-2.39696	0.296086	2.24046
71	H	-2.99201	1.113087	1.817924
72	H	-3.04246	-0.23475	2.959038
73	H	-1.57923	0.745144	2.808256
74	H	-4.5645	-4.58873	1.053061

(*R*,*R*)-**21C Input**

```
%mem=12GB
%nprocshared=12
#                opt      freq              b3lyp/gen       geom=connectivity   pseudo=read

Title                Card     Required

                 0        1
                    Mo         2.09174418    -2.37101084                0
                    O          0.69287118    -0.86437684               -2.156763
                    N          4.18557718    -2.51119184               -0.522953
                    N          4.94064718    -3.71263884               -0.338903
                    N          2.61487818    -3.76050484                1.735527
                    N          3.59804818    -4.77828584                1.537245
                    N          2.12525318    -4.28578084               -1.117818
                    N          3.09380018    -5.30348584               -0.878013
                    N         -0.00215282    -3.06195584                0.205494
                    N          1.49934318    -1.44795184               -1.317419
                    C          6.23489618    -3.51395584               -0.816416
                    C          6.34033018    -2.20874684               -1.299718
                    C          5.06758618    -1.61893684               -1.108258
                    C          3.82260418    -5.44797884                2.735934
                    C          3.00483718    -4.88861184                3.721188
                    C          2.28043418    -3.85767884                3.07921
                    C          2.85372018    -6.37692684               -1.730092
```

C	1.73656218	-6.08102484	-2.516968
C	1.31425518	-4.79004084	-2.119853
C	-0.45134282	-4.04867284	1.086559
B	4.24559318	-5.02193484	0.137413
H	5.00577918	-5.91659884	0.182033
H	6.96804418	-4.32677384	-0.767497
H	7.22274418	-1.73663684	-1.735727
H	4.72809018	-0.60533484	-1.34754
H	4.54791318	-6.26833484	2.78111
H	2.94010118	-5.18310084	4.770408
H	1.54139718	-3.17113584	3.506552
H	3.50299518	-7.25940384	-1.702137
H	1.28667018	-6.71312884	-3.284947
H	0.47963118	-4.18723384	-2.496126
H	0.31971218	-4.47731584	1.741967
C	-1.76985782	-4.49594884	1.165983
H	-2.01723982	-5.27774684	1.889976
C	-0.98644882	-2.54926384	-0.65148
H	-0.60050082	-1.79221584	-1.388381
C	-2.77141082	-3.93729784	0.309652
C	-2.32219382	-2.95149684	-0.624863
H	-3.01778182	-2.49816984	-1.337781
N	-4.13255182	-4.31564684	0.406436
C	-4.50731582	-5.51879484	1.212924
H	-5.60586682	-5.60764284	1.212433
H	-4.07193482	-6.45272184	0.802683
H	-4.16684282	-5.39616384	2.256744
C	-5.09354382	-3.88232784	-0.655591
H	-4.84924382	-4.31620784	-1.646585
H	-6.10437182	-4.20942984	-0.362253
H	-5.09202582	-2.78083884	-0.739214
C	2.80373718	-0.65838684	1.07271
C	1.39701018	-0.96826084	1.445798
H	1.27150318	-1.37736884	2.459423
C	3.89220818	-0.83106984	2.173248
H	3.70794518	-1.71584984	2.797893
H	4.89464018	-0.93457184	1.726582
C	0.27003418	0.04598716	1.095728
H	-0.11039582	-0.14452884	0.080315
C	2.99096218	0.70639916	0.334476
H	4.06145218	0.97286016	0.291548
H	2.61897018	0.65995116	-0.701098
H	-0.58435482	-0.11039384	1.7762
C	0.66704018	1.58701016	1.156825

C	2.22287318	1.83301016	1.098174
H	0.30904718	1.99179916	2.120562
H	2.42120318	2.81471916	0.633461
H	2.60855518	1.87915516	2.130877
C	-0.09298582	2.35198616	0.036556
C	0.33922218	2.11020316	-1.422892
H	1.33164418	2.55610016	-1.604268
H	0.41261618	1.02621716	-1.665801
H	-0.37486682	2.58292916	-2.113352
C	-1.10529582	3.18044616	0.335529
H	-1.66771082	3.71301516	-0.439412
H	-1.41693482	3.36333316	1.369807
H	3.91807718	0.04956416	2.839107

1	10	1	49	1	50	1
2	10	1				
3	4	1	13	1		
4	11	1	21	1		
5	6	1	16	1		
6	14	1	21	1		
7	8	1	19	1		
8	17	1	21	1		
9	20	1	35	1		
10						
11	12	1.5	23	1		
12	13	1.5	24	1		
13	25	1				
14	15	1.5	26	1		
15	16	1.5	27	1		
16	28	1				
17	18	1.5	29	1		
18	19	1.5	30	1		
19	31	1				
20	32	1	33	1.5		
21	22	1				
22						
23						
24						
25						
26						
27						
28						
29						
30						

31						
32						
33	34	1	37	1.5		
34						
35	36	1	38	1.5		
36						
37	38	1.5	40	1		
38	39	1				
39						
40	41	1	45	1		
41	42	1	43	1	44	1
42						
43						
44						
45	46	1	47	1	48	1
46						
47						
48						
49	50	1	52	1	57	1
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51						
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55	56	1	60	1	61	1
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57	58	1	59	1	62	1
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60						
61	62	1	63	1	66	1
62	64	1	65	1		
63						
64						
65						
66	67	1	71	2		
67	68	1	69	1	70	1
68						
69						
70						
71	72	1	73	1		
72						
73						
74						

Mo 0
LANL2DZ
*****
H B C N O 0
6-31G(d)
*****

Mo 0
LANL2DZ

(*R*,*R*)-**21C Output Coordinates**

Tag	Symbol	X	Y	Z
1	Mo	0.664107	0.167478	-0.30497
2	O	-0.30187	1.230701	-2.91201
3	N	2.842426	0.600179	-0.64919
4	N	3.795527	-0.29981	-0.28051
5	N	1.468056	-0.7956	1.701631
6	N	2.651209	-1.46494	1.658416
7	N	1.357391	-1.85522	-1.0953
8	N	2.518754	-2.4167	-0.66955
9	N	-1.31686	-0.97302	-0.07076
10	N	0.123145	0.798197	-1.86555
11	C	5.014994	0.139416	-0.67187
12	C	4.858796	1.356926	-1.31416
13	C	3.476838	1.598592	-1.27485
14	C	2.976679	-1.91053	2.89068
15	C	1.979454	-1.52728	3.77678
16	C	1.060193	-0.83163	2.979625
17	C	2.71437	-3.59852	-1.29553
18	C	1.648806	-3.82109	-2.15601
19	C	0.827527	-2.69514	-1.99271
20	C	-1.49773	-1.96831	0.822067
21	B	3.425096	-1.66576	0.331567
22	H	4.420922	-2.30435	0.544291
23	H	5.897279	-0.44891	-0.46532
24	H	5.628114	1.979492	-1.74632
25	H	2.911264	2.434255	-1.65898
26	H	3.8903	-2.46588	3.046445
27	H	1.929191	-1.71788	4.838526
28	H	0.134997	-0.35082	3.265374
29	H	3.595302	-4.18836	-1.0864
30	H	1.493736	-4.66725	-2.80897

31	H	-0.10735	-2.44689	-2.47496
32	H	-0.66418	-2.16616	1.485232
33	C	-2.65274	-2.72517	0.924463
34	H	-2.69381	-3.50223	1.677416
35	C	-2.34588	-0.74724	-0.91805
36	H	-2.19425	0.031713	-1.65585
37	C	-3.74026	-2.47934	0.053519
38	C	-3.53771	-1.45036	-0.89698
39	H	-4.29827	-1.19188	-1.62296
40	N	-4.90887	-3.1923	0.121808
41	C	-5.04588	-4.2734	1.08616
42	H	-6.04391	-4.70535	1.000405
43	H	-4.3119	-5.07301	0.913355
44	H	-4.92187	-3.91163	2.11531
45	C	-5.98116	-2.92484	-0.82559
46	H	-5.67321	-3.12407	-1.86159
47	H	-6.83117	-3.56849	-0.59491
48	H	-6.32006	-1.88267	-0.76351
49	C	0.733334	2.298861	0.625338
50	C	-0.51349	1.668272	0.909883
51	H	-0.64701	1.259926	1.915563
52	C	1.77122	2.502376	1.718361
53	H	1.7381	1.719521	2.479661
54	H	2.790864	2.536445	1.316904
55	C	-1.76352	2.327274	0.344014
56	H	-1.80435	2.231955	-0.74661
57	C	0.613293	3.496162	-0.32288
58	H	1.580312	4.003354	-0.43516
59	H	0.309126	3.183228	-1.32552
60	H	-2.67364	1.858121	0.736573
61	C	-1.74889	3.837521	0.722115
62	C	-0.43208	4.513101	0.210234
63	H	-1.73588	3.875399	1.818877
64	H	-0.65522	5.235087	-0.58525
65	H	0.001535	5.09727	1.030772
66	C	-2.99664	4.577757	0.26937
67	C	-3.34868	4.537365	-1.20047
68	H	-2.5059	4.849125	-1.83055
69	H	-3.61201	3.520621	-1.51998
70	H	-4.19848	5.19025	-1.42394
71	C	-3.764	5.239625	1.144057
72	H	-4.655	5.780719	0.832497
73	H	-3.5275	5.266832	2.205472
74	H	1.594425	3.463583	2.228285

(*S*,*R*)-**21A Input**

```
%mem=12GB
%nprocshared=12
#                opt    freq              b3lyp/gen      geom=connectivity   pseudo=read

Title             Card  Required

                0     1
                Mo       -3.23437968   -5.69119197                0
                O        -4.66336568   -5.41106497             -2.594792
                N        -1.62998868   -4.24403497             -0.040771
                N        -1.28377168   -3.45384297              1.102252
                N        -2.70648968   -6.03095897              2.191091
                N        -2.20990268   -4.93524597              2.962523
                N        -4.21406068   -3.89999697               0.87329
                N        -3.61880168   -3.12915997              1.914582
                N        -5.26828668   -6.43684597              0.466542
                N        -3.86541668   -5.43096097             -1.574658
                C        -0.31688468   -2.51940197               0.73094
                C        -0.01894868   -2.69157397             -0.621292
                C        -0.84530268   -3.75106097             -1.069689
                C        -1.86938368   -5.38000097              4.236508
                C        -2.12913068   -6.75041697              4.316259
                C        -2.63797168   -7.11965197               3.04933
                C        -4.47133068   -2.08445397              2.258116
                C        -5.61972968   -2.16597197              1.464857
                C        -5.43041268   -3.28826897               0.62366
                C        -5.74888368   -6.74065397              1.741808
                B        -2.17128868   -3.48785097              2.383136
                H        -1.78188668   -2.72739697              3.189665
                H         0.07292432   -1.81122497              1.470608
                H         0.70280032   -2.12722597             -1.214802
                H        -0.92231268   -4.19778797             -2.067006
                H        -1.47139368   -4.67718897              4.977226
                H        -1.96846368   -7.40345797              5.176183
                H        -2.95103968   -8.10887697              2.698108
                H        -4.18333168   -1.37131797              3.038832
                H        -6.48201868   -1.49682197              1.485025
                H        -6.09003568   -3.69195897             -0.153162
                H        -5.03079468   -6.59075897              2.560582
                C        -7.03772368   -7.20315397              2.009828
                H        -7.31733668   -7.40953497              3.047003
```

C	-6.20056868	-6.59727097	-0.567833				
H	-5.81860568	-6.27278097	-1.575738				
C	-7.96790868	-7.39713897	0.940328				
C	-7.50386368	-7.05299997	-0.36912				
H	-8.16567068	-7.13638097	-1.236682				
N	-9.26137068	-7.93222297	1.162632				
C	-9.78625568	-8.02668997	2.560796				
H	-10.77179568	-8.51905897	2.528047				
H	-9.89834968	-7.03142997	3.037291				
H	-9.10822668	-8.64241997	3.178371				
C	-10.27514968	-7.88080097	0.062876				
H	-10.54555368	-6.84121597	-0.213248				
H	-11.18194568	-8.40682397	0.403348				
H	-9.88629868	-8.39710697	-0.832773				
C	-1.70534868	-7.08871297	-0.64177				
C	-2.98972368	-7.75793597	-0.299175				
H	-2.99638268	-8.39202997	0.597106				
C	-0.48084668	-7.45877897	0.281589				
C	0.83304432	-6.66412497	-0.023799				
C	-0.13932968	-8.99364397	0.207658				
H	-0.75185368	-7.24599397	1.329937				
C	1.91999932	-6.95272197	1.058298				
H	1.22248732	-6.96006397	-1.011773				
H	0.62951432	-5.58250597	-0.054636				
C	1.14763432	-9.35122697	0.966993				
H	-0.03429468	-9.30264797	-0.849812				
H	-0.97890468	-9.58041997	0.621113				
C	2.07363732	-8.45933797	1.352533				
H	2.89333032	-6.54395097	0.729284				
H	-3.55151168	-8.22561097	-1.118415				
C	-1.32685068	-7.10519697	-2.153318				
H	-2.22581368	-6.98751297	-2.776264				
H	-0.84298668	-8.05650097	-2.437629				
H	-0.62635368	-6.29744797	-2.416776				
C	3.33777032	-8.86885397	2.125316				
H	4.24650332	-8.60047197	1.559345				
H	3.35241532	-9.95272497	2.313578				
H	3.38926932	-8.34525297	3.095615				
H	1.65964532	-6.42657197	1.997171				
H	1.29504732	10.41812497	-1.191531				

1	10	1	49	1	50	1
2	10	1				

3	4	1	13	1		
4	11	1	21	1		
5	6	1	16	1		
6	14	1	21	1		
7	8	1	19	1		
8	17	1	21	1		
9	20	1	35	1		
10						
11	12	1.5	23	1		
12	13	1.5	24	1		
13	25	1				
14	15	1.5	26	1		
15	16	1.5	27	1		
16	28	1				
17	18	1.5	29	1		
18	19	1.5	30	1		
19	31	1				
20	32	1	33	1.5		
21	22	1				
22						
23						
24						
25						
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27						
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30						
31						
32						
33	34	1	37	1.5		
34						
35	36	1	38	1.5		
36						
37	38	1.5	40	1		
38	39	1				
39						
40	41	1	45	1		
41	42	1	43	1	44	1
42						
43						
44						
45	46	1	47	1	48	1
46						

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49 50 1 52 1 65 1
50 51 1 64 1
51
52 53 1 54 1 55 1
53 56 1 57 1 58 1
54 59 1 60 1 61 1
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56 62 1 63 1 73 1
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59 62 2 74 1
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62 69 1
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65 66 1 67 1 68 1
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69 70 1 71 1 72 1
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Mo 0
LANL2DZ
*****
H B C N O 0
6-31G(d)
*****

Mo 0
LANL2DZ

(*S*,*R*)-**21A Output Coordinates**

Tag	Symbol	X	Y	Z
1	Mo	-0.11986	0.301018	-0.75634
2	O	-0.9787	0.708427	-3.5782

3	N	1.616701	1.727153	-0.8672
4	N	1.934274	2.513148	0.200336
5	N	0.463423	0.091794	1.509883
6	N	0.97131	1.180617	2.147459
7	N	-1.04116	2.215437	0.073457
8	N	-0.38633	2.961565	1.001807
9	N	-2.19994	-0.52503	-0.27654
10	N	-0.60206	0.562725	-2.44088
11	C	2.902694	3.392917	-0.15366
12	C	3.22703	3.180591	-1.48285
13	C	2.384789	2.131838	-1.88533
14	C	1.288664	0.863978	3.421411
15	C	0.981148	-0.47278	3.633864
16	C	0.466723	-0.90764	2.404607
17	C	-1.12761	4.044359	1.325743
18	C	-2.30492	4.006731	0.592007
19	C	-2.1979	2.839669	-0.17976
20	C	-2.74599	-0.47225	0.956095
21	B	1.039458	2.562684	1.456868
22	H	1.466474	3.375416	2.232556
23	H	3.278387	4.106148	0.565622
24	H	3.962631	3.70355	-2.0758
25	H	2.296965	1.650734	-2.84767
26	H	1.706056	1.610485	4.081643
27	H	1.115217	-1.04619	4.539019
28	H	0.110451	-1.88787	2.120469
29	H	-0.76197	4.760694	2.047488
30	H	-3.1147	4.721184	0.607036
31	H	-2.88542	2.42352	-0.90261
32	H	-2.1138	-0.06381	1.735604
33	C	-4.02853	-0.89836	1.258593
34	H	-4.37128	-0.81339	2.282132
35	C	-2.99391	-1.01289	-1.25551
36	H	-2.56377	-1.0306	-2.25033
37	C	-4.8594	-1.42193	0.240219
38	C	-4.28925	-1.45538	-1.05535
39	H	-4.84478	-1.82075	-1.90982
40	N	-6.13275	-1.86436	0.489644
41	C	-6.69053	-1.75586	1.829298
42	H	-7.69813	-2.1739	1.832587
43	H	-6.75298	-0.71118	2.165321
44	H	-6.09108	-2.31484	2.5596
45	C	-6.96363	-2.34557	-0.60445
46	H	-7.15365	-1.56265	-1.35204

47	H	-7.92439	-2.67452	-0.20598
48	H	-6.49944	-3.19982	-1.11382
49	C	1.449143	-1.37487	-1.37714
50	C	0.170244	-1.89898	-1.04811
51	H	0.044434	-2.43707	-0.10696
52	C	2.606582	-1.69281	-0.41085
53	C	3.902404	-0.89081	-0.62319
54	C	2.956595	-3.20386	-0.45534
55	H	2.268656	-1.48532	0.609895
56	C	4.916021	-1.17411	0.496326
57	H	4.352634	-1.16749	-1.58681
58	H	3.692837	0.180463	-0.66573
59	C	4.189939	-3.54703	0.343228
60	H	3.092998	-3.52986	-1.49872
61	H	2.104307	-3.78759	-0.08087
62	C	5.076692	-2.64992	0.794842
63	H	5.89471	-0.74647	0.230614
64	H	-0.486	-2.26685	-1.83743
65	C	1.841224	-1.30929	-2.84658
66	H	0.966453	-1.18042	-3.48931
67	H	2.349372	-2.23584	-3.15815
68	H	2.536167	-0.49045	-3.06206
69	C	6.272309	-3.04327	1.624263
70	H	7.21268	-2.76281	1.128146
71	H	6.298438	-4.12133	1.81652
72	H	6.269691	-2.52644	2.59519
73	H	4.612064	-0.65051	1.417913
74	H	4.348685	-4.60404	0.564253

(*S*,*R*)-**21B Input**

```
%mem=12GB
%nprocshared=12
#                opt    freq              b3lyp/gen        geom=connectivity   pseudo=read

Title              Card  Required

                0      1
                Mo      -2.06695417     -9.56591662                0
                O       -0.62906117     -9.25523362             2.58663
                N       -3.66401417     -8.11310262            0.039029
                N       -4.02238517     -7.33908862           -1.111669
                N       -2.60122517     -9.93170462           -2.182073
                N       -3.11272317     -8.84787662           -2.960184
```

N	-1.08855817	-7.78982962	-0.90413
N	-1.69340917	-7.03050362	-1.94848
N	-0.03597317	-10.32363962	-0.463104
N	-1.42994317	-9.28587762	1.569086
C	-4.98406317	-6.39808962	-0.741968
C	-5.26629917	-6.55126162	0.61579
C	-4.43581817	-7.60515162	1.069617
C	-3.45835617	-9.30814762	-4.227292
C	-3.18753217	-10.67711262	-4.295508
C	-2.66644517	-11.02951862	-3.028721
C	-0.84248517	-5.99180262	-2.31359
C	0.31400883	-6.06590462	-1.531439
C	0.13147983	-7.17748662	-0.674686
C	0.44231483	-10.64076962	-1.735955
B	-3.14616317	-7.39238862	-2.399334
H	-3.54085317	-6.64247262	-3.213117
H	-5.38171117	-5.69977462	-1.486836
H	-5.98073917	-5.97784562	1.209446
H	-4.34865417	-8.03891262	2.071732
H	-3.86750317	-8.61616362	-4.972133
H	-3.34843017	-11.33951662	-5.148186
H	-2.33950617	-12.01176462	-2.670388
H	-1.13727317	-5.28772062	-3.099964
H	1.17727383	-5.39875962	-1.568793
H	0.79844083	-7.57291362	0.1001
H	-0.27586417	-10.49564062	-2.555478
C	1.72928783	-11.11015662	-2.001107
H	2.00703783	-11.32706062	-3.036632
C	0.89735483	-10.47653362	0.571529
H	0.51859483	-10.13922962	1.576332
C	2.66008083	-11.29704562	-0.930915
C	2.19895183	-10.93828762	0.375642
H	2.86178183	-11.01477762	1.243061
N	3.95140783	-11.83883162	-1.149488
C	4.47433083	-11.94840762	-2.547316
H	5.45798983	-12.44427962	-2.511038
H	4.58972383	-10.95810362	-3.033259
H	3.79319483	-12.56727462	-3.158282
C	4.96688483	-11.77926862	-0.051655
H	5.24068683	-10.73774662	0.213583
H	5.87165883	-12.31135562	-0.388049
H	4.57774883	-12.28537762	0.849672
C	-3.60271817	-10.94487062	0.661585
C	-2.31844017	-11.62681162	0.341997

H	-2.31436017	-12.28347962	-0.538412
H	-1.76071217	-12.07645662	1.174081
C	-3.9860585	-10.92575196	2.15298859
C	-3.86994979	-12.30612504	2.88661444
C	-5.44155812	-10.37685187	2.37869589
H	-3.30606186	-10.22959609	2.67261607
C	-4.46271125	-12.27222594	4.30496284
H	-4.38397974	-13.09168566	2.30145567
H	-2.80989875	-12.60509959	2.9510525
C	-5.7123487	-10.12131536	3.89328085
H	-6.17685181	-11.10626438	2.00112209
H	-5.58014223	-9.4391259	1.81445012
C	-5.27906968	-11.31406668	4.77065611
H	-3.62875218	-12.301357	4.97471179
C	-5.8254302	-11.32685372	6.20740637
H	-5.44684575	-12.1952935	6.76677369
H	-6.92843852	-11.36598103	6.20632526
H	-5.53047867	-10.40946993	6.74566559
C	-4.78383634	-11.34411146	-0.24238769
H	-5.47042796	-10.52657433	-0.31397675
H	-5.28253362	-12.1930582	0.17652812
H	-4.41919411	-11.59009635	-1.21779913
H	-4.9901678	-13.19514019	4.42710567
H	-6.14792368	-9.2232983	4.27894885

1	10	1	49	1	50	1
2	10	1				
3	4	1	13	1		
4	11	1	21	1		
5	6	1	16	1		
6	14	1	21	1		
7	8	1	19	1		
8	17	1	21	1		
9	20	1	35	1		
10						
11	12	1.5	23	1		
12	13	1.5	24	1		
13	25	1				
14	15	1.5	26	1		
15	16	1.5	27	1		
16	28	1				
17	18	1.5	29	1		
18	19	1.5	30	1		
19	31	1				

20	32	1	33	1.5		
21	22	1				
22						
23						
24						
25						
26						
27						
28						
29						
30						
31						
32						
33	34	1	37	1.5		
34						
35	36	1	38	1.5		
36						
37	38	1.5	40	1		
38	39	1				
39						
40	41	1	45	1		
41	42	1	43	1	44	1
42						
43						
44						
45	46	1	47	1	48	1
46						
47						
48						
49	50	1	53	1	69	1
50	51	1	52	1		
51						
52						
53	54	1	55	1	56	1
54	57	1	58	1	59	1
55	60	1	61	1	62	1
56						
57	63	1	64	1	73	1
58						
59						
60	63	2	74	1		
61						
62						
63	65	1				

64
65 66 1 67 1 68 1
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69 70 1 71 1 72 1
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74

Mo 0
LANL2DZ
*****
H B C N O 0
6-31G(d)
*****

Mo 0
LANL2DZ

(*S*,*R*)-**21B Output Coordinates**

Tag	Symbol	X	Y	Z
1	Mo	0.155096	0.334142	-0.11006
2	O	1.045497	-1.37163	-2.38046
3	N	1.425611	2.202036	-0.44062
4	N	0.851406	3.435902	-0.32829
5	N	-0.78436	1.691744	1.601525
6	N	-1.00107	3.008893	1.338004
7	N	-1.24336	1.592402	-1.3822
8	N	-1.45098	2.912664	-1.14209
9	N	-1.69098	-1.00403	0.026825
10	N	0.725115	-0.64734	-1.46941
11	C	1.746142	4.393228	-0.66548
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(*S*,*R*)-**21C Output Coordinates**

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72	H	3.408686	4.49881	1.977967
73	H	4.345559	5.533479	0.885827
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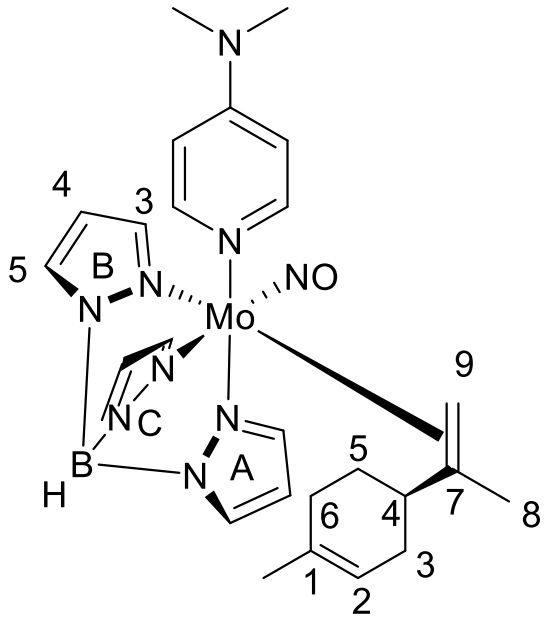
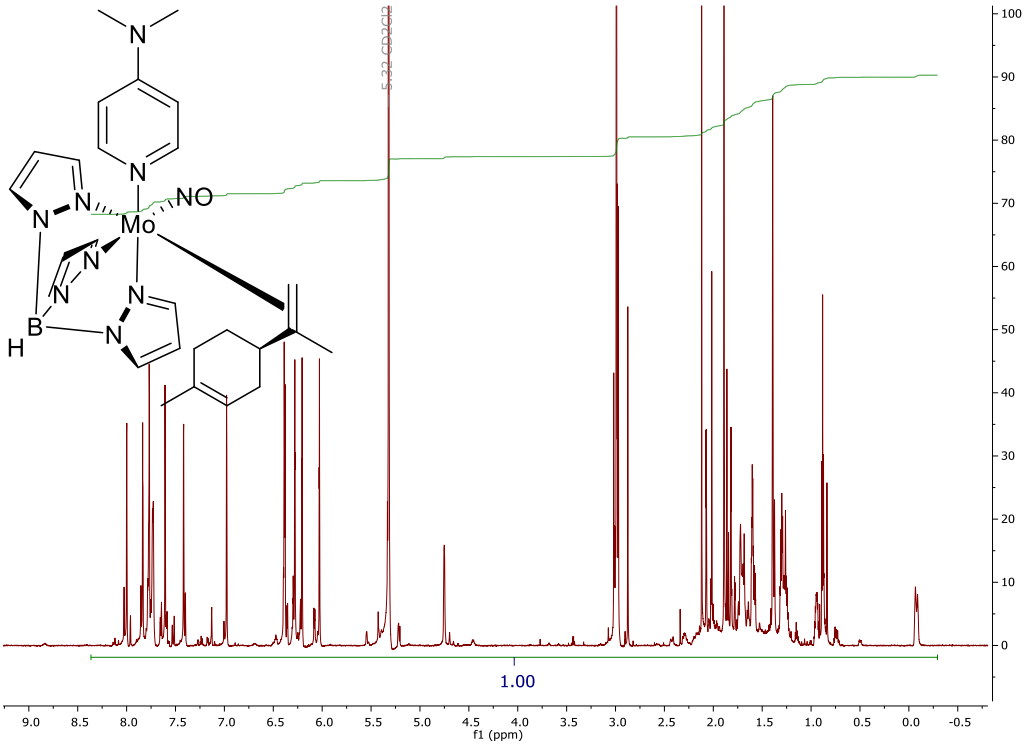
Mo$_R$Tp(NO)(DMAP)(η^2-*R*-limonene) (*R*,*R*)- **21A**

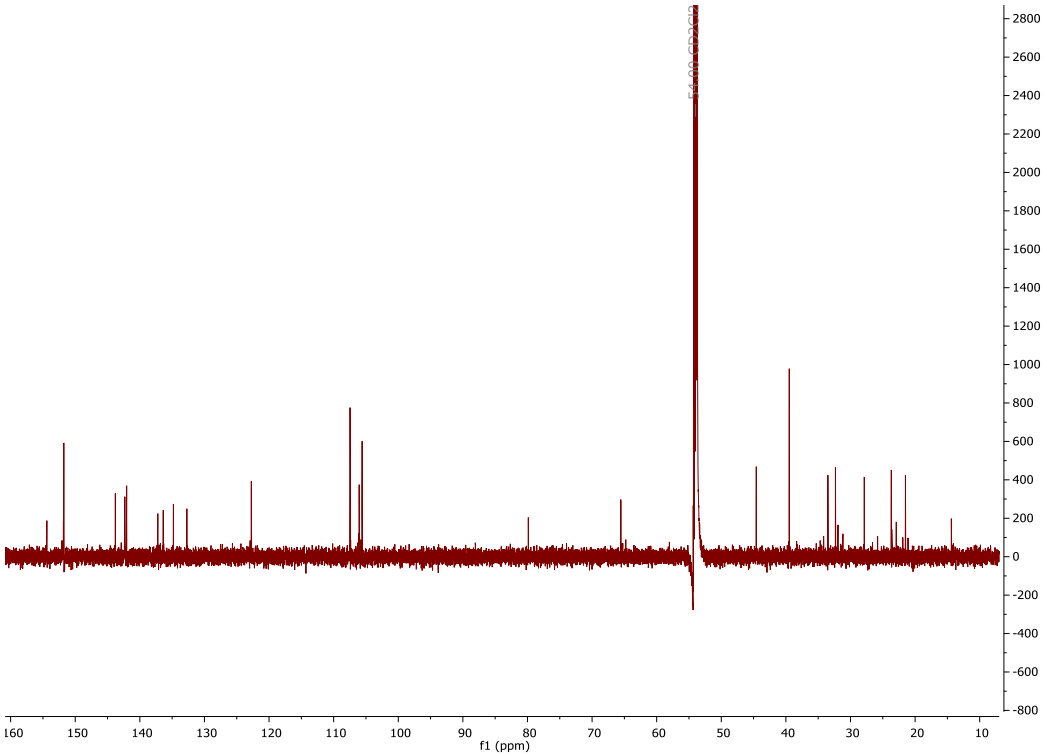


To a 4 dram vial charged with a stir pea, Mo_RTp(NO)(DMAP)(η^2-*R*-α-pinene) (0.10g , 0.17 mmol) was combined with *R*-limonene (2 mL, 12 mmol) and HFIP (0.1g, 0.60 mmol). The vial was capped and allowed to mix for 4 h. The reaction solution was added to a 15 mL medium porosity fritted disk, 3/4 full of silica, and the excess limonene was eluted with 40 mL of hexanes. The yellow band was then eluted with ~60 ml of ether. The yellow filtrate was evaporated *in vacuo* to dryness and dissolved in ~0.5 mL THF. The THF solution was added to 20 mL stirring pentane and then concentrated to 10 mL *in vacuo*. The yellow solid was then collected on a 15 mL fine porosity fritted disk and washed with pentane (3 x 10 mL). The solid was then desiccated yielding **9**A (0.026 g, 0.044 mmol, 26% recovered, ~23% yield). ^{1}H NMR (d_2-DCM, δ): 8.00 (1H, d, PzA3), 7.84 (1H, d, PzA5), 7.77 (1H, d, PzC5), 7.73 (2H, m, DMAP H2 and H6), 7.61 (1H, d, PzB5), 7.42 (1H, d, PzC3), 6.98 (1H, d, PzB3), 6.39 (2H, m, DMAP H3 and H5), 6.28 (1H, t, PzA4), 6.21 (1H, t, PzC4), 6.03 (1H, t, PzB4), 4.75 (1H, bs, H2), 2.99 (6H, s, DMAP methyl), 2.08 (1H, d, *J* = 3.0, H9x proximal to NO), 1.89 (3H, s, 8 methyl), 1.82 (1H, d, *J* = 3.0, H9y proximal to TpC), 1.73 (2H, b, H5x and H6x), 1.60 (2H, m, H5y and H6y), 1.39 (3H, s, 1 methyl), 1.30 (1H, m, H3), 0.91 (1H, m, H4), -0.06 (1H, b, H3). ^{13}C NMR (d_2-DCM, δ): 153.8 (DMAP 4), 151.2 (DMAP 2 and 6), 143.21 (PzA3), 141.7 (PzC3), 141.5 (PzB3), 136.6 (PzA5), 135.8 (PzC5), 134.2 (PzB5), 132.1 (C1), 122.2 (C2), 106.9 (DMAP 3 and 5), 105.5 (PzA4), 105.0 (2C, PzB4 and PzC4), 79.3 (C7), 65.0 (C9), 44.0 (C4), 32.9 (C5/6), 31.7 (C5/6), 27.3 (C3), 23.1 (C1 Methyl), 20.9 (C8).

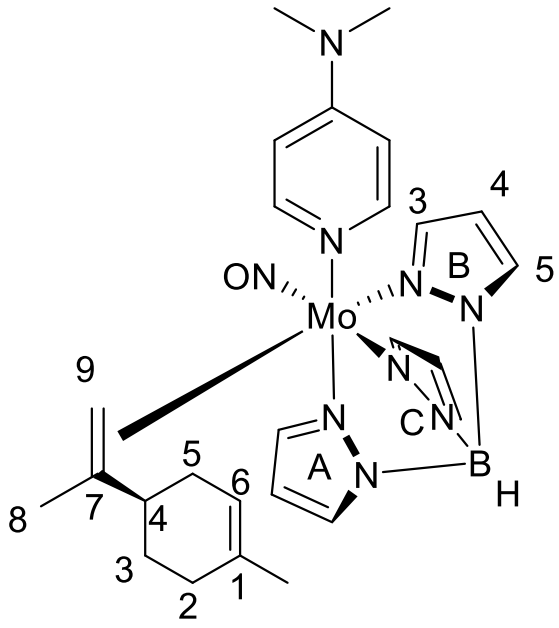
^{1}H NMR (CD_2CL_2) of R_{Mo},*R*-**21**A (unidentified side product present)



^{13}C NMR (CD_2CL_2) of R_{Mo},*R*-**21**A (unidentified side product present)



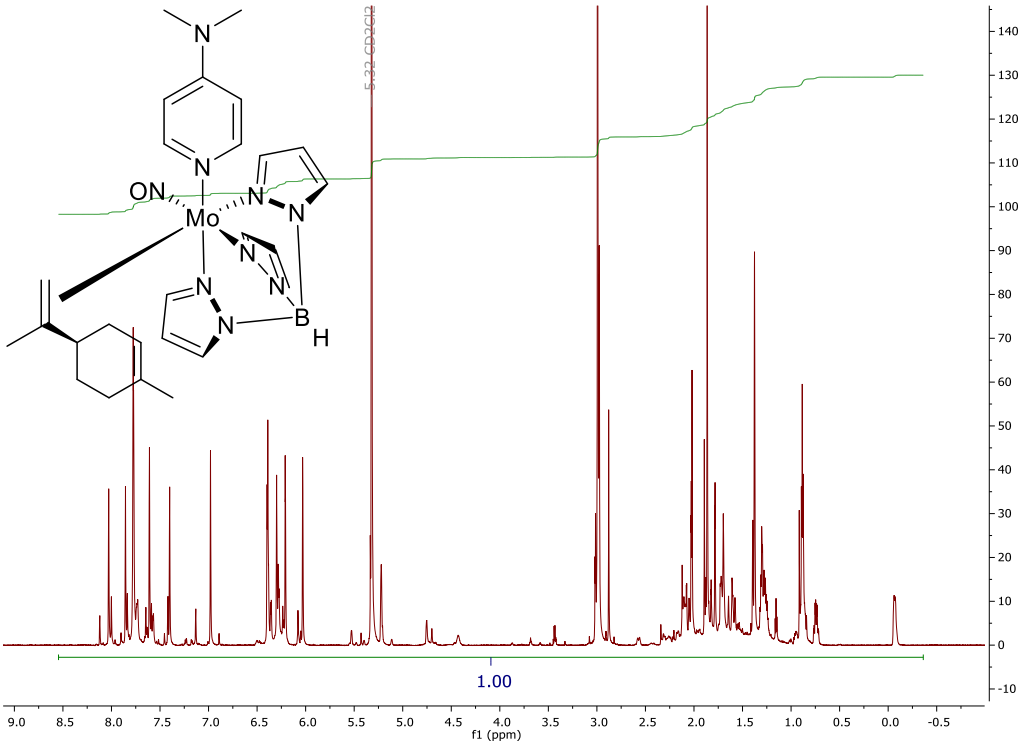
Mo$_S$Tp(NO)(DMAP)(η^2-*R*-limonene) (*S*,*R*)- **21A**



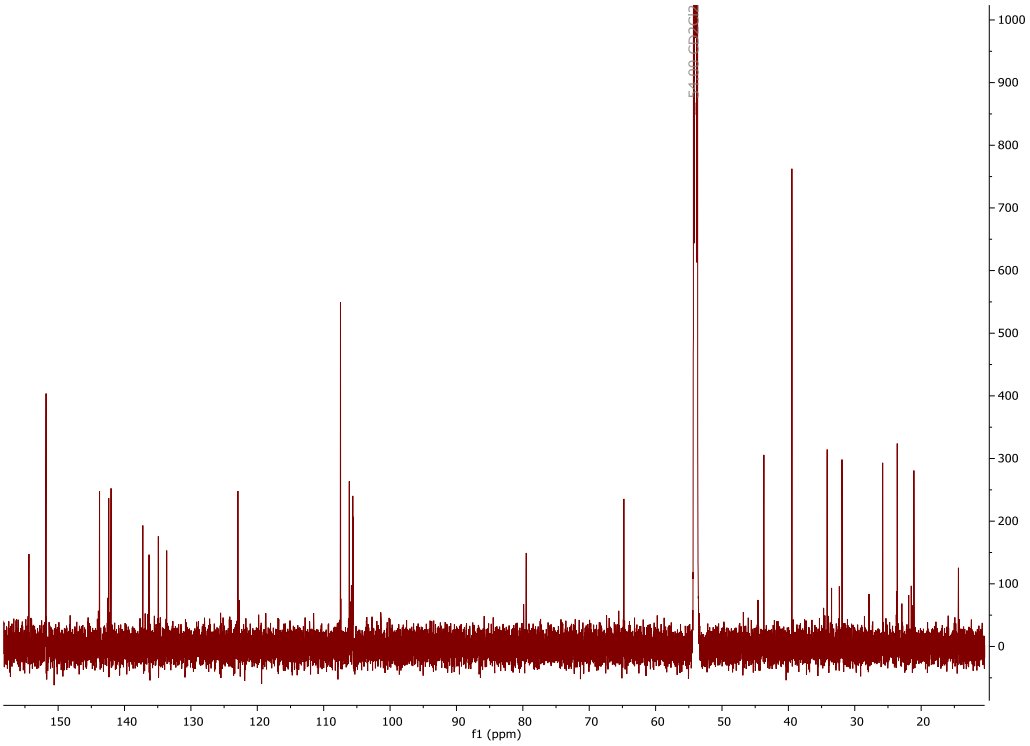
To a 4 dram vial charged with a stir pea, Mo_STp(NO)(DMAP)(η^2-*S*-α-pinene) (0.10g , 0.167 mmol) was combined with *R*-limonene (2 mL, 12 mmol) and HFIP (0.10g, 0.60 mmol). The vial was capped and allowed to mix for 4 h. The reaction solution was added to a 15 mL medium porosity fritted disk, 3/4 full of silica, and the excess limonene was eluted with ~40 mL of hexanes. The yellow band was then eluted with ~60 ml of ether. The yellow filtrate was evaporated *in vacuo* to dryness and dissolved in ~0.5 mL THF. The THF solution was added to 20 mL stirring pentane and then concentrated to 10 mL *in vacuo*. The yellow solid was then collected on a 15 mL fine porosity fritted disk and washed with pentane (3x10 mL). The solid was then desiccated yielding **9**B (0.0076 g, 0.013mmol, 8% recovered, ~5% yield)

^{1}H NMR (d_2-DCM, δ): 8.03 (1H, d, PzA3), 7.86 (1H, d, PzA5), 7.78 (3H, m, PzC5 and DMAP H2 and H6), 7.61 (1H, d, PzB5), 7.40 (1H, d, PzC3), 6.98 (1H, d, PzB3), 6.40 (2H, m, DMAP H3 and H5), 6.30 (1H, t, PzA4), 6.21 (1H, t, PzC4), 6.03 (1H, t, PzB4), 5.22 (1H, b, H6) 2.99 (6H, s, DMAP Methyls), 2.08 (1H, b, H5x), 2.03 (1H, d, J = 3.0, H9x proximal to NO), 1.87 (3H, s, 8 methyl), 1.79 (1H, d, *J* = 3.0, H9y proximal to TpC), 1.70 (1H, b, H5y), 1.38 (3H, s, 1 Methyl), 1.30 (1H, broad, H2x), 0.92 (1H, m, H4), 0.88 (1H, b, H2y), 0.75 (1H, m, H3x), -0.05 (1H, b, H3y), ^{13}C NMR (d_2-DCM, δ): 154.4 (DMAP 4), 151.8 (DMAP 2 and 6), 143.8 (PzA3), 142.4 (PzC3), 142.0 (PzB3), 137.3 (PzA5), 134.9 (PzC5), 133.7 (PzB5), 122.9 (C6), 122.7 (C1), 107.5 (DMAP 3 and 5), 106.1 (PzA4), 105.6 (PzC4), 105.6 (PzB4), 79.5 (C7), 64.8 (C9), 34.2 (C 5), 31.9 (C2), 25.8 (C3), 23.6 (C1 methyl), 21.1 (2C, C4 and C8).

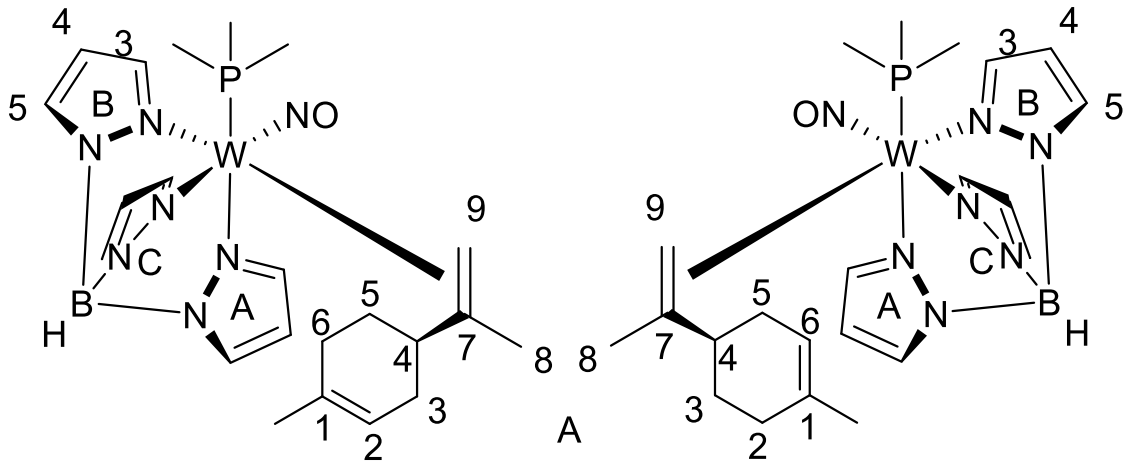
^{1}H NMR (CD_2CL_2) of S_{Mo},*R*-**21**A (unidentified side product present)



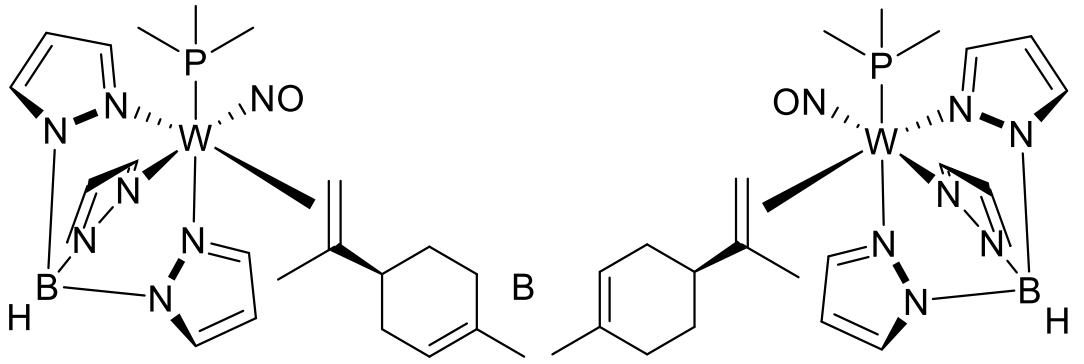
^{13}C NMR (CD_2CL_2) of S_{Mo},*R*-**21**A (unidentified side product present)



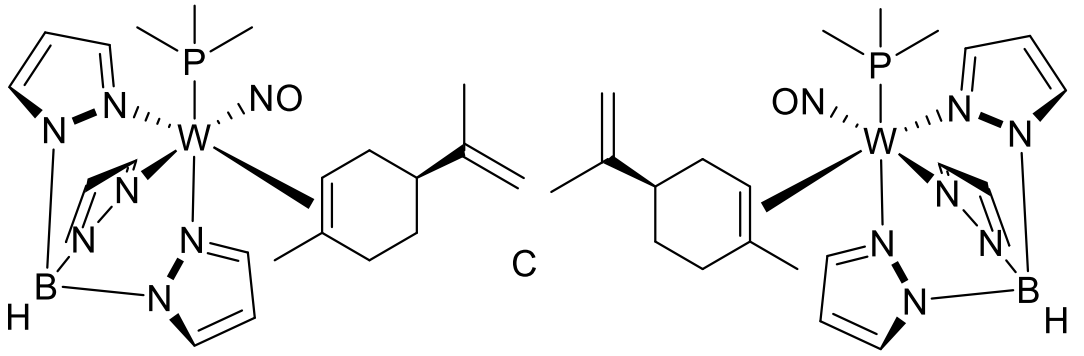
WTp(NO)(PMe$_3$)(η^2-*R*-limonene) (*R*,*R*)- **22A** and (*S*,*R*)- **22A**



A



B



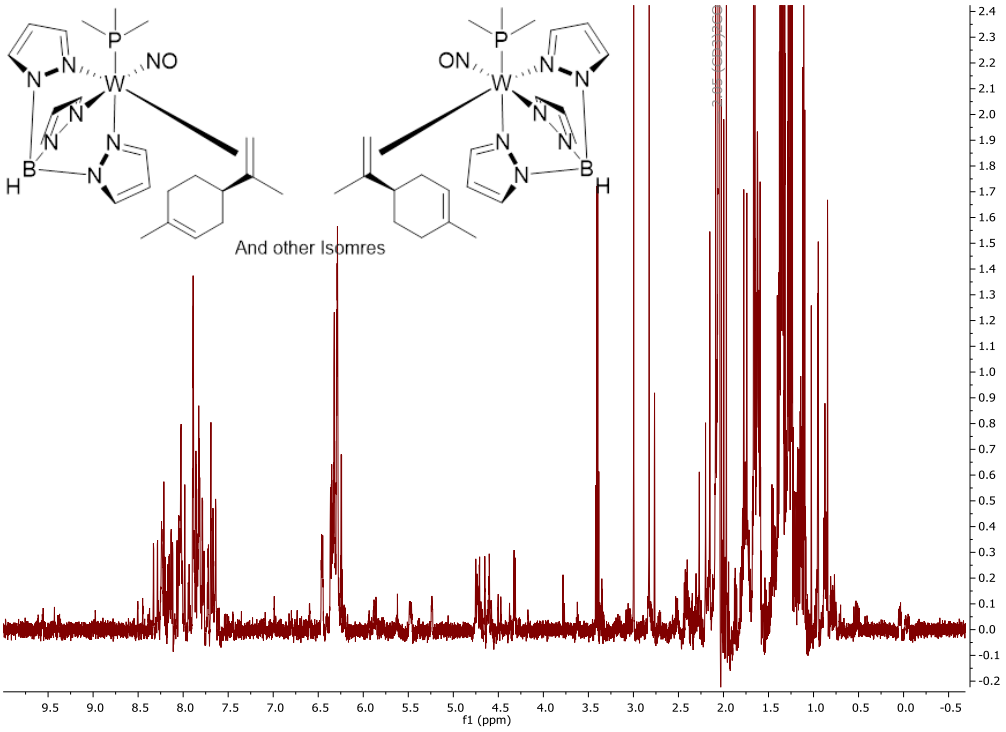
C

Among others

To a 4 dram vial charged with a stir pea, WTp(NO)(PMe_3)(η^2-benzene) (0.25 g, 0.42 mmol) was combined with (*R*)-Limonene (1 mL, 6.2 mmol) and 3 ml of THF. The vial was capped and allowed to mix 18 h. About 4 mL of ether was added to the reaction solution, and then loaded onto a 15 mL medium porosity fritted disk, ~3/4 full of silica. An orange band was eluted with ~25 mL ether. The filtrate was evaporated *in vacuo*

and then dissolved in about 2 mL DCM and added to 75 mL stirring pentane. The pentane solution was concentrated to about 10 mL and the solid precipitate was collected on 15 mL fine porosity fritted disk. The solid was dried to yield a yellow solid (0.065 g, 0.10 mmol, 24% yield). IR: υ_{NO}: 1544 cm^{-1} υ_{BH}: 2483 cm^{-1} (mix of diastereomers). CV: E_{pa}: 23 mV. ^{1}H NMR (d_6-acetone, δ): **W_S**: 8.13 (1H, d, PzA3) , 7.99 (1H, d, PzB3), 7.90 (1H, d PzC5), 7.87 (1H, d PzA5), 7.84 (1H, d PzB5), 7.64 (1H, d PzC3), 6.30 (1H, t PzA4), 6.28 (1H, t PzB4), 6.25 (1H, t PzC4), 5.25 (1H, bs, H6), 2.09 (1H, m, H5x), 2.01 (3H, s, H8), 1.82 (2H, m, H9x proximal to NO and H5y), 1.62 (1H, dd, *J* = 5.4, H9y proximal to PzC), 1.35 (9H, d, *J* = 8.1, PMe_3), 1.34 (3H, s, H1 methyl), 1.30 (1H m, H2x), 0.88 (1H, m, H2y), 0.80 (1H, m, H3x), 0.77 (1H, m, H4), 0.06 (1H, m, H3y). ^{1}H NMR (d_6-acetone, δ): **W_R**: 8.12 (1H, d ,PzA3), 7.98 (2H ,d, Pz3/5), 7.86 (1H, d, Pz3/5), 7.86 (2H,d, Pz3/5), 7.82 (1H,d, Pz3/5), 7.67 (1H,d,PzC3), 6.30 (1H, t, Pz4), 6.29 (1H, t, Pz4), 6.24, (1H, t, Pz4), 4.73 (1H, bs, H2), 2.13 (1H, m, H5x), 1.99 (3H, s, H8), 1.87 (1h, dd, *J* = 5.4, H9 proximal to NO), 1.74 (2H, m, H5y and H6), 1.62 (1H, d, *J* = 5.4, H 9 proximal to PzC) 1.59 (1H, m, H5y), 1.35 (4H, m, H3x and 1 methyl), 1.32 (9H, d, *J* = 8.2,PMe_3), 0.80 (1H, m, H4), -0.05 (1H, m, H3y). ^{13}C NMR (d_6-acetone, δ): Unambiguous assignment of Tp protons was not possible: Pz3: (144.4, 144.4, 144.0, 143.9, 143.3, 143.2), Pz5: (137.2, 137.1 (2C), 137.0, 136.5, 136.4),Pz4: (106.4 (2C), 106.4, 106.3, 106.3, 106.3). **W(S)**: 133.2(C1), 123.7 (C6), 58.5 (C7), 49.6 (C9), 44.7 (C4), 34.3 (C5), 32.3 (C2), 28.6 (C3), 23.6 (C1 methyl), 23.1 (C8), 13.6 (d, J = 27.9, PMe_3). **W(R)**: 132.5 (C1), 123.3 (C2), 59.1 (C7), 50.3 (C9), 43.7 (C4), 33.8 (C6), 32.6 (C5), 26.6 (C3), 23.5 (C1 methyl), 22.9 (C8),13.9 (d, J = 27.5, PMe_3). ^{31}P NMR (THF, δ) All isomers: -11.0, -11.9, -12.2, -12.8, -13.2, -13.5, -14.4, -14.6, -15.4, -15.4.

^{1}H NMR (d^6-Acetone) of **22**



Gaussian DFT of:

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31									
32									
33	34	1	35	1	36	1			
34	37	1	38	1	39	1			
35	40	1	41	1	42	1			
36									
37	43	2	54	1					
38									
39									
40	43	1	44	1	45	1			
41									
42									
43	46	1							
44									
45									
46	47	1	48	1	49	1			
47									
48									
49									
50	51	1	52	1	53	1			
51									
52									
53									
54									

55							
56	57	1	61	1	65	1	
57	58	1	59	1	60	1	
58							
59							
60							
61	62	1	63	1	64	1	
62							
63							
64							
65	66	1	67	1	68	1	
66							
67							
68							

(*R*,*R*)-**22B Output Coordinates**

Tag	Symbol	X	Y	Z
1	O	-1.10419	-0.96006	-2.76445
2	N	0.084435	1.922535	-0.29555
3	N	1.108536	2.78312	0.100908
4	N	1.633191	0.174546	1.66924
5	N	2.450865	1.297808	1.669205
6	N	2.146493	0.391087	-1.26484
7	N	2.965064	1.411448	-0.79425
8	N	-0.55355	-0.66766	-1.66524
9	C	0.760858	4.071143	-0.21272
10	C	-0.49479	4.057304	-0.82946
11	C	-0.86957	2.692448	-0.86834
12	C	3.162633	1.351596	2.832489
13	C	2.813045	0.244876	3.619261
14	C	1.857697	-0.45834	2.850993
15	C	3.954477	1.658048	-1.7047
16	C	3.786267	0.788757	-2.79205
17	C	2.636955	0.025198	-2.47606
18	B	2.511995	2.232507	0.445388
19	H	3.276473	3.131116	0.65246
20	H	1.425842	4.892344	0.008385
21	H	-1.05439	4.900789	-1.20177
22	H	-1.74563	2.23542	-1.29601
23	H	3.856886	2.156262	3.021665
24	H	3.185041	-0.00901	4.599404
25	H	1.318696	-1.35719	3.103208
26	H	4.68915	2.430041	-1.53155

27	H	4.389169	0.729437	-3.68459
28	H	2.132919	-0.72783	-3.06244
29	C	-1.64766	-0.19915	1.106863
30	C	-0.99905	-1.50305	1.187761
31	H	-0.54473	-1.79096	2.139757
32	H	-1.47485	-2.35187	0.693869
33	C	-3.03249	-0.15309	0.383354
34	C	-4.00346	-1.23313	0.954171
35	C	-3.77529	1.207059	0.469204
36	H	-2.88671	-0.38655	-0.68016
37	C	-5.42309	-1.09835	0.429458
38	H	-4.00335	-1.1827	2.057138
39	H	-3.63183	-2.23613	0.702186
40	C	-5.0207	1.211924	-0.44286
41	H	-4.10046	1.3767	1.506201
42	H	-3.1217	2.044953	0.210288
43	C	-5.89772	-0.01425	-0.2263
44	H	-5.61655	2.121285	-0.26192
45	H	-4.71433	1.25605	-1.50244
46	C	-7.30518	0.052265	-0.78442
47	H	-7.85671	-0.87955	-0.61037
48	H	-7.87552	0.877459	-0.33039
49	H	-7.28937	0.239145	-1.86943
50	C	-1.58618	0.685396	2.362604
51	H	-1.63073	1.754693	2.119788
52	H	-2.43454	0.46757	3.033899
53	H	-0.66909	0.517705	2.935636
54	H	-6.08302	-1.95482	0.585668
55	W	0.306395	-0.28178	-0.14607
56	P	1.494932	-2.63267	-0.22619
57	C	1.189375	-3.92314	1.115305
58	H	1.57327	-3.56321	2.074894
59	H	0.117524	-4.11118	1.212056
60	H	1.700984	-4.85682	0.854846
61	C	3.383306	-2.64223	-0.256
62	H	3.747472	-2.0526	-1.1005
63	H	3.757834	-2.19289	0.669537
64	H	3.75795	-3.66916	-0.33853
65	C	1.054348	-3.61268	-1.77135
66	H	-0.02894	-3.75884	-1.80433
67	H	1.338508	-3.04817	-2.66344
68	H	1.563159	-4.58368	-1.77198

(*R*,*R*)-**22C Input**

```
%mem=12GB
%nprocshared=12
#                opt    freq              b3lyp/sdd       geom=connectivity

Title            Card   Required

                 0      1
                        O          0.19235075     1.55220907          11.33583384
                        N          3.68505675    -0.09460593          12.96964384
                        N          4.44012675    -1.29605293          13.15369384
                        N          2.11435775    -1.34391893          15.22812384
                        N          3.09752775    -2.36169993          15.02984184
                        N          1.62473275    -1.86919493          12.37477884
                        N          2.59327975    -2.88689993          12.61458384
                        N          0.99882275     0.96863407          12.17517784
                        C          5.73437575    -1.09736993          12.67618084
                        C          5.83980975     0.20783907          12.19287884
                        C          4.56706575     0.79764907          12.38433884
                        C          3.32208375    -3.03139293          16.22853084
                        C          2.50431675    -2.47202593          17.21378484
                        C          1.77991375    -1.44109293          16.57180684
                        C          2.35319975    -3.96034093          11.76250484
                        C          1.23604175    -3.66443893          10.97562884
                        C          0.81373475    -2.37345493          11.37274384
                        B          3.74507275    -2.60534893          13.63000984
                        H          4.50525875    -3.50001293          13.67462984
                        H          6.46752375    -1.91018793          12.72509984
                        H          6.72222375     0.67994907          11.75686984
                        H          4.22756975     1.81125107          12.14505684
                        H          4.04739275    -3.85174893          16.27370684
                        H          2.43958075    -2.76651493          18.26300484
                        H          1.04087675    -0.75454993          16.99914884
                        H          3.00247475    -4.84281793          11.79045984
                        H          0.78614975    -4.29654293          10.20764984
                        H         -0.02088925    -1.77064793          10.99647084
                        C          2.30321675     1.75819907          14.56530684
                        C          0.89648975     1.44832507          14.93839484
                        H          0.77098275     1.03921707          15.95201984
                        C          3.39168775     1.58551607          15.66584484
                        H          3.20742475     0.70073607          16.29048984
                        H          4.39411975     1.48201407          15.21917884
                        C         -0.23048625     2.46257307          14.58832484
```

H	-0.61091625	2.27205707	13.57291184
C	2.49044175	3.12298507	13.82707284
H	3.56093175	3.38944607	13.78414484
H	2.11844975	3.07653707	12.79149884
H	-1.08487525	2.30619207	15.26879684
C	0.16651975	4.00359607	14.64942184
C	1.72235275	4.24959607	14.59077084
H	-0.19147325	4.40838507	15.61315884
H	1.92068275	5.23130507	14.12605784
H	2.10803475	4.29574107	15.62347384
C	-0.59350625	4.76857207	13.52915284
C	-0.16129825	4.52678907	12.06970484
H	0.83112375	4.97268607	11.88832884
H	-0.08790425	3.44280307	11.82679584
H	-0.87538725	4.99951507	11.37924484
C	-1.60581625	5.59703207	13.82812584
H	-2.16823125	6.12960107	13.05318484
H	-1.91745525	5.77991907	14.86240384
H	3.41755675	2.46615007	16.33170384
W	1.59122375	0.04557507	13.49259684
P	-0.50267325	-0.64536993	13.69809084
C	-1.08786696	-1.93084063	14.8459207
H	-1.47505053	-2.75772256	14.28801823
H	-0.27341339	-2.26209554	15.45570392
H	-1.85917931	-1.52844722	15.46886275
C	-1.72766337	0.07507953	14.83508326
H	-1.43185407	-0.11562042	15.84554374
H	-1.78608446	1.13124419	14.67382821
H	-2.68523782	-0.36682443	14.65432911
C	-1.78027275	0.02009558	12.58575313
H	-1.34608372	0.7597336	11.94597545
H	-2.18402828	-0.77285953	11.99152786
H	-2.56182215	0.46464774	13.16579961

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3	9	1	18	1
4	5	1	14	1
5	12	1	18	1
6	7	1	17	1
7	15	1	18	1
8	55	1		
9	10	1.5	20	1
10	11	1.5	21	1

11	22	1							
12	13	1.5	23	1					
13	14	1.5	24	1					
14	25	1							
15	16	1.5	26	1					
16	17	1.5	27	1					
17	28	1							
18	19	1							
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22									
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25									
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27									
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29	30	1	32	1	37	1	55	1	
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32	33	1	34	1	54	1			
33									
34									
35	36	1	40	1	41	1			
36									
37	38	1	39	1	42	1			
38									
39									
40									
41	42	1	43	1	46	1			
42	44	1	45	1					
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46	47	1	51	2					
47	48	1	49	1	50	1			
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50									
51	52	1	53	1					
52									
53									
54									

55							
56	57	1	61	1	65	1	
57	58	1	59	1	60	1	
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59							
60							
61	62	1	63	1	64	1	
62							
63							
64							
65	66	1	67	1	68	1	
66							
67							
68							

(*R*,*R*)-**22C Output Coordinates**

Tag	Symbol	X	Y	Z
1	O	-0.98375	-0.27951	-3.02504
2	N	1.329815	1.869076	-0.54925
3	N	2.641427	2.018527	-0.10253
4	N	1.363619	-0.07159	1.747369
5	N	2.693582	0.331837	1.784403
6	N	2.177565	-0.72801	-1.06046
7	N	3.39867	-0.29916	-0.55525
8	N	-0.52383	-0.13144	-1.85535
9	C	3.105109	3.253769	-0.46765
10	C	2.091366	3.922087	-1.16457
11	C	1.003984	3.016412	-1.19069
12	C	3.178081	0.20287	3.053699
13	C	2.154577	-0.29399	3.873716
14	C	1.043807	-0.44773	3.013629
15	C	4.411625	-0.8033	-1.32288
16	C	3.849825	-1.5756	-2.34935
17	C	2.451004	-1.48795	-2.15078
18	B	3.413229	0.826209	0.509344
19	H	4.538497	1.142837	0.770889
20	H	4.108017	3.564788	-0.21682
21	H	2.130131	4.911507	-1.59224
22	H	0.028066	3.130598	-1.63285
23	H	4.197693	0.469071	3.28783
24	H	2.20256	-0.50377	4.930672
25	H	0.046093	-0.78088	3.250157
26	H	5.443126	-0.57129	-1.10411

27	H	4.369768	-2.10511	-3.13217
28	H	1.647358	-1.89474	-2.74593
29	C	-1.34061	1.436842	0.573541
30	C	-1.75805	0.069575	0.888274
31	H	-1.66862	-0.2206	1.942657
32	C	-0.90023	2.363186	1.715973
33	H	-0.38166	1.826846	2.517772
34	H	-0.23162	3.159032	1.359999
35	C	-3.08374	-0.38228	0.260362
36	H	-2.98169	-0.48476	-0.82647
37	C	-2.2807	2.149202	-0.42104
38	H	-1.98834	3.202401	-0.54427
39	H	-2.22896	1.685239	-1.41225
40	H	-3.40291	-1.36131	0.648032
41	C	-4.19354	0.6719	0.581603
42	C	-3.75892	2.097224	0.074397
43	H	-4.26712	0.716755	1.678481
44	H	-4.41576	2.428636	-0.74162
45	H	-3.90217	2.816163	0.892081
46	C	-5.56847	0.263335	0.055456
47	C	-5.69617	-0.02178	-1.43252
48	H	-5.29628	0.80396	-2.03681
49	H	-5.1273	-0.91856	-1.71549
50	H	-6.74185	-0.18126	-1.71919
51	C	-6.63381	0.156512	0.882893
52	H	-7.62015	-0.12343	0.517203
53	H	-6.54799	0.350892	1.950836
54	H	-1.77944	2.854683	2.166294
55	W	0.208989	-0.02192	-0.22841
56	P	-0.25229	-2.58327	0.165303
57	C	1.24125	-3.74101	0.169093
58	H	1.74802	-3.70997	-0.79782
59	H	1.947226	-3.4169	0.940384
60	H	0.919278	-4.76793	0.378079
61	C	-1.09662	-3.18399	1.742872
62	H	-0.42317	-3.04819	2.594686
63	H	-2.01443	-2.61818	1.914697
64	H	-1.33833	-4.2491	1.650303
65	C	-1.34114	-3.34829	-1.16487
66	H	-2.35278	-2.94536	-1.07195
67	H	-0.962	-3.07375	-2.15306
68	H	-1.36793	-4.43926	-1.06135

(*S*,*R*)-**22A Input**

```
%mem=12GB
%nprocshared=12
#                opt    freq            b3lyp/sdd       geom=connectivity

Title            Card   Required

                 0      1
                        O       1.70677906    7.77912041    5.98687462
                        N       4.74015606    8.94615041    8.54089562
                        N       5.08637306    9.73634241    9.68391862
                        N       3.66365506    7.15922641   10.77275762
                        N       4.16024206    8.25493941   11.54418962
                        N       2.15608406    9.29018841    9.45495662
                        N       2.75134306   10.06102541   10.49624862
                        N       2.50472806    7.75922441    7.00700862
                        C       6.05326006   10.67078341    9.31260662
                        C       6.35119606   10.49861141    7.96037462
                        C       5.52484206    9.43912441    7.51197762
                        C       4.50076106    7.81018441   12.81817462
                        C       4.24101406    6.43976841   12.89792562
                        C       3.73217306    6.07053341   11.63099662
                        C       1.89881406   11.10573141   10.83978262
                        C       0.75041506   11.02421341   10.04652362
                        C       0.93973206    9.90191641    9.20532662
                        B       4.19885606    9.70233441   10.96480262
                        H       4.58825806   10.46278841   11.77133162
                        H       6.44306906   11.37896041   10.05227462
                        H       7.07294506   11.06295941    7.36686462
                        H       5.44783206    8.99239741    6.51466062
                        H       4.89875106    8.51299641   13.55889262
                        H       4.40168106    5.78672741   13.75784962
                        H       3.41910506    5.08130841   11.27977462
                        H       2.18681306   11.81886741   11.62049862
                        H      -0.11187394   11.69336341   10.06669162
                        H       0.28010906    9.49822641    8.42850462
                        C       4.66479606    6.10147241    7.93989662
                        C       3.38042106    5.43224941    8.28249162
                        H       3.37376206    4.79815541    9.17877262
                        C       5.88929806    5.73140641    8.86325562
                        C       7.20318906    6.52606041    8.55786762
                        C       6.23081506    4.19654141    8.78932462
                        H       5.61829106    5.94419141    9.91160362
```

C	8.29014406	6.23746341	9.63996462
H	7.59263206	6.23012141	7.56989362
H	6.99965906	7.60767941	8.52703062
C	7.51777906	3.83895841	9.54865962
H	6.33585006	3.88753741	7.73185462
H	5.39124006	3.60976541	9.20277962
C	8.44378206	4.73084741	9.93419962
H	9.26347506	6.64623441	9.31095062
H	2.81863306	4.96457441	7.46325162
C	5.04329406	6.08498841	6.42834862
H	4.14433106	6.20267241	5.80540262
H	5.52715806	5.13368441	6.14403762
H	5.74379106	6.89273741	6.16489062
C	9.70791506	4.32133141	10.70698262
H	10.61664806	4.58971341	10.14101162
H	9.72256006	3.23746041	10.89524462
H	9.75941406	4.84493241	11.67728162
H	8.02979006	6.76361341	10.57883762
H	7.66519206	2.77206041	9.77319762
W	3.13576506	7.49899341	8.58166662
P	1.10185806	6.75333941	9.04820862
C	0.72074519	4.9745694	9.1041573
H	0.98222246	4.52421233	8.16943373
H	1.28112186	4.51431916	9.89095314
H	-0.32516957	4.83941678	9.28497791
C	0.47541393	6.35733457	10.71048054
H	1.24934276	6.51961444	11.43131299
H	-0.3598859	6.98681292	10.93615995
H	0.16849101	5.33276037	10.741238
C	-0.10862181	6.54504274	7.70517066
H	-0.95372461	7.17601101	7.88567083
H	0.3434438	6.81237382	6.772931
H	-0.42724009	5.52428327	7.66732223

1	8	1		
2	3	1	11	1
3	9	1	18	1
4	5	1	14	1
5	12	1	18	1
6	7	1	17	1
7	15	1	18	1
8	55	1		
9	10	1.5	20	1
10	11	1.5	21	1

11	22	1							
12	13	1.5	23	1					
13	14	1.5	24	1					
14	25	1							
15	16	1.5	26	1					
16	17	1.5	27	1					
17	28	1							
18	19	1							
19									
20									
21									
22									
23									
24									
25									
26									
27									
28									
29	30	1	32	1	45	1	55	1	
30	31	1	44	1	55	1			
31									
32	33	1	34	1	35	1			
33	36	1	37	1	38	1			
34	39	1	40	1	41	1			
35									
36	42	1	43	1	53	1			
37									
38									
39	42	2	54	1					
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41									
42	49	1							
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45	46	1	47	1	48	1			
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49	50	1	51	1	52	1			
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53									
54									

55							
56	57	1	61	1	65	1	
57	58	1	59	1	60	1	
58							
59							
60							
61	62	1	63	1	64	1	
62							
63							
64							
65	66	1	67	1	68	1	
66							
67							
68							

(*S*,*R*)-**22A Output Coordinates**

Tag	Symbol	X	Y	Z
1	O	-2.05251	-0.87281	-3.16408
2	N	0.147387	1.620681	-1.07028
3	N	0.187279	2.68405	-0.16858
4	N	0.076326	0.147317	1.6071
5	N	0.051517	1.460565	2.061583
6	N	-2.29553	1.122111	0.092305
7	N	-2.02013	2.244779	0.864244
8	N	-1.45329	-0.66151	-2.07259
9	C	0.643806	3.803989	-0.81424
10	C	0.89795	3.476083	-2.1505
11	C	0.563593	2.104751	-2.26425
12	C	0.540248	1.515985	3.335024
13	C	0.895643	0.219147	3.732928
14	C	0.58737	-0.59813	2.621815
15	C	-3.15379	2.997528	0.99451
16	C	-4.19237	2.362785	0.298452
17	C	-3.60417	1.201846	-0.25826
18	B	-0.54107	2.58999	1.193142
19	H	-0.47563	3.633706	1.77718
20	H	0.740848	4.743127	-0.2907
21	H	1.264678	4.126665	-2.92871
22	H	0.599875	1.460976	-3.12763
23	H	0.601861	2.454261	3.865264
24	H	1.321317	-0.08587	4.675908
25	H	0.732157	-1.66	2.502091
26	H	-3.1449	3.924192	1.548478

27	H	-5.21228	2.697622	0.192207
28	H	-4.04077	0.457864	-0.90675
29	C	1.37424	-1.1829	-1.14031
30	C	0.547273	-2.2128	-0.52041
31	H	0.859596	-2.59296	0.456439
32	C	2.658441	-0.78796	-0.35453
33	C	3.416435	0.450581	-0.8916
34	C	3.660063	-1.98193	-0.2876
35	H	2.378408	-0.56005	0.682642
36	C	4.568294	0.853485	0.056461
37	H	3.834946	0.222645	-1.88335
38	H	2.735829	1.297692	-1.0148
39	C	5.000991	-1.60128	0.315241
40	H	3.817382	-2.39553	-1.29709
41	H	3.217095	-2.79982	0.300344
42	C	5.425569	-0.32829	0.490154
43	H	5.207816	1.606873	-0.43119
44	H	0.132004	-3.00082	-1.15356
45	C	1.581984	-1.27868	-2.65836
46	H	0.685512	-1.65982	-3.15799
47	H	2.415515	-1.95947	-2.90089
48	H	1.830053	-0.311	-3.11255
49	C	6.760456	0.005351	1.126458
50	H	7.406682	0.557697	0.426858
51	H	7.297177	-0.89637	1.44535
52	H	6.627214	0.651546	2.008259
53	H	4.156849	1.347782	0.954074
54	H	5.650099	-2.42443	0.622911
55	W	-0.68629	-0.34787	-0.48785
56	P	-2.30055	-2.08676	0.657355
57	C	-1.62926	-3.67794	1.415152
58	H	-1.05729	-4.23081	0.66619
59	H	-0.9727	-3.44363	2.258842
60	H	-2.45967	-4.29834	1.771347
61	C	-3.35744	-1.46384	2.093009
62	H	-2.69992	-1.14267	2.907406
63	H	-3.95643	-0.60824	1.772362
64	H	-4.01977	-2.25969	2.45308
65	C	-3.58637	-2.77562	-0.53224
66	H	-4.20713	-1.96373	-0.92055
67	H	-3.07499	-3.23745	-1.3814
68	H	-4.2214	-3.51481	-0.03021

(*S*,*R*)-**22B Input**

```
%mem=12GB
%nprocshared=12
#                opt    freq              b3lyp/sdd       geom=connectivity

Title            Card   Required

                 0      1
                    O       -10.77920828    -3.12173899             0
                    N       -10.36784528     0.38568901       2.077549
                    N       -10.94725128     1.65056201       2.193221
                    N       -12.55278828    -0.16483999       4.078303
                    N       -12.79712028     1.18453401        3.84457
                    N       -12.99458928    -0.22468299       1.122961
                    N       -13.23525828     1.11981301       1.364491
                    N       -11.06870728    -2.41261299       0.998534
                    C       -10.02745628     2.60959601       1.865535
                    C        -8.82835928     1.97645501       1.523499
                    C        -9.09207128     0.59397501       1.670517
                    C       -13.36616928     1.75149201        4.94823
                    C       -13.50972128     0.76268401       5.931864
                    C       -12.98968028    -0.41243999       5.341713
                    C       -14.09562928     1.60751201       0.420776
                    C       -14.42927828     0.56443201      -0.455344
                    C       -13.71298728    -0.56012599       0.023241
                    B       -12.44781828     1.83561101       2.486189
                    H       -12.72885628     3.00123101       2.512078
                    H       -10.28729928     3.65701901       1.894054
                    H        -7.90375928     2.43837101       1.214777
                    H        -8.43596228    -0.23892499       1.500205
                    H       -13.62411528     2.79972101       4.962754
                    H       -13.91961028     0.87496101       6.923443
                    H       -12.91742128    -1.40049999       5.766707
                    H       -14.40056528     2.64328901       0.428053
                    H       -15.07943428     0.61206901      -1.314906
                    H       -13.66723528    -1.56455499      -0.369371
                    C        -9.79452728    -2.26378999       3.667972
                    C       -11.04714628    -2.87982699        4.01093
                    H       -11.54181328    -2.60413199       4.942466
                    H       -11.21452328    -3.92451199       3.742232
                    C        -8.78581128    -3.22480799       2.985476
                    C        -8.04676928    -4.08766199       4.051775
                    C        -7.73295228    -2.59141499       2.045801
```

H	-9.37343428	-3.92087599	2.368881
C	-7.25954128	-5.23910299	3.390837
H	-7.34508828	-3.45605099	4.616589
H	-8.77381828	-4.49197999	4.769876
C	-6.63742628	-3.56223299	1.637716
H	-7.26850928	-1.71411399	2.527617
H	-8.23629728	-2.23587599	1.136214
C	-6.41462228	-4.76438899	2.215847
H	-7.95795328	-6.01948599	3.042204
C	-5.33623028	-5.71381499	1.732876
H	-5.76730528	-6.68551899	1.445344
H	-4.60024228	-5.91745799	2.52617
H	-4.79970628	-5.31275099	0.86458
C	-9.19221728	-1.22909399	4.621643
H	-8.48969828	-0.55367199	4.118002
H	-8.64120028	-1.72054699	5.440202
H	-9.97097828	-0.60644599	5.076026
H	-6.61001228	-5.72764499	4.135273
H	-6.00736928	-3.25166699	0.801464
W	-11.68946735	-1.3374096	2.56652463
P	-13.45317028	-2.76435099	2.509835
C	-13.40279326	-4.34081237	2.00463196
H	-14.0579515	-4.46845339	1.16834525
H	-12.40328349	-4.59113081	1.71615164
H	-13.71459839	-4.98133679	2.80300908
C	-14.00894597	-3.93524279	3.78753833
H	-13.28147144	-4.71173015	3.90044617
H	-14.12687537	-3.41904	4.71733795
H	-14.94523825	-4.36333937	3.49600775
C	-14.75923692	-1.88206772	2.0011459
H	-14.53737678	-0.83833721	2.0805481
H	-14.97780681	-2.12371691	0.98196345
H	-15.60632065	-2.11414379	2.61228405

1	8	1.5		
2	3	1	11	1.5
3	9	1.5	18	1
4	5	1	14	1.5
5	12	1.5	18	1
6	7	1	17	1.5
7	15	1.5	18	1
8	55	1		
9	10	1.5	20	1
10	11	1.5	21	1

11	22	1				
12	13	1.5	23	1		
13	14	1.5	24	1		
14	25	1				
15	16	1.5	26	1		
16	17	1.5	27	1		
17	28	1				
18	19	1				
19						
20						
21						
22						
23						
24						
25						
26						
27						
28						
29	30	1.5	33	1	49	1
30	31	1	32	1		
31						
32						
33	34	1	35	1	36	1
34	37	1	38	1	39	1
35	40	1	41	1	42	1
36						
37	43	1	44	1	53	1
38						
39						
40	43	2	54	1		
41						
42						
43	45	1				
44						
45	46	1	47	1	48	1
46						
47						
48						
49	50	1	51	1	52	1
50						
51						
52						
53						
54						

55						
56	57	1	61	1	65	1
57	58	1	59	1	60	1
58						
59						
60						
61	62	1	63	1	64	1
62						
63						
64						
65	66	1	67	1	68	1
66						
67						
68						

(*S*,*R*)-**22B Output Coordinates**

Tag	Symbol	X	Y	Z
1	O	1.254968	-0.92072	-2.62816
2	N	-0.43371	2.018299	-0.19476
3	N	-1.66378	2.654939	-0.00786
4	N	-1.81042	0.089477	1.615176
5	N	-2.85987	0.987428	1.449294
6	N	-2.06475	0.116676	-1.40489
7	N	-3.11989	0.953451	-1.06562
8	N	0.686145	-0.58669	-1.54774
9	C	-1.51112	4.002076	-0.1852
10	C	-0.17249	4.262371	-0.49781
11	C	0.456415	2.996301	-0.49242
12	C	-3.66232	0.972419	2.552478
13	C	-3.14151	0.048158	3.468603
14	C	-1.98893	-0.47395	2.840549
15	C	-4.00425	1.016439	-2.10591
16	C	-3.52372	0.209249	-3.14698
17	C	-2.303	-0.32201	-2.66653
18	B	-2.97236	1.856083	0.180922
19	H	-3.90842	2.598159	0.273947
20	H	-2.35226	4.671118	-0.08338
21	H	0.282901	5.218948	-0.69986
22	H	1.48323	2.751658	-0.68892
23	H	-4.53054	1.610839	2.615161
24	H	-3.52957	-0.2027	4.443235
25	H	-1.29271	-1.20304	3.218866
26	H	-4.88989	1.631221	-2.04656

27	H	-3.97664	0.043661	-4.11185
28	H	-1.58351	-0.95172	-3.16792
29	C	1.632325	0.163709	1.160731
30	C	1.048514	-1.13818	1.468003
31	H	0.565387	-1.26325	2.439695
32	H	1.614923	-2.02759	1.180842
33	C	3.017287	0.056991	0.461176
34	C	4.143549	-0.25011	1.491447
35	C	3.461151	1.25832	-0.40671
36	H	2.962147	-0.80844	-0.21608
37	C	5.45368	-0.65372	0.78175
38	H	4.333822	0.640822	2.108312
39	H	3.820873	-1.0531	2.16913
40	C	4.910068	1.16268	-0.85565
41	H	3.32558	2.202212	0.149534
42	H	2.823211	1.309619	-1.3003
43	C	5.820192	0.301065	-0.34715
44	H	5.360648	-1.67527	0.374267
45	C	7.241111	0.21581	-0.86791
46	H	7.470027	-0.80151	-1.22176
47	H	7.970266	0.445843	-0.07558
48	H	7.412012	0.908766	-1.70049
49	C	1.526353	1.254015	2.236715
50	H	1.71368	2.258207	1.835848
51	H	2.255938	1.084982	3.044894
52	H	0.529551	1.270873	2.693815
53	H	6.280466	-0.69447	1.509391
54	H	5.210508	1.836966	-1.66041
55	W	-0.27491	-0.22151	-0.08507
56	P	-0.97142	-2.74917	-0.10968
57	C	0.336842	-3.80881	-0.94832
58	H	0.611697	-3.35403	-1.9045
59	H	1.231094	-3.84039	-0.31877
60	H	-0.03383	-4.82836	-1.10506
61	C	-1.23244	-3.67322	1.513623
62	H	-0.36812	-3.52271	2.165559
63	H	-2.13133	-3.29919	2.012729
64	H	-1.35232	-4.74441	1.314958
65	C	-2.53644	-3.27013	-1.03036
66	H	-3.39401	-2.70769	-0.64896
67	H	-2.43096	-3.06007	-2.0974
68	H	-2.71112	-4.34347	-0.89138

(*S*,*R*)-**22C Input**

```
%mem=12GB
%nprocshared=12
#                opt    freq            b3lyp/sdd     geom=connectivity

Title            Card   Required

                 0      1
                        O       8.83912815    4.6094903     6.71606239
                        N       5.14231815    3.7704493     8.51587639
                        N       4.18931015    2.7288183     8.75323839
                        N       6.50173315    2.3355933    10.79598139
                        N       5.35040315    1.5020733    10.64775039
                        N       6.83395715    1.6208053     7.95673639
                        N       5.70136015    0.8066583     8.24822439
                        N       7.96982415    4.2547473     7.61269039
                        C       2.93767815    3.1436663     8.30306039
                        C       3.05213715    4.4338743     7.78347439
                        C       4.41451115    4.7902663     7.92578539
                        C       5.03334315    0.9220983    11.87202039
                        C       5.95633515    1.3582913    12.82569239
                        C       6.83959715    2.2221843    12.13784039
                        C       5.72391515   -0.3219057     7.43461239
                        C       6.86012815   -0.2633187     6.62207739
                        C       7.51886915    0.9417523     6.96394339
                        B       4.64255515    1.3314273     9.26725039
                        H       3.73190615    0.5944233     9.35633239
                        H       2.07348615    2.4763853     8.39482639
                        H       2.25589015    5.0454543     7.35507739
                        H       4.91847615    5.7216283     7.64740139
                        H       4.17480715    0.2461103    11.95543639
                        H       5.98865515    1.0909293    13.88360839
                        H       7.69887115    2.7756383    12.53173139
                        H       4.92501715   -1.0688157     7.50481739
                        H       7.17141515   -0.9935897     5.87273239
                        H       8.44090015    1.3690413     6.55296539
                        C       6.90936415    5.4165943     9.98280639
                        C       8.21544815    4.8205323    10.38135239
                        H       8.20640615    4.3947353    11.39649639
                        C       5.81742315    5.5131793    11.09025339
                        H       5.81665915    4.6280673    11.74207939
                        H       4.81068215    5.6103113    10.65182039
                        C       9.56534015    5.5654323    10.16023939
```

H	10.36741515	4.8570173	9.88073139
C	6.94299715	6.7380963	9.12797339
H	6.06316515	7.3572273	9.37723139
H	6.88538915	6.5197953	8.04765739
H	9.87223015	6.0179253	11.12193139
C	9.49837115	6.7026313	9.07948539
C	8.23490715	7.5840763	9.35672939
H	9.37672315	6.2260303	8.08667039
H	8.22766415	8.4582513	8.68171639
H	8.26214115	7.9585653	10.39426339
C	10.80987715	7.5311523	9.04278639
C	11.63722215	7.4687533	7.98878739
H	11.41394315	6.8406273	7.11920039
H	12.56961015	8.0433743	7.94643939
C	11.13132515	8.4308853	10.25055639
H	10.36925415	9.2199983	10.36288839
H	11.14387015	7.8484033	11.18641239
H	12.11263415	8.9121023	10.12626739
H	5.98578815	6.3997753	11.72759239
W	7.24718715	3.5393963	8.99244939
P	9.17206715	2.4744513	9.20180539
C	9.51159909	1.119251	10.36823165
H	8.64802244	0.94708415	10.97609179
H	9.74677058	0.22944726	9.8224811
H	10.33961912	1.38448332	10.9918779
C	10.55332337	2.88763146	8.09103385
H	10.80819914	2.02978943	7.50448002
H	10.26318308	3.68881047	7.44386246
H	11.40064479	3.18720799	8.67172335
C	10.60477919	2.82926518	10.2666262
H	10.30724341	2.7793382	11.29321266
H	11.37332095	2.10790824	10.08253999
H	10.97608157	3.80914842	10.05014669

1	8	1		
2	3	1	11	1
3	9	1	18	1
4	5	1	14	1
5	12	1	18	1
6	7	1	17	1
7	15	1	18	1
8	55	1		
9	10	1.5	20	1
10	11	1.5	21	1

11	22	1							
12	13	1.5	23	1					
13	14	1.5	24	1					
14	25	1							
15	16	1.5	26	1					
16	17	1.5	27	1					
17	28	1							
18	19	1							
19									
20									
21									
22									
23									
24									
25									
26									
27									
28									
29	30	1	32	1	37	1	55	1	
30	31	1	35	1	55	1			
31									
32	33	1	34	1	54	1			
33									
34									
35	36	1	40	1	41	1			
36									
37	38	1	39	1	42	1			
38									
39									
40									
41	42	1	43	1	46	1			
42	44	1	45	1					
43									
44									
45									
46	47	2	50	1					
47	48	1	49	1					
48									
49									
50	51	1	52	1	53	1			
51									
52									
53									
54									

55							
56	57	1	61	1	65	1	
57	58	1	59	1	60	1	
58							
59							
60							
61	62	1	63	1	64	1	
62							
63							
64							
65	66	1	67	1	68	1	
66							
67							
68							

(*S*,*R*)-**22C Output Coordinates**

Tag	Symbol	X	Y	Z
1	O	1.332934	-0.03281	-2.82161
2	N	-1.37225	1.861382	-0.51707
3	N	-2.73625	1.87485	-0.22559
4	N	-1.50844	-0.1846	1.678826
5	N	-2.86473	0.099945	1.570543
6	N	-1.93784	-0.76867	-1.23803
7	N	-3.24045	-0.46913	-0.86078
8	N	0.764021	0.039885	-1.69313
9	C	-3.26373	3.0869	-0.5807
10	C	-2.24076	3.878769	-1.11488
11	C	-1.08108	3.070336	-1.05498
12	C	-3.48058	-0.12878	2.766672
13	C	-2.51884	-0.57323	3.685531
14	C	-1.30605	-0.59047	2.960383
15	C	-4.11304	-1.01565	-1.76084
16	C	-3.37367	-1.68574	-2.74566
17	C	-2.01881	-1.49246	-2.38304
18	B	-3.47069	0.596351	0.238747
19	H	-4.64111	0.811041	0.377012
20	H	-4.31293	3.296771	-0.4373
21	H	-2.3181	4.885663	-1.49367
22	H	-0.07632	3.298155	-1.36857
23	H	-4.54041	0.038182	2.8857
24	H	-2.67031	-0.83507	4.720888
25	H	-0.31718	-0.84808	3.304124
26	H	-5.1789	-0.88035	-1.65441

27	H	-3.75371	-2.21547	-3.60506
28	H	-1.12061	-1.79955	-2.89732
29	C	1.211576	1.573842	0.860151
30	C	1.668532	0.227174	1.205609
31	H	1.392184	-0.08344	2.22094
32	C	0.572314	2.418824	1.974064
33	H	-0.00578	1.816754	2.683406
34	H	-0.0956	3.191696	1.570272
35	C	3.092979	-0.2555	0.864614
36	H	3.114269	-1.30996	0.556383
37	C	2.115181	2.43811	-0.06173
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53	H	7.245958	0.168102	0.598644
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55	W	-0.13948	0.038553	-0.15102
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65	C	1.179391	-3.12882	1.827085
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67	H	1.443629	-4.18757	1.723398
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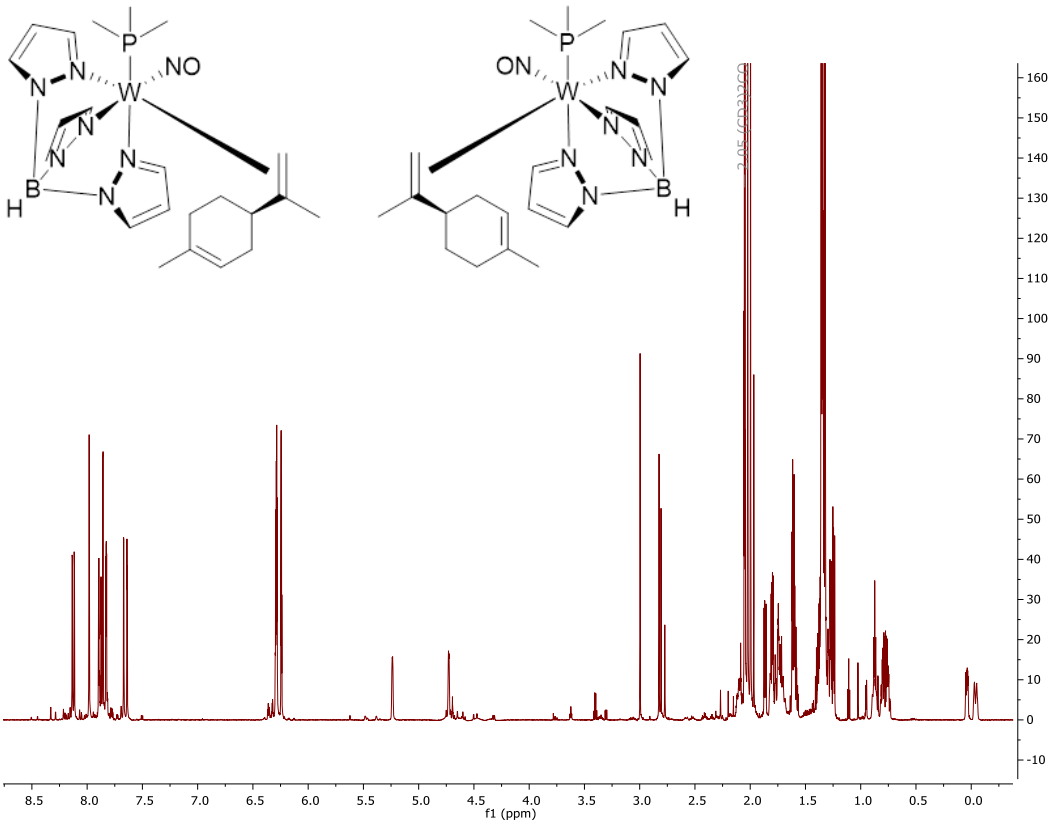
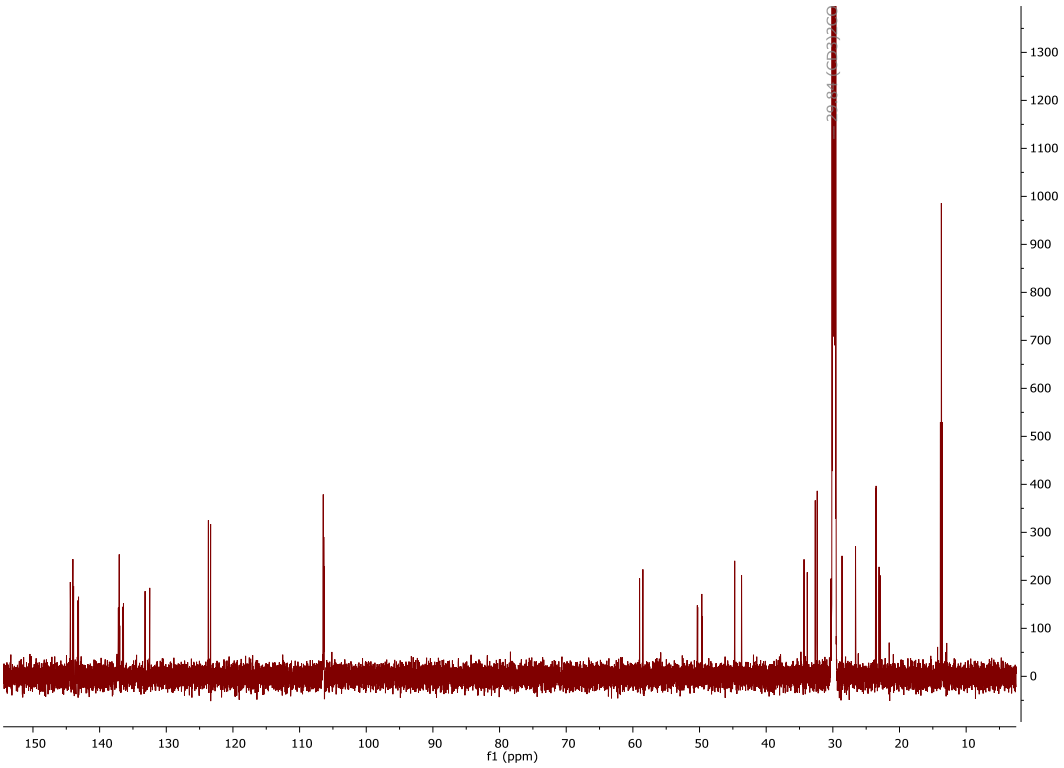
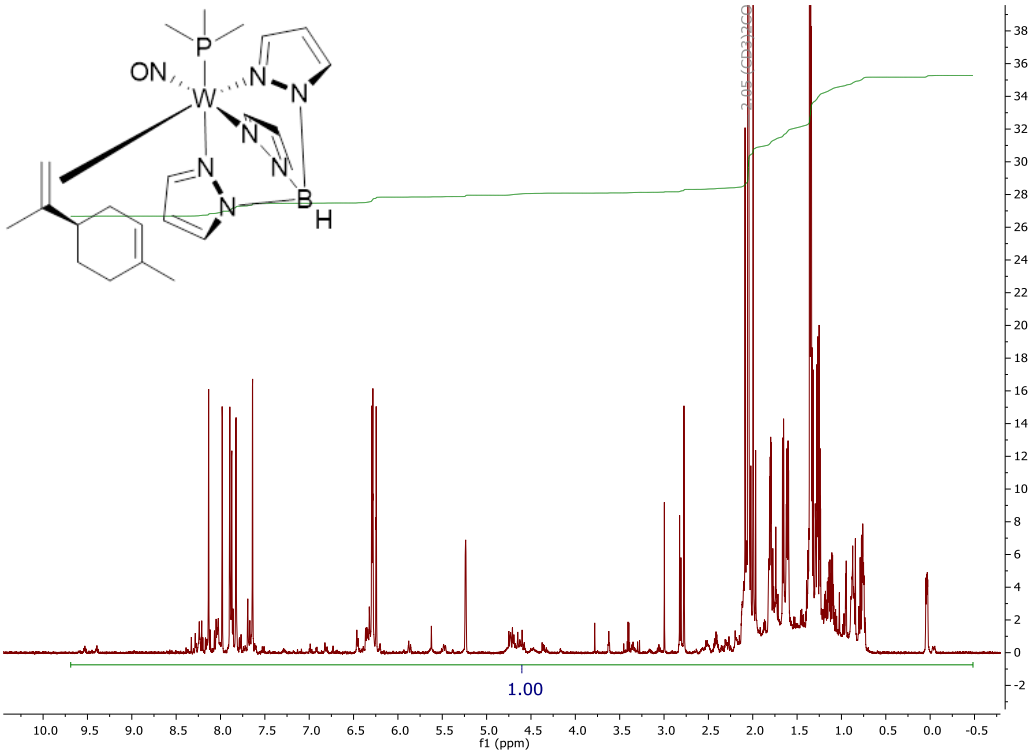
^{1}H NMR (d^{6}-Acetone) of R_{Mo},*R*- and S_{Mo},*R*- **22**A



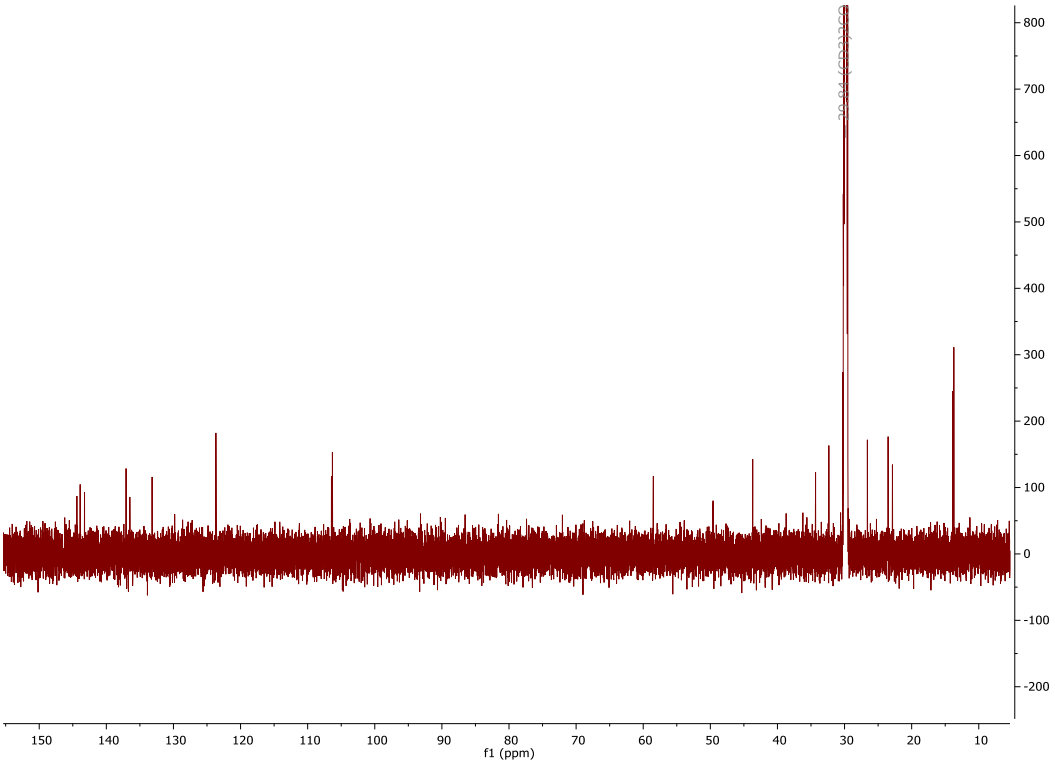
^{13}C NMR (d^{6}-Acetone) of R_{Mo},*R*- and S_{Mo},*R*- **22**A



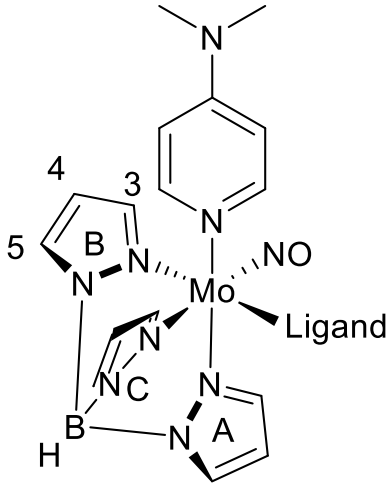
^{1}H NMR (d^{6}-Acetone) of S_{Mo},*R*- **22**A



^{13}C NMR (d^{6}-Acetone) of S_{Mo},*R*- **22**A

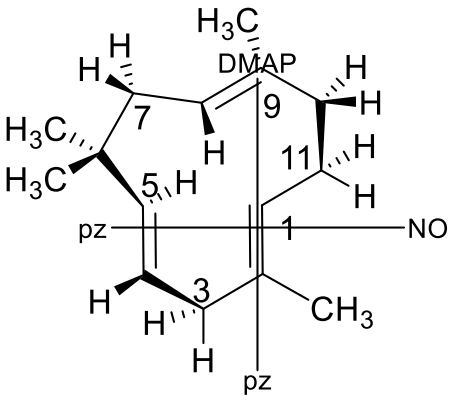


MoTp(NO)(DMAP)(η²-α-humulene) (23)



Among others

Ligand =



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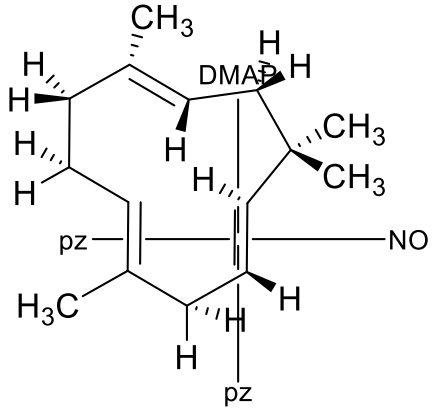

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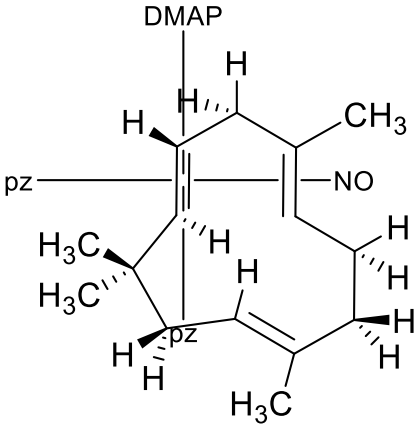
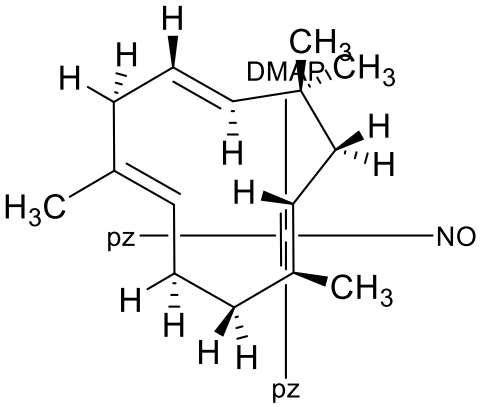


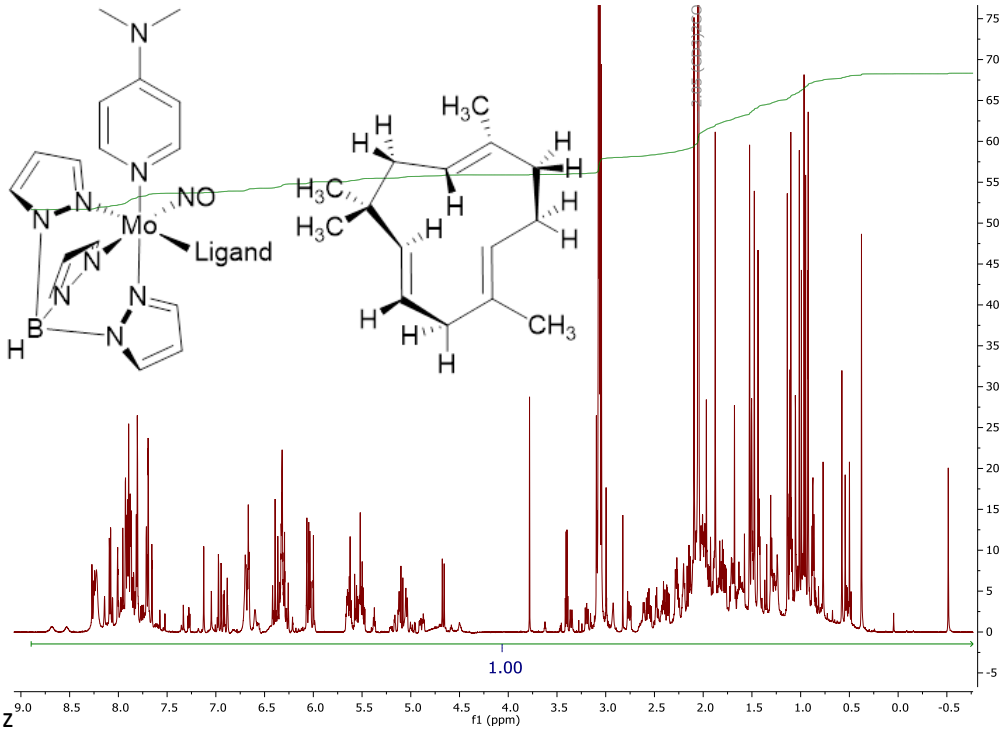
C



D

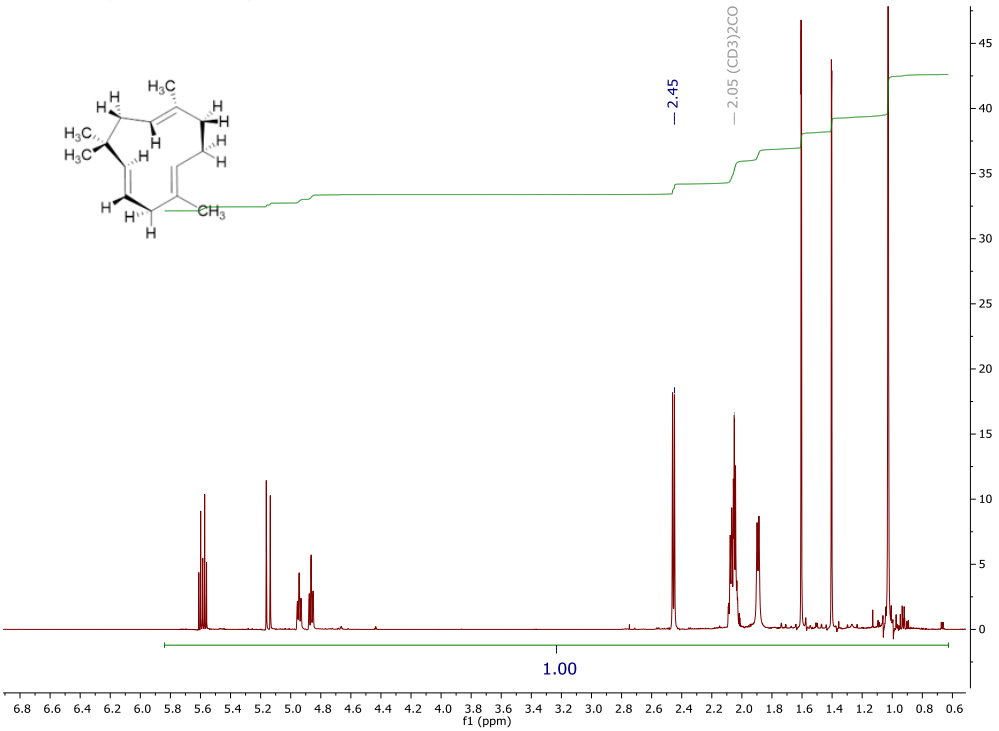
To a 4 dram vial charged with a stir pea, MoTp(NO)(DMAP)(η^2-trifluorotoluene) (1.0 g , 1.7 mmol) was combined with α-humulene (1 mL, 4.3 mol) and 10 mL of THF. The vial was then capped and the solution was allowed to mix for 4 h. About 10 mL of ether was added to the reaction vial and the solution was transferred to a 60 mL medium porosity fritted disk, 3/4 full of silica. The orange band was eluted with ~300 mL of ether. The filtrate was concentrated *in vacuo* to about 10 mL and then was added to 100 mL stirring pentane. The solution was then concentrated to 50 mL and the dark yellow solid was collected on a 30 mL fine porosity fritted disk. The solid was then washed with pentane (3x20 mL), dessicated, and collected (0.15 g, 0.23 mmol, 14%). IR υ_{NO}: 1557 cm^{-1}, υ_{BH}: 2466 cm^{-1}. CV E_{pa}: Broad 55 mV, **23**A: 0 mV. ^{1}H NMR (d_6-Acetone, δ) **23A**: 8.22 (2H, b, DMAP H2 and H6), 8.07 (1H, d, PzA5), 7.92 (1H, d, PzC3), 7.89 (1H, d, PzA3), 7.82 (1H, d, PzC5), 7.72 (1H, d, PzB3), 7.12 (1H, d, PzB5) , 6.66 (2H, m, DMAP H3 and H5), 6.40 (1H, t, PzC4), 6.33 (1H, t, PzA4), 6.06 (1H, t, PzB4), 5.47 (1H, m, H4), 5.02 (1H, m, H8), 4.66 (1H, d, J = 15.7, H5), 3.06 (6H, s, DMAP Methyls), 2.25 (1H, m, H11x), 2.08 (4H, bs, 2 methyl and H11y), 2.06 (2H, m, H10x), 2.02 (1H, m, H10y), 2.00 (1H, m, H7x syn to metal), 1.76 (1H, m, H1), 1.67 (1H, m, H7y anti to metal), 1.49 (1H, m, H3x anti to metal), 1.43 (3H, s, 9 methyl), 1.08 (1H, m, H3y syn to metal), 0.99 (6H, m, 6 methyls).^{13}C NMR (d_6-Acetone, δ) **23A**: 154.8 (DMAP 4), 151.3 (DMAP 2 and 6), 143.1 (PzA5 and PzC5), 141.8 (PzB5), 137.2 (PzC3 and PzA3), 136.7 (C5), 135.3 (PzB3), 133.6 (C9), 131.9 (C4), 126.7 (C8), 108.2 (DMAP 3 and 5), 106.4 (PzC4), 106.2 (PzA4) , 105.9 (PzB4), 69.0 (C1 or C2), 68.0 (C1 or C2), 44.2 C3), 40.5 (C11), 39.1(C6x or C7y), 37.4 (C6x or C7y), 31.1 (6x methyl syn to metal), 26.2 (6y methyl anti to metal), 20.6 (2 methyl), 15.5 (9 methyl). Anal. Cald for $C_{31}HBMoN_9O$: C, 55.95; H, 6.66; N, 18.94. Found: C, 55.92; H, 6.83; N, 18.54.

^{1}H NMR (d^6-Acetone) of **23** mixture of Isomers

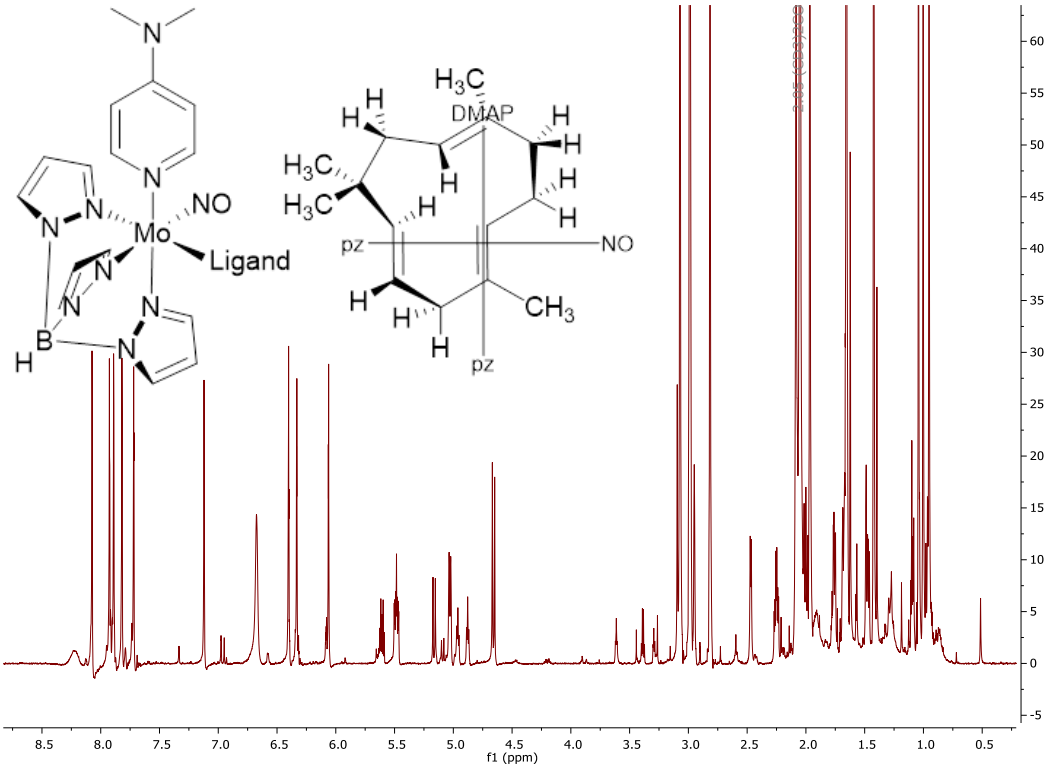


Z

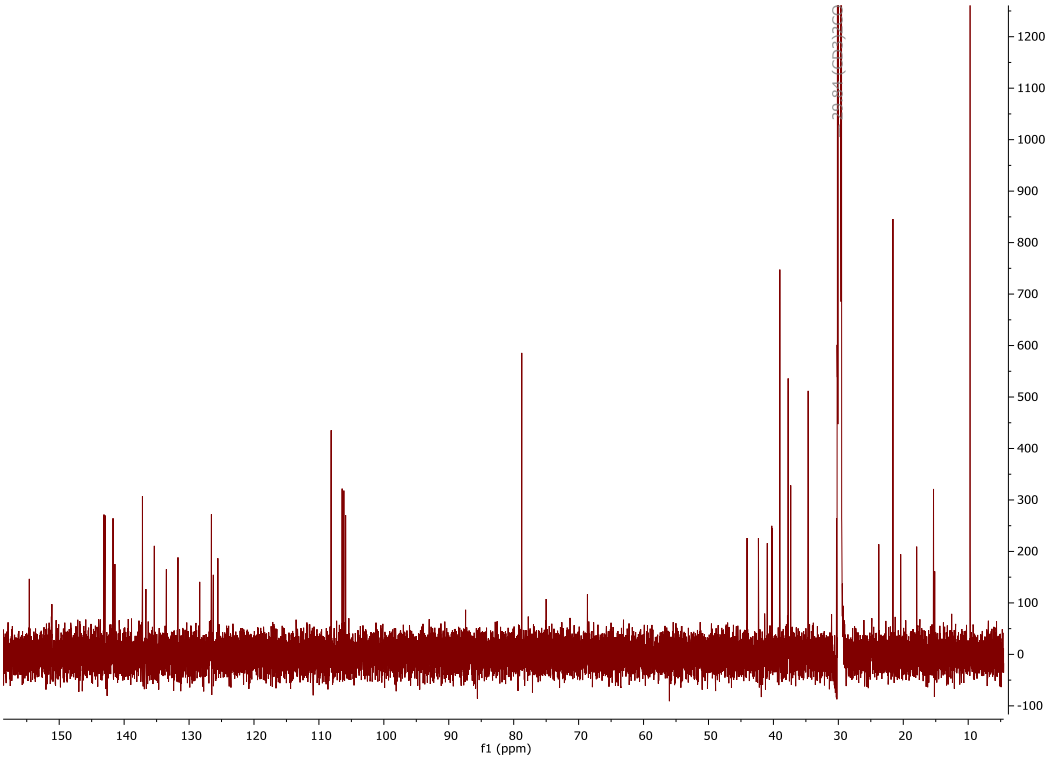
^{1}H NMR (d^6-Acetone) of α-Humulene



^{1}H NMR (d^{6}-Acetone) of **23**A (Free ligand impurity in sample)



^{13}C NMR (d^{6}-Acetone) of **23**A (Free ligand impurity in sample)



Gaussian DFT of:

23A Input

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23A Output Coordinates

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60	C	4.417501	0.290897	0.872577
61	C	5.648087	1.180681	0.878365
62	C	6.312905	1.143677	2.269702
63	H	6.713575	0.146286	2.48683
64	H	7.140605	1.861885	2.330007
65	H	5.593313	1.394215	3.059133

66	C	6.690121	0.761453	-0.17473
67	H	6.309313	0.841733	-1.19794
68	H	7.579543	1.399203	-0.10269
69	H	7.004017	-0.27698	-0.01856
70	C	5.163745	2.656341	0.596725
71	H	4.687618	3.044224	1.504417
72	H	6.058919	3.27488	0.425158
73	H	4.621721	-0.64765	-0.99352
74	H	3.760862	0.428574	1.736275
75	C	4.218918	2.721561	-0.57183
76	C	2.958712	3.181227	-0.62246
77	H	4.583994	2.22105	-1.46868
78	C	2.278462	3.944534	0.488932
79	H	1.406088	3.401709	0.87816
80	H	2.944003	4.157341	1.329574
81	H	1.900034	4.906767	0.114852
82	C	2.110758	2.894874	-1.84538
83	H	1.760864	3.836082	-2.30049
84	H	2.731419	2.39529	-2.59749
85	C	0.845541	2.023671	-1.56746
86	H	0.097667	2.658844	-1.07804
87	H	0.416687	1.755376	-2.54012

23B Input

```
%mem=12GB
%nprocshared=12
#                opt    freq              b3lyp/gen        geom=connectivity    pseudo=read

Title             Card   Required

                0      1
                   Mo       -5.29281213      -4.54752588      -0.05953037
                   O        -4.12439413      -5.24969588      -2.69767937
                   N        -6.01501513      -2.52747988      -0.33926537
                   N        -5.70996413      -1.45956788       0.56122663
                   N        -5.49505013      -4.11571488       2.18041763
                   N        -5.22745713      -2.79996788       2.66838263
                   N        -3.43636013      -3.33836888       0.23058863
                   N        -3.38070513      -2.18577988       1.06795063
                   N        -3.77266413      -6.07905188       0.46621763
                   N        -4.82719913      -4.85145688      -1.68142937
                   C        -6.28463713      -0.28353388       0.08187263
                   C        -6.96544013      -0.56610188      -1.10377937
```

C	-6.78189813	-1.95050788	-1.33690037
C	-5.50868413	-2.74090988	4.02967963
C	-5.95997513	-3.99509488	4.44806363
C	-5.94445713	-4.81254488	3.29448863
C	-2.10777713	-1.62762088	1.00144963
C	-1.32537613	-2.40380788	0.14214063
C	-2.17010913	-3.44161888	-0.31872437
C	-3.42179613	-6.47708588	1.75820263
B	-4.69765913	-1.67416288	1.72684263
H	-4.52190013	-0.67933788	2.32658963
H	-6.15556013	0.65430412	0.63359163
H	-7.52637613	0.13501312	-1.72462737
H	-7.15749413	-2.57536388	-2.15530437
H	-5.36194513	-1.80587688	4.58214263
H	-6.26690513	-4.28403788	5.45508663
H	-6.25001113	-5.85983688	3.19589163
H	-1.87198713	-0.72271688	1.57290163
H	-0.27988513	-2.23930188	-0.12533537
H	-1.94903013	-4.25140588	-1.02300037
H	-4.00769213	-6.01923388	2.56696463
C	-2.40182613	-7.38035888	2.05772563
H	-2.20435313	-7.62166588	3.10620763
C	-2.98952813	-6.64143188	-0.55273637
H	-3.25849913	-6.27711788	-1.58520937
C	-1.63363713	-7.97220088	1.00545263
C	-1.95833213	-7.55231488	-0.32400937
H	-1.39986113	-7.93611288	-1.18337237
N	-0.63398713	-8.93953788	1.26405263
C	-0.17075413	-9.16538388	2.66858063
H	0.55757787	-9.99251788	2.66453263
H	0.31113087	-8.26524688	3.10156163
H	-1.02471113	-9.45401688	3.30745963
C	0.28941487	-9.35820088	0.16370763
H	0.92473887	-8.52181388	-0.19224937
H	0.93922987	-10.16299988	0.54419263
H	-0.29246513	-9.75110188	-0.68925737
C	-7.37832913	-4.92266088	-0.22872337
C	-6.67771413	-6.16314088	0.20142363
H	-6.81473413	-6.37617288	1.27293963
C	-8.37236013	-4.17803988	0.72949363
H	-7.92350013	-4.07610888	1.72925763
H	-8.53746113	-3.15669688	0.33770463
C	-9.75159913	-4.86713388	0.88906963
C	-10.10255513	-5.43353588	2.06160163

C	-11.34338213	-6.28755988	2.34930063
C	-10.99848413	-7.83481988	2.28500963
H	-10.28360613	-8.06610888	3.09333963
H	-11.92116513	-8.41347088	2.46887663
H	-9.38723213	-5.37789188	2.89478763
C	-10.38123513	-8.18818488	0.91690463
C	-9.05909513	-8.01910888	0.72657863
C	-8.32550413	-8.03900788	-0.62331937
H	-8.32442113	-9.06168788	-1.04774437
H	-8.88418613	-7.40684188	-1.33688137
C	-6.81840113	-7.52766688	-0.58808337
C	-5.96112313	-8.63639888	0.12099363
H	-6.27588113	-8.76104688	1.16815363
H	-6.08426213	-9.60340188	-0.39102237
H	-4.89495513	-8.37418288	0.10945663
C	-6.38163213	-7.44018588	-2.09219037
H	-6.95293013	-6.65832088	-2.61389937
H	-5.31440113	-7.20459688	-2.19879437
H	-6.57882913	-8.40019488	-2.59473337
H	-7.76750713	-4.93859488	-1.25828237
C	-10.63981513	-4.84584888	-0.36591037
H	-10.20315213	-5.47414288	-1.15993337
H	-11.65583713	-5.20979788	-0.16072237
H	-10.71052713	-3.81810588	-0.76012237
H	-12.14644913	-6.07356688	1.62535463
H	-11.73485813	-6.06229488	3.35836063
C	-11.37152113	-8.56372788	-0.19552037
H	-12.14826913	-7.78891388	-0.30945237
H	-10.86347813	-8.69023588	-1.16165037
H	-11.88536113	-9.50913488	0.05104163
H	-8.44682113	-7.76062688	1.59998263

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8	17	1	21	1		
9	20	1	35	1		
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11	12	1.5	23	1		
12	13	1.5	24	1		

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33	34	1	37	1.5		
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37	38	1.5	40	1		
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45	46	1	47	1	48	1
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54						
55	56	2	77	1		
56	57	1	61	1		

57 58 1 81 1 82 1
58 59 1 60 1 62 1
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62 63 2 83 1
63 64 1 87 1
64 65 1 66 1 67 1
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68 69 1 70 1 71 1
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72 73 1 74 1 75 1
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87

Mo 0
LANL2DZ
*****
H B C N O 0
6-31G(d)
*****

Mo 0
LANL2DZ

23B Output Coordinates

Tag	Symbol	X	Y	Z
1	Mo	0.380246	0.684342	-0.60993
2	O	0.843254	0.365263	-3.5304
3	N	-0.46257	2.743942	-0.9167
4	N	-0.14551	3.769392	-0.08111
5	N	0.174961	1.233793	1.687613
6	N	0.407169	2.520752	2.060077
7	N	2.250495	1.994334	-0.34339
8	N	2.21363	3.123062	0.411633
9	N	1.952891	-0.92769	-0.12563
10	N	0.625908	0.46615	-2.34837
11	C	-0.70451	4.916423	-0.53434
12	C	-1.40692	4.635064	-1.69514
13	C	-1.21956	3.258166	-1.89253
14	C	0.177479	2.67002	3.382406
15	C	-0.21835	1.446206	3.902865
16	C	-0.20471	0.583162	2.79882
17	C	3.420744	3.73045	0.392126
18	C	4.277857	2.977506	-0.39696
19	C	3.491428	1.901928	-0.83634
20	C	2.357803	-1.23014	1.124741
21	B	0.888034	3.590977	1.050654
22	H	1.051767	4.63408	1.62471
23	H	-0.55542	5.843038	0.000799
24	H	-1.97212	5.321382	-2.30807
25	H	-1.59277	2.614937	-2.67638
26	H	0.312168	3.632612	3.854148
27	H	-0.48255	1.215873	4.924243
28	H	-0.46554	-0.46489	2.750558
29	H	3.577182	4.651967	0.934308
30	H	5.313503	3.180367	-0.62643
31	H	3.757708	1.075089	-1.47874
32	H	1.814106	-0.74994	1.928735
33	C	3.401913	-2.08907	1.422368
34	H	3.642897	-2.2651	2.46316
35	C	2.656276	-1.50439	-1.1261
36	H	2.350318	-1.24721	-2.13361
37	C	4.127711	-2.71106	0.378861
38	C	3.714034	-2.37539	-0.93286
39	H	4.206256	-2.7864	-1.80525
40	N	5.161963	-3.57527	0.620499
41	C	5.552052	-3.87898	1.989574
42	H	6.384218	-4.58404	1.976664
43	H	5.877663	-2.97875	2.528247

44	H	4.727968	-4.33675	2.553079
45	C	5.875784	-4.18627	-0.49165
46	H	6.362559	-3.43271	-1.12554
47	H	6.649076	-4.84834	-0.0999
48	H	5.204927	-4.78398	-1.12288
49	C	-1.83571	0.18934	-0.71336
50	C	-1.16589	-0.99815	-0.28951
51	H	-1.1944	-1.14324	0.794534
52	C	-2.76508	0.993466	0.212322
53	H	-2.32155	1.066346	1.208345
54	H	-2.85156	2.01848	-0.17183
55	C	-4.15481	0.388836	0.337206
56	C	-4.55484	-0.16856	1.49272
57	C	-5.77527	-1.01363	1.737986
58	C	-5.42457	-2.54229	1.708817
59	H	-4.7192	-2.74758	2.524262
60	H	-6.33805	-3.11461	1.923627
61	H	-3.85466	-0.13117	2.330413
62	C	-4.81487	-2.94108	0.382552
63	C	-3.48649	-2.84765	0.217371
64	C	-2.71628	-2.88804	-1.0804
65	H	-2.68213	-3.91245	-1.48525
66	H	-3.24897	-2.29171	-1.83384
67	C	-1.23674	-2.37133	-1.01192
68	C	-0.41118	-3.41544	-0.22997
69	H	-0.77168	-3.52339	0.800895
70	H	-0.48592	-4.40103	-0.70754
71	H	0.645285	-3.14208	-0.18655
72	C	-0.73794	-2.33126	-2.46762
73	H	-1.22961	-1.54243	-3.04579
74	H	0.337394	-2.15542	-2.5246
75	H	-0.94769	-3.28811	-2.96405
76	H	-2.14819	0.218289	-1.75946
77	C	-4.99218	0.440902	-0.91822
78	H	-4.56924	-0.19676	-1.70556
79	H	-6.02665	0.126332	-0.75954
80	H	-5.01083	1.463479	-1.32081
81	H	-6.55813	-0.81469	0.997713
82	H	-6.21094	-0.78474	2.720673
83	C	-5.78207	-3.26527	-0.7301
84	H	-6.52977	-2.47076	-0.86295
85	H	-5.28184	-3.41706	-1.69063
86	H	-6.34379	-4.18215	-0.49945
87	H	-2.9016	-2.62432	1.107651

23C Input

```
%mem=12GB
%nprocshared=12
#                opt    freq              b3lyp/gen       geom=connectivity   pseudo=read

Title             Card  Required

                0     1
                Mo       -4.47820154    -2.10408393                0
                O        -4.02965554    -3.28546893           -2.695151
                N        -5.30786654    -0.16148693           -0.424912
                N        -4.87363554     1.02484107            0.244396
                N        -4.25150054    -1.40251893            2.149335
                N        -3.98103154    -0.02008093            2.396839
                N        -2.63618154    -0.87732293           -0.223886
                N        -2.47142554     0.38282207            0.422321
                N        -2.86100154    -3.56871693            0.382308
                N        -4.40088554    -2.66347893           -1.621721
                C        -5.52528754     2.12416407           -0.313818
                C        -6.38025654     1.67579407           -1.322337
                C        -6.22306854     0.26892207           -1.369704
                C        -3.95783254     0.20876107            3.769841
                C        -4.21177554    -0.99596493            4.429771
                C        -4.38819354    -1.96202793            3.411547
                C        -1.23061454     0.91502007            0.084664
                C        -0.57647554     0.01735307           -0.763968
                C        -1.46562454    -1.07004593           -0.937423
                C        -2.15745054    -3.72067893             1.57919
                B        -3.66940454     0.97330807            1.231493
                H        -3.41849354     2.04071507            1.653433
                H        -5.31886454     3.13284307            0.061014
                H        -7.03733554     2.28366907           -1.947202
                H        -6.71654854    -0.46724593           -2.014648
                H        -3.76001354     1.21477807            4.156957
                H        -4.26666354    -1.15888193            5.507836
                H        -4.60852654    -3.03012593            3.512012
                H        -0.92303054     1.89027107            0.478647
                H         0.41391546     0.13430407           -1.207987
                H        -1.34058454    -1.97777893           -1.538657
                H        -2.46576654    -3.04926093            2.392855
                C        -1.12493854    -4.63704193             1.77787
                H        -0.63438354    -4.67299793            2.754918
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C	-2.43120654	-4.40188793	-0.660962
H	-2.96033254	-4.21950693	-1.637421
C	-0.72039154	-5.50588993	0.714817
C	-1.40426254	-5.33801293	-0.530619
H	-1.13117254	-5.93791593	-1.404207
N	0.27653046	-6.49504493	0.897027
C	1.13102546	-6.46204893	2.124903
H	1.79522846	-7.34141293	2.10824
H	1.75188246	-5.54475493	2.181099
H	0.49781346	-6.51912293	3.02835
C	0.82882746	-7.21027893	-0.295829
H	1.36482046	-6.52676993	-0.985394
H	1.53083646	-7.98275993	0.05809
H	0.01207146	-7.70632593	-0.84997
C	-6.54232054	-2.62844293	0.295838
C	-5.63684754	-3.74920793	0.668777
H	-5.54113954	-3.91588193	1.750469
C	-7.69033754	-2.11575293	1.274967
C	-5.69469454	-5.11591093	-0.093172
H	-6.98618054	-2.77365293	-0.697613
H	-6.16237754	-4.96192093	-1.079099
H	-4.66953654	-5.49310393	-0.279361
C	-7.76744254	-2.96136393	2.594831
H	-6.86811554	-2.81482993	3.208509
H	-8.63696954	-2.64520293	3.191843
H	-7.87039054	-4.03172793	2.366842
C	-7.58223054	-0.60492493	1.695479
H	-6.63446154	-0.41026993	2.215517
H	-7.64040854	0.05416307	0.818906
H	-8.40892854	-0.34485493	2.375365
C	-9.09471654	-2.26464493	0.524287
H	-9.89854954	-2.04420293	1.247081
H	-9.13944754	-1.49186493	-0.264198
C	-9.30570654	-3.63348293	-0.131421
C	-9.95331254	-4.71169393	0.345695
H	-8.81235254	-3.74078793	-1.106448
C	-10.72790254	-4.75763393	1.671674
H	-11.76084154	-5.10572193	1.499001
H	-10.25478054	-5.46652693	2.372759
H	-10.76899954	-3.77145893	2.154267
C	-9.94205854	-6.03607393	-0.465492
H	-10.54229454	-5.92068493	-1.387999
H	-10.41810654	-6.83219593	0.132241
C	-8.49558754	-6.50470093	-0.873097

H	-8.03081154	-5.74085493	-1.515628
H	-8.59929454	-7.42631893	-1.478508
C	-7.61025354	-6.80133693	0.343106
C	-6.44016454	-6.22871693	0.689118
H	-8.00666254	-7.59434893	0.995121
C	-5.70445354	-6.72520193	1.951388
H	-5.56671954	-5.90701893	2.677541
H	-6.26468654	-7.53340293	2.444298
H	-4.70153154	-7.10421493	1.689867

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4	11	1	21	1		
5	6	1	16	1		
6	14	1	21	1		
7	8	1	19	1		
8	17	1	21	1		
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18	19	1.5	30	1		
19	31	1				
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6-31G(d)
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Mo 0
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23C Output Coordinates

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23D Input

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H B C N O 0
6-31G(d)
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Mo 0
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23D Output Coordinates

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19	C	3.34247	2.185184	-0.48952
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21	B	0.455953	3.639475	1.173607
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27	H	-1.1795	0.950154	4.723557
28	H	-0.86157	-0.57205	2.460604
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30	H	5.066827	3.513536	0.0218
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35	C	2.550459	-1.43126	-1.01884
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61	C	-4.93659	-1.53671	1.814325
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63	H	-5.87413	-0.47112	3.463191
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65	H	-4.86443	-1.84143	3.965714
66	C	-4.49144	-2.95721	1.456547
67	H	-3.82536	-3.29632	2.265964
68	H	-5.38141	-3.60442	1.534524
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73	C	-1.70566	-3.47588	-1.29663
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77	H	-1.88657	-3.44557	0.90076
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79	H	-2.0044	-3.53804	-3.44899
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81	H	-3.1974	-2.54055	-2.61337
82	C	-0.89446	-4.79279	-1.31156
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85	H	-0.22526	-4.82726	-2.18101

86	H	-4.10755	-1.06962	-0.81151
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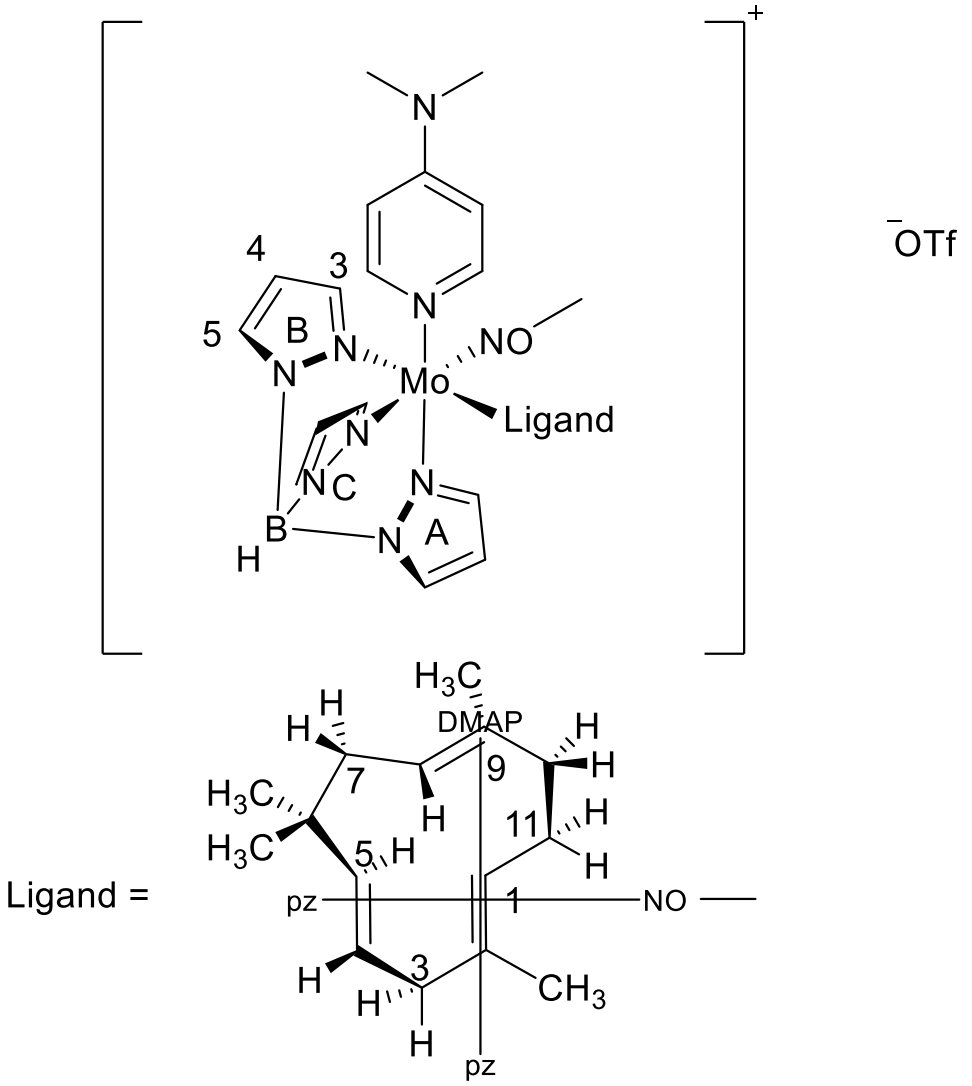
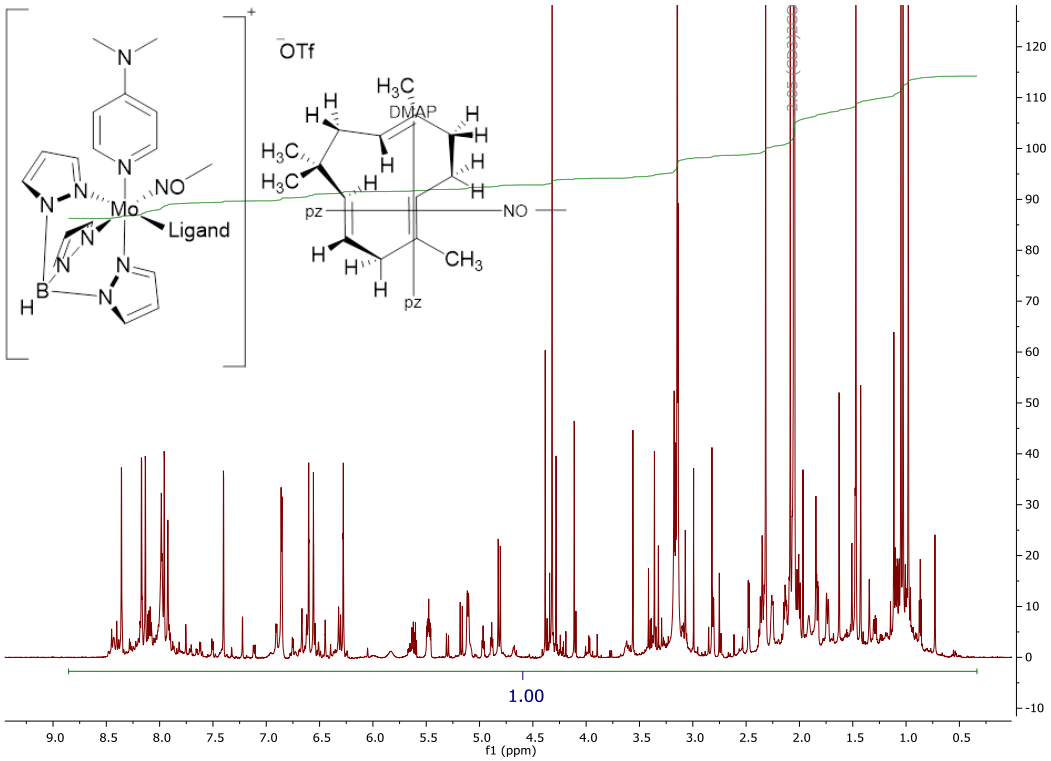
(MoTp(NO-Me)(DMAP)(η²-α -Humulene))(OTf) (**23A•CH₃**)



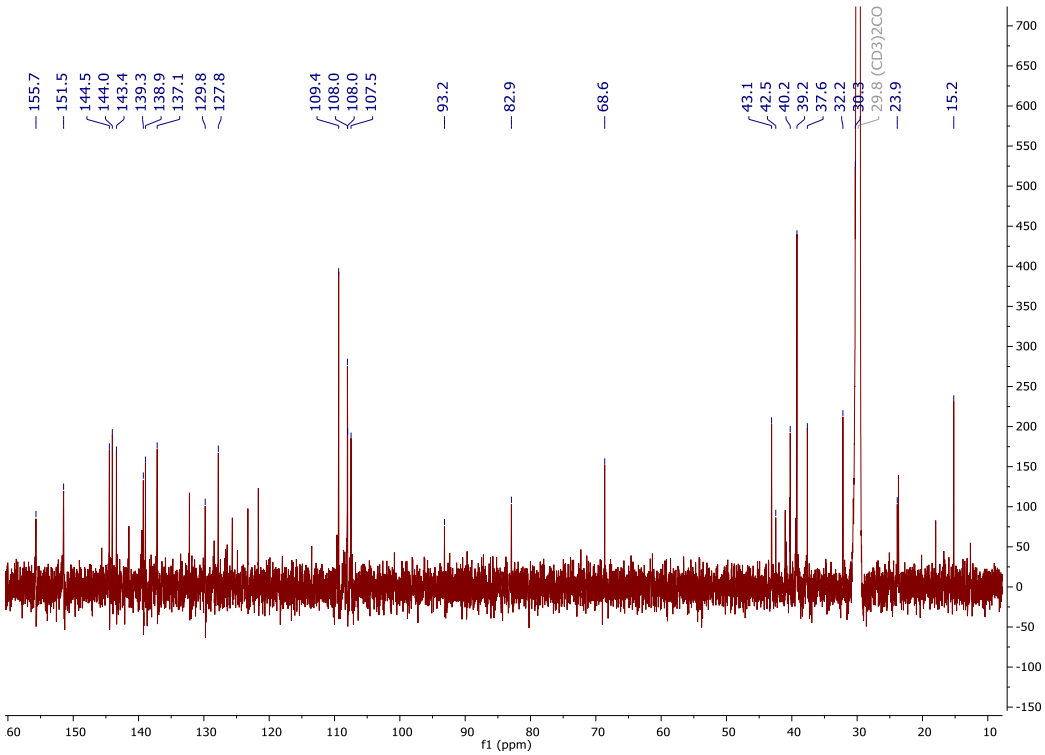
In a 4 dram vial, MoTp(NO)(DMAP)(η²-α -Humulene) (0.10g, 0.15 mmol, Mixture of Diastereomers) was dissolved in DCM (2 mL). An excess of methyl triflate (~10 drops from a 2 mL pasture pipette) was then added. Immediately the solution was added to 100 mL of ether. The solution was reduced *in vacuo* to about 25 mL. 75 mL of pentane was added and the volume was reduced *in vacuo* to 75 mL. The yellow brown solid was then collected on a 15 mL fine porosity fritted disk and washed with pentane (3x10 mL). The solid was desiccated and collected (0.093g, 0.11 mmol, 77% mass recovered, ~70% yield). IR υ_{NO}: 1623 cm^{-1} υ_{BH}: 2497 cm^{-1}. CV E_{pc}: -1400 mV E_{pa}: -380 mV. ^1H NMR (d_6-Acetone, δ): 8.37 (1H, d, PzA3), 8.19 (1H,

d, PzA5), 8.15 (1H, d, PzC5), 8.01 (2H, b, DMAP H2 and H6),7.98 (1H, d, PzB5), 7.93 (1H, d, PzC3), 7.41 (1H, d, PzB3) , 6.85 (2H, m, DMAP H3 and H5), 6.61 (1H, t, PzA4), 6.56 (1H, t, PzC4), 6.29 (1H, t, PzB4), 5.48 (1H, m, H4), 5.10 (1H, m, H8), 4.89 (1H, d, *J* = 15.4, H5), 4.32 (3H, s, NO Methyl), 3.15 (6H, s, DMAP Methyls), 2.80 (1H, m, H1), 2.35 (2H, m, H11x syn and 10x syn), 2.32 (3H, s, H2 methyl), 2.25 (1H, m, H10y anti), 2.15 (1H, m, H11y syn), 2.06 (1H, m, H7x syn), 1.83 (1H, m, H3x anti), 1.73 (1H, m, H7y anti), 1.46 (3H, s, 9 methyl), 1.04 (3H, s, 6x methyl anti), 1.08 (1H, m, H3 syn), 0.98 (3H, s, 6x methyl syn). ^{13}C NMR (d_6-Acetone, δ): 155.7 (DMAP-4), 151.5 (DMAP 2 and 6), 144.5 (PzC3), 144.0 (PzA3), 143.4 (PzB3), 139.3 (PzA5, C5), 138.9 (PzC5), 137.1(PzB5), 129.8 (C4), 127.8 (2C, C9 and C8), 109.4 (DMAP 3 and 5), 108.0 (2C, PzA4 and PzC4), 107.5 (PzB4), 93.2 (C2), 82.9 (C1), 68.6 (NO-Methyl), 43.1 (C3), 42.5 (C7), 40.2 (C10 or C11), 40.2 (C10 or C11), 39.2 (DMAP Methyls), 37.6 (C6), 32.2 (C2 methyl), 30.3 (C6 methyl syn), 23.7 (C6 methyl anti), and 15.21 (C9 methyl).

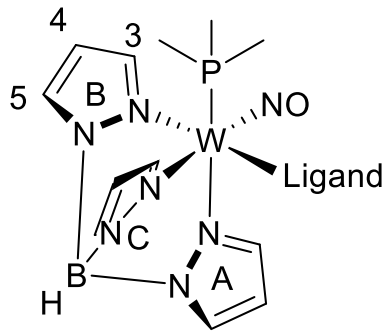
^{1}H NMR (d^{6}-Acetone) of **23** • Me (impure due to decomposition and free ligand ejection)



^{13}C NMR (d^{6}-Acetone) of **23** • Me (Marked peaks are complex, Free ligand impurity in sample)



WTp(NO)(PMe$_3$)(η^2 α-humulene) (**24**) (Pictured **24A**)



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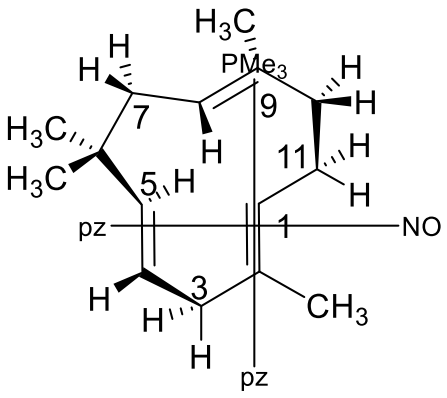

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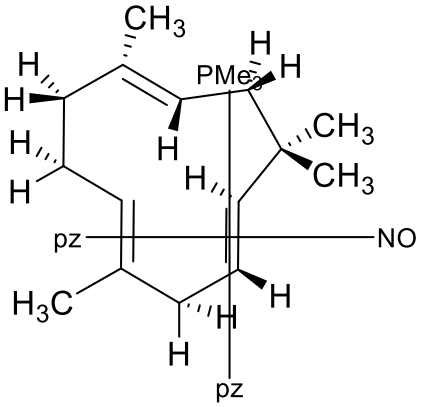

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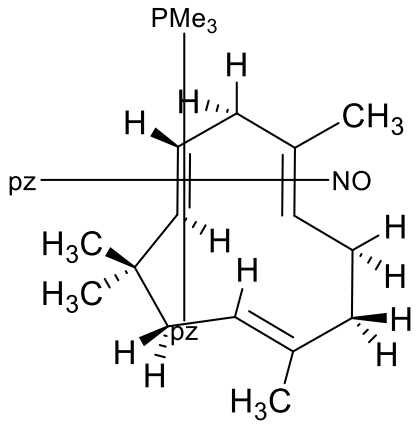

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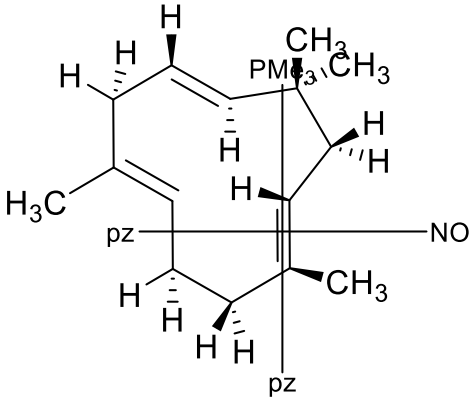
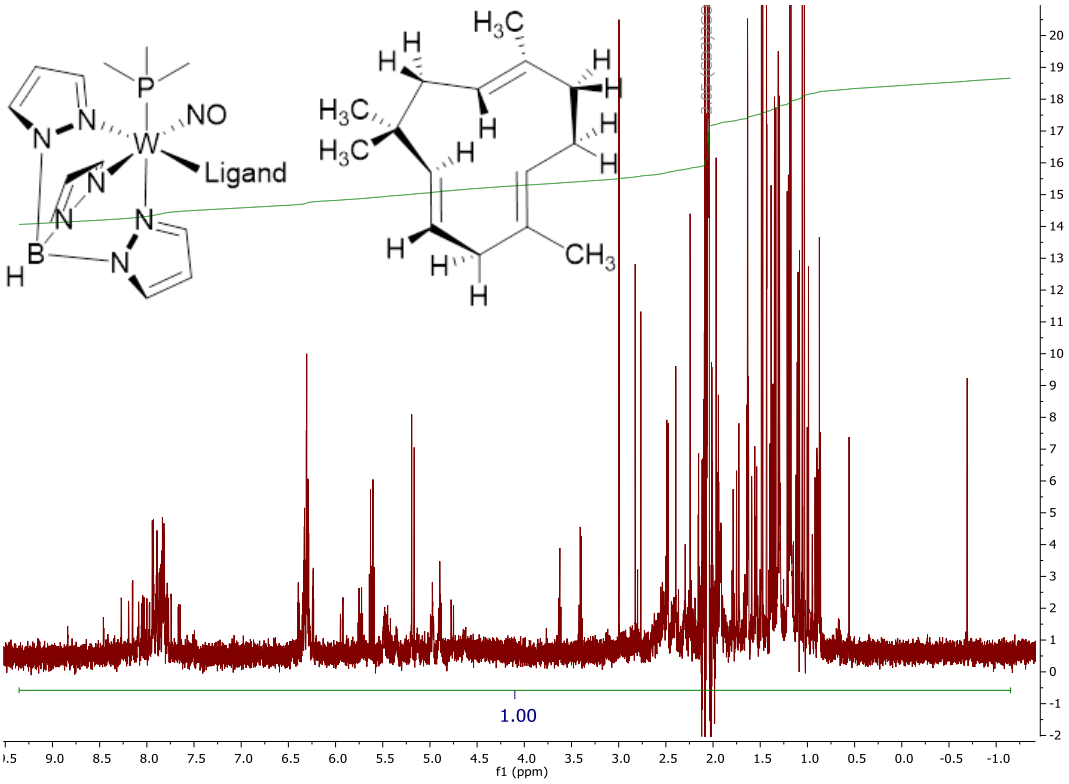


D

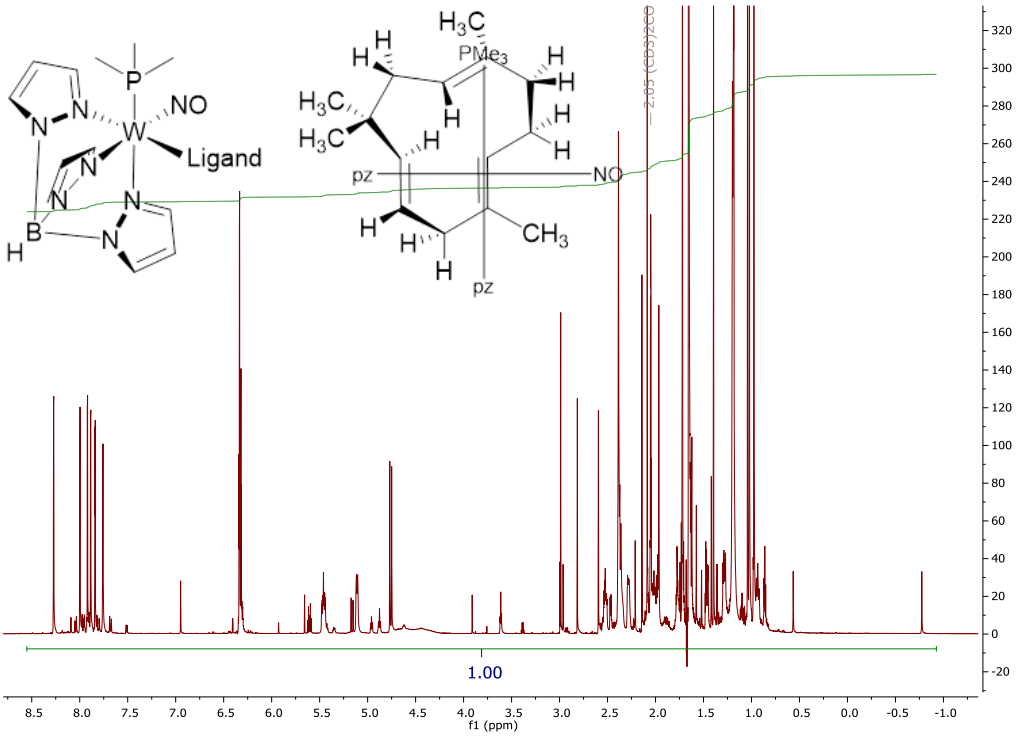
To a four-dram vial charged with a stir pea, WTp(NO)(PMe$_3$)(η^2-benzene) (0.25 g, 0.41 mmol) was combined with α-humulene (1.0 mL, 4.2 mmol) and 3 mL of THF. The vial was capped and allowed to mix 18 h. About 4 mL of ether was added to the reaction solution, and then loaded onto a 15 mL medium

porosity fritted disk, ~3/4 full of silica, and an orange band was eluted with ~25 mL ether. The filtrate was evaporated *in vacuo* to dryness and then dissolved with about 2 mL DCM and added to 75 mL stirring pentane. The pentane solution was concentrated to about 10 mL and the resulting precipitate was collected on 15 mL fine porosity fritted disk. The solid was desiccated to yield a yellow product (0.064 g, 0.090 mol, 21% mass recovery, ~10% yield due to permethylferrocenium impurity). IR: υ_{NO}: 1540 cm^{-1} υ_{BH}: 2486 cm^{-1}. CV: E_{pa}: + 302 mV.^{1}H NMR-(d_6-Acetone, δ) **24A**: 8.27 (1H, d, PzA3), 8.00 (1H, d, PzB3), 7.92 (1H, d PzB/C5), 7.88(1H, d PzB/C5), 7.84 (1H, d PzA5), 7.76 (1H, d PzC3), 6.34 (1H, d PzB/C4), 6.33 (1H, d PzB/C4), 6.32 (1H, d PzA4), 5.46 (1H, m, H4), 5.10 (1H, m, H8), 4.77 (1H, d, *J* = 15.8, H5), 2.53(1H, m, H10x or H11x syn), 2.47 (1H, m, H10x or H11x anti), 2.38 (3H, s, H2 methyl), 2.36 (1H, m, H10y or H11y anti), 2.03 (1H, m, H7x syn), 2.00 (1H, m, H10y or H11y syn), 1.98 (1H, m, H1), 1.77 (1H, m, H7y anti), 1.71 (3H, s, 9 methyl),) 1.47 (1H, m, H3x), 1.19 (9H, d, *J* = 7.3, PMe_3), 0.97 (3H, s, 6x methyl syn), 1.02 (3H, s, 6y methyl anti), 0.93 (1H, m, H3y syn). ^{13}C NMR-(d_6-Acetone, δ) **24A**: 143.8 (PzC3), 143.2 (PzB3), 142.9 (PzA3), 139.7 (humulene 9), 137.2 (Pz5), 137.1 (humulene 5 and Pz5), 136.3 (Pz5), 133.3 (humulene 4), 126.9 (humulene 8), 106.9 (Pz4), 106.8 (Pz4), 106.2 (Pz4), 64.1 (humulene 2), 55.3 (humulene 1), 44.5 (humulene 3), 40.9 (humulene 10), 40.2 (humulene 7), 34.6 (humulene 6), 32.1 (humulene 11), 30.6 (humulene 6 methyl anti), 30.2 (humulene 6 syn), 23.0 (humulene 2 methyl), 16.5 (humulene 9 methyl) 13.5 (d, J = 23.7, PMe_3). ^{31}P NMR-(THF, δ) **24A**: -13.14.

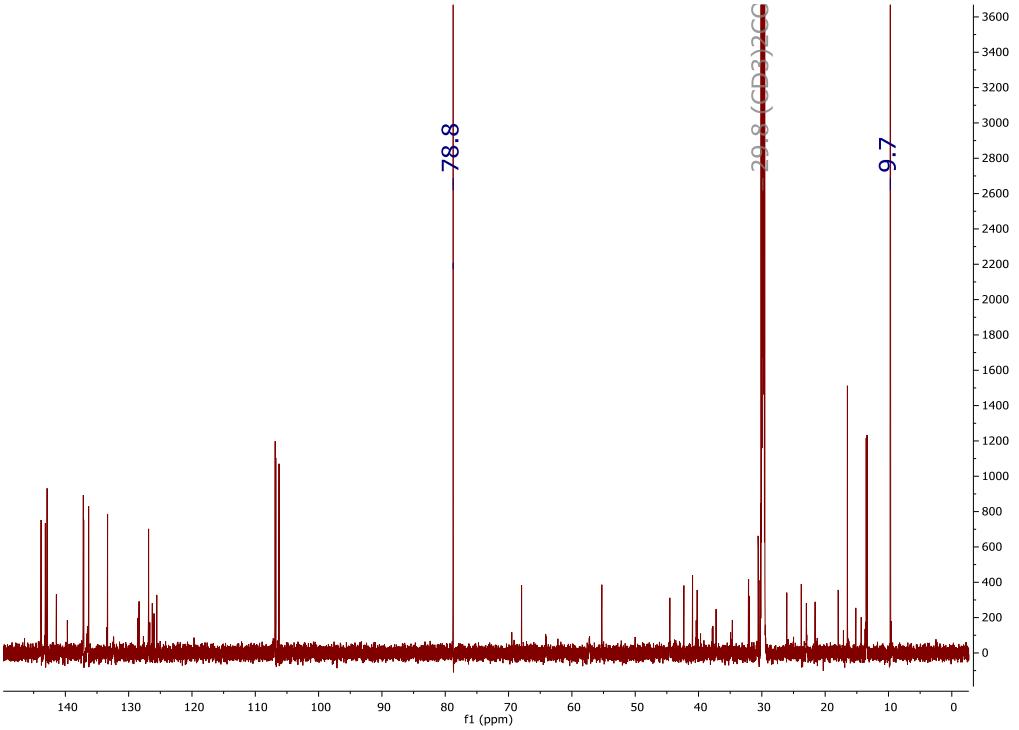
^{1}H NMR (d^{6}-Acetone) of **24**, mix of isomers



^{1}H NMR (d^{6}-Acetone) of **24**A (Singlet at 1.65 is permethylferrocene impurity and some free ligand is present)



^{13}C NMR (d^{6}-Acetone) of**24**A (Signals marked are permethylferrocene impurity and some free ligand is present)



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C	-18.57572267	-5.17912183	-2.85196064
C	-17.30250867	-5.96952383	2.51461936
C	-17.75379967	-7.22370883	2.93300336
C	-17.73828167	-8.04115883	1.77942836
C	-13.90160167	-4.85623483	-0.51361064
C	-13.11920067	-5.63242183	-1.37291964
C	-13.96393367	-6.67023283	-1.83378464
B	-16.49148367	-4.90277683	0.21178236
H	-16.31572467	-3.90795183	0.81152936
H	-17.94938467	-2.57430983	-0.88146864
H	-19.32020067	-3.09360083	-3.23968764
H	-18.95131867	-5.80397783	-3.67036464
H	-17.15576967	-5.03449083	3.06708236
H	-18.06072967	-7.51265183	3.94002636
H	-18.04383567	-9.08845083	1.68083136
H	-13.66581167	-3.95133083	0.05784136
H	-12.07370967	-5.46791583	-1.64039564
H	-13.74285467	-7.48001983	-2.53806064
C	-19.17215367	-8.15127483	-1.74378364
C	-18.47153867	-9.39175483	-1.31363664
H	-18.60855867	-9.60478683	-0.24212064
C	-20.16618467	-7.40665383	-0.78556664
H	-19.71732467	-7.30472283	0.21419736
H	-20.33128567	-6.38531083	-1.17735564
C	-21.54542367	-8.09574783	-0.62599064
C	-21.89637967	-8.66214983	0.54654136
C	-23.13720667	-9.51617383	0.83424036
C	-22.79230867	-11.06343383	0.76994936

H	-22.07743067	-11.29472283	1.57827936
H	-23.71498967	-11.64208483	0.95381636
H	-21.18105667	-8.60650583	1.37972736
C	-22.17505967	-11.41679883	-0.59815564
C	-20.85291967	-11.24772283	-0.78848164
C	-20.11932867	-11.26762183	-2.13837964
H	-20.11824567	-12.29030183	-2.56280464
H	-20.67801067	-10.63545583	-2.85194164
C	-18.61222567	-10.75628083	-2.10314364
C	-17.75494767	-11.86501283	-1.39406664
H	-18.06970567	-11.98966083	-0.34690664
H	-17.87808667	-12.83201583	-1.90608264
H	-16.68877967	-11.60279683	-1.40560364
C	-18.17545667	-10.66879983	-3.60725064
H	-18.74675467	-9.88693483	-4.12895964
H	-17.10822567	-10.43321083	-3.71385464
H	-18.37265367	-11.62880883	-4.10979364
H	-19.56133167	-8.16720883	-2.77334264
C	-22.43363967	-8.07446283	-1.88097064
H	-21.99697667	-8.70275683	-2.67499364
H	-23.44966167	-8.43841183	-1.67578264
H	-22.50435167	-7.04671983	-2.27518264
H	-23.94027367	-9.30218083	0.11029436
H	-23.52868267	-9.29090883	1.84330036
C	-23.16534567	-11.79234183	-1.71058064
H	-23.94209367	-11.01752783	-1.82451264
H	-22.65730267	-11.91884983	-2.67671064
H	-23.67918567	-12.73774883	-1.46401864
H	-20.24064567	-10.98924083	0.08492236
W	-17.08663667	-7.77613983	-1.57459064
P	-15.56648867	-9.30766583	-1.04884264
C	-15.43026964	-11.10070792	-0.7680501
H	-16.01347489	-11.3731953	0.08665585
H	-15.79145012	-11.62486292	-1.62811417
H	-14.40579909	-11.3582162	-0.59761072
C	-15.10928184	-9.82633343	0.63470892
H	-14.09168144	-9.55713809	0.82686329
H	-15.74675952	-9.34000339	1.34323224
H	-15.22060725	-10.88678968	0.7238111
C	-14.55044207	-10.03730192	-2.37084131
H	-14.88230703	-9.67021168	-3.31953009
H	-13.52554195	-9.7678998	-2.2228472
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24B Output Coordinates

Tag	Symbol	X	Y	Z
1	O	-0.13001	1.018255	-3.27327
2	N	-1.14668	-1.86999	-0.89159
3	N	-2.21319	-2.54415	-0.30414

4	N	-1.42782	-0.32472	1.699106
5	N	-2.48982	-1.20992	1.843049
6	N	-2.90286	0.260857	-0.83561
7	N	-3.78683	-0.63337	-0.24386
8	N	-0.32005	0.695577	-2.0671
9	C	-2.29932	-3.80261	-0.83849
10	C	-1.28309	-3.95263	-1.78997
11	C	-0.59184	-2.71674	-1.78957
12	C	-2.74622	-1.40536	3.169602
13	C	-1.84217	-0.63663	3.917316
14	C	-1.04061	0.018502	2.954969
15	C	-5.03423	-0.46162	-0.77759
16	C	-4.97177	0.561294	-1.73421
17	C	-3.6168	0.971869	-1.74453
18	B	-3.21422	-1.79624	0.608993
19	H	-4.09207	-2.53089	0.961255
20	H	-3.06866	-4.48896	-0.51837
21	H	-1.07283	-4.82056	-2.39485
22	H	0.256565	-2.40382	-2.37737
23	H	-3.53865	-2.06455	3.490178
24	H	-1.76827	-0.56968	4.991301
25	H	-0.20682	0.685409	3.105759
26	H	-5.86311	-1.07743	-0.46235
27	H	-5.77638	0.93798	-2.34602
28	H	-3.12754	1.701538	-2.37154
29	C	1.381554	-0.61142	-0.01077
30	C	1.369244	0.805163	0.35607
31	H	1.404641	1.004486	1.431321
32	C	1.929835	-1.75696	0.9256
33	C	2.221834	1.819327	-0.45126
34	H	1.752052	-0.765	-1.0242
35	H	2.30421	1.451157	-1.47914
36	H	1.703902	2.790876	-0.52117
37	C	2.654561	-1.16001	2.163378
38	H	1.949708	-0.64288	2.827648
39	H	3.125128	-1.96159	2.751315
40	H	3.429586	-0.44709	1.86386
41	C	0.891838	-2.78742	1.451263
42	H	0.143064	-2.31591	2.094185
43	H	0.372518	-3.29659	0.634936
44	H	1.407072	-3.55548	2.048194
45	C	2.989448	-2.60254	0.093931
46	H	3.513768	-3.26137	0.801118
47	H	2.424564	-3.25892	-0.58571

48	C	3.967287	-1.79118	-0.72908
49	C	5.200508	-1.33741	-0.40462
50	H	3.582586	-1.47565	-1.70067
51	C	5.940092	-1.67419	0.875517
52	H	6.945407	-2.06001	0.648449
53	H	6.078651	-0.77313	1.492938
54	H	5.418573	-2.4203	1.48265
55	C	5.910316	-0.36201	-1.35222
56	H	6.137292	-0.85155	-2.31172
57	H	6.876351	-0.06408	-0.9189
58	C	5.076203	0.927779	-1.64567
59	H	4.146312	0.65264	-2.15413
60	H	5.652275	1.547105	-2.35333
61	C	4.795771	1.729857	-0.39298
62	C	3.60588	2.099145	0.146034
63	H	5.700033	2.033926	0.144848
64	C	3.598601	2.911789	1.435003
65	H	3.024419	2.408913	2.226927
66	H	4.613792	3.077628	1.814539
67	H	3.136372	3.899244	1.276824
68	W	-0.69403	0.233516	-0.37881
69	P	-1.2052	2.715321	0.36047
70	C	-2.94966	3.022907	1.017458
71	H	-3.69109	2.766094	0.258039
72	H	-3.11705	2.392421	1.896486
73	H	-3.0647	4.076184	1.298923
74	C	-1.0812	3.976518	-1.03214
75	H	-0.06235	3.979816	-1.42779
76	H	-1.75542	3.692272	-1.84475
77	H	-1.34382	4.977953	-0.67144
78	C	-0.22339	3.558328	1.731888
79	H	-0.4041	3.04182	2.679717
80	H	0.843013	3.529588	1.508687
81	H	-0.54755	4.600857	1.830819

24C Input

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%mem=12GB
%nprocshared=12
#                opt    freq              b3lyp/sdd        geom=connectivity

Title            Card   Required

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N	-11.56214108	-5.98980715	2.149335
N	-11.29167208	-4.60736915	2.396839
N	-9.94682208	-5.46461115	-0.223886
N	-9.78206608	-4.20446615	0.422321
N	-11.71152608	-7.25076715	-1.621721
C	-12.83592808	-2.46312415	-0.313818
C	-13.69089708	-2.91149415	-1.322337
C	-13.53370908	-4.31836615	-1.369704
C	-11.26847308	-4.37852715	3.769841
C	-11.52241608	-5.58325315	4.429771
C	-11.69883408	-6.54931615	3.411547
C	-8.54125508	-3.67226815	0.084664
C	-7.88711608	-4.56993515	-0.763968
C	-8.77626508	-5.65733415	-0.937423
B	-10.98004508	-3.61398015	1.231493
H	-10.72913408	-2.54657315	1.653433
H	-12.62950508	-1.45444515	0.061014
H	-14.34797608	-2.30361915	-1.947202
H	-14.02718908	-5.05453415	-2.014648
H	-11.07065408	-3.37251015	4.156957
H	-11.57730408	-5.74617015	5.507836
H	-11.91916708	-7.61741415	3.512012
H	-8.23367108	-2.69701715	0.478647
H	-6.89672508	-4.45298415	-1.207987
H	-8.65122508	-6.56506715	-1.538657
C	-13.85296108	-7.21573115	0.295838
C	-12.94748808	-8.33649615	0.668777
H	-12.85178008	-8.50317015	1.750469
C	-15.00097808	-6.70304115	1.274967
C	-13.00533508	-9.70319915	-0.093172
H	-14.29682108	-7.36094115	-0.697613
H	-13.47301808	-9.54920915	-1.079099
H	-11.98017708	-10.08039215	-0.279361
C	-15.07808308	-7.54865215	2.594831
H	-14.17875608	-7.40211815	3.208509
H	-15.94761008	-7.23249115	3.191843
H	-15.18103108	-8.61901615	2.366842
C	-14.89287108	-5.19221315	1.695479
H	-13.94510208	-4.99755815	2.215517
H	-14.95104908	-4.53312515	0.818906
H	-15.71956908	-4.93214315	2.375365

C	-16.40535708	-6.85193315	0.524287
H	-17.20919008	-6.63149115	1.247081
H	-16.45008808	-6.07915315	-0.264198
C	-16.61634708	-8.22077115	-0.131421
C	-17.26395308	-9.29898215	0.345695
H	-16.12299308	-8.32807615	-1.106448
C	-18.03854308	-9.34492215	1.671674
H	-19.07148208	-9.69301015	1.499001
H	-17.56542108	-10.05381515	2.372759
H	-18.07964008	-8.35874715	2.154267
C	-17.25269908	-10.62336215	-0.465492
H	-17.85293508	-10.50797315	-1.387999
H	-17.72874708	-11.41948415	0.132241
C	-15.80622808	-11.09198915	-0.873097
H	-15.34145208	-10.32814315	-1.515628
H	-15.90993508	-12.01360715	-1.478508
C	-14.92089408	-11.38862515	0.343106
C	-13.75080508	-10.81600515	0.689118
H	-15.31730308	-12.18163715	0.995121
C	-13.01509408	-11.31249015	1.951388
H	-12.87736008	-10.49430715	2.677541
H	-13.57532708	-12.12069115	2.444298
H	-12.01217208	-11.69150315	1.689867
W	-11.78884208	-6.69137215	0
P	-10.17164208	-8.15600515	0.382308
C	-9.25482535	-8.35403103	1.94199798
H	-8.22023098	-8.13602723	1.77771515
H	-9.64893272	-7.68174001	2.67521293
H	-9.35630493	-9.36074764	2.29002606
C	-9.61394759	-9.23711329	-0.97142094
H	-10.20530492	-9.05067241	-1.84345093
H	-8.5856338	-9.03579301	-1.18807939
H	-9.72302887	-10.26047077	-0.67860574
C	-10.12955786	-9.8609748	1.01768772
H	-10.47471226	-9.87281564	2.03042077
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H	-9.12657006	-10.23160698	0.97835235

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81						

24C Output Coordinates

Tag	Symbol	X	Y	Z
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2	N	-1.17439	-1.81185	-1.11586
3	N	-1.99448	-2.70386	-0.42972
4	N	-1.00463	-0.69629	1.681775
5	N	-1.91356	-1.72356	1.906205
6	N	-3.07588	0.018433	-0.3546
7	N	-3.70792	-1.05661	0.259434
8	N	-1.02355	0.983401	-2.01309
9	C	-2.05095	-3.88567	-1.11936

10	C	-1.26263	-3.76825	-2.27038
11	C	-0.73764	-2.45417	-2.22474
12	C	-1.82714	-2.13752	3.203699
13	C	-0.84581	-1.37321	3.851988
14	C	-0.36165	-0.48968	2.861276
15	C	-5.04979	-1.00389	-0.00171
16	C	-5.30449	0.121103	-0.79798
17	C	-4.03813	0.719517	-1.00507
18	B	-2.83938	-2.23063	0.778027
19	H	-3.53016	-3.12099	1.183531
20	H	-2.64281	-4.71158	-0.75463
21	H	-1.09419	-4.51494	-3.03028
22	H	-0.08429	-1.95149	-2.92032
23	H	-2.45479	-2.9335	3.57477
24	H	-0.52448	-1.45082	4.878661
25	H	0.418809	0.250514	2.935086
26	H	-5.71846	-1.76514	0.371252
27	H	-6.25578	0.447599	-1.18787
28	H	-3.77488	1.575831	-1.60767
29	C	1.270734	-0.46086	-0.62106
30	C	1.382572	0.874484	-0.03891
31	H	1.600913	0.856236	1.037926
32	C	1.681804	-1.73648	0.162376
33	H	1.373502	-1.6409	1.208626
34	H	1.139847	-2.59747	-0.25679
35	C	3.181204	-2.02683	0.122991
36	C	3.932073	-1.93823	1.249854
37	C	5.441365	-1.94846	1.355542
38	C	6.01621	-0.47744	1.439168
39	H	5.623715	-0.01041	2.353436
40	H	7.109698	-0.53891	1.546164
41	H	3.412599	-1.69019	2.180317
42	C	5.617183	0.334133	0.215858
43	C	4.421235	0.968726	0.205394
44	C	3.694987	1.542718	-0.99614
45	H	4.242593	2.405471	-1.41124
46	H	3.67399	0.789288	-1.79871
47	C	2.213445	2.012729	-0.73544
48	C	2.291147	3.271763	0.167856
49	H	2.712742	3.039735	1.15591
50	H	2.937326	4.031752	-0.29336
51	H	1.306434	3.725757	0.314401
52	C	1.653957	2.43555	-2.11557
53	H	1.53133	1.577666	-2.78614

54	H	0.675461	2.915391	-2.03241
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56	H	1.52313	-0.53365	-1.6835
57	C	3.737211	-2.37822	-1.24486
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59	H	4.752161	-2.7852	-1.20055
60	H	3.093621	-3.12458	-1.73383
61	H	5.901233	-2.4588	0.49973
62	H	5.762161	-2.48792	2.259075
63	C	6.521337	0.215561	-0.99756
64	H	6.688173	-0.83773	-1.27141
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66	H	7.511963	0.645963	-0.78652
67	H	3.863903	0.978177	1.142054
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69	P	-1.43863	2.479502	0.92382
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73	H	-0.73893	2.430099	3.290555
74	C	-3.14563	2.46668	1.740211
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77	H	-3.25804	3.357403	2.369446
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79	H	-0.5789	4.330774	-0.48863
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24D Input

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Title             Card  Required

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24D Output Coordinates

Tag	Symbol	X	Y	Z
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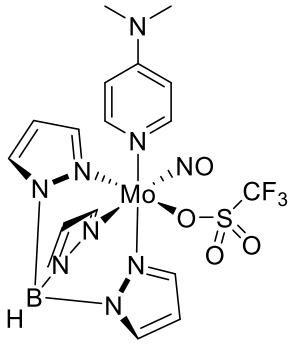
2	N	1.684901	1.402126	-1.45885
3	N	2.478337	2.334555	-0.78721
4	N	0.746339	1.073431	1.404869
5	N	1.771502	1.986159	1.621787
6	N	3.037709	-0.39888	0.12102
7	N	3.708361	0.710704	0.620268
8	N	1.116829	-1.56653	-1.67575
9	C	2.933671	3.267831	-1.68061
10	C	2.446235	2.944943	-2.95113
11	C	1.680452	1.769349	-2.76281
12	C	1.516426	2.706696	2.75231
13	C	0.301458	2.26584	3.296355
14	C	-0.14032	1.249074	2.420214
15	C	5.040721	0.423547	0.735091

16	C	5.250284	-0.89456	0.305618
17	C	3.971098	-1.36285	-0.08073
18	B	2.970276	2.075128	0.656417
19	H	3.715935	2.944275	1.008067
20	H	3.572104	4.076142	-1.35737
21	H	2.620986	3.470772	-3.8765
22	H	1.157252	1.176056	-3.49261
23	H	2.199239	3.4725	3.087864
24	H	-0.19433	2.632289	4.181359
25	H	-1.05046	0.672868	2.45873
26	H	5.740516	1.165219	1.089931
27	H	6.186292	-1.42879	0.25914
28	H	3.689391	-2.31008	-0.51553
29	C	-1.12546	0.400067	-1.27662
30	C	-1.41216	-0.6635	-0.30951
31	H	-1.79761	-0.28109	0.640572
32	C	-1.54408	1.832372	-0.87557
33	H	-1.36483	1.9919	0.191865
34	C	-1.32204	0.153104	-2.77842
35	H	-0.9325	-0.8147	-3.10779
36	H	-2.38611	0.197902	-3.05444
37	H	-0.83024	0.935628	-3.36969
38	H	-0.92605	2.568173	-1.41104
39	C	-3.06743	2.121684	-1.1623
40	C	-3.76905	2.854816	-0.03487
41	C	-4.72696	2.440281	0.836254
42	C	-5.26479	3.415722	1.879391
43	H	-4.77446	4.393366	1.811381
44	H	-6.34785	3.570387	1.755514
45	H	-5.11649	3.02992	2.900194
46	C	-5.38776	1.055461	0.969037
47	H	-5.18891	0.703812	1.995864
48	H	-6.4792	1.215647	0.922119
49	H	-3.15354	2.73018	-2.07588
50	C	-4.99603	-0.03312	-0.00479
51	C	-4.21681	-1.08984	0.305959
52	H	-5.35808	0.088897	-1.02465
53	C	-3.64144	-2.13162	-0.6467
54	C	-2.04448	-2.02141	-0.65943
55	H	-1.68577	-2.77563	0.053985
56	H	-1.69076	-2.3584	-1.64182
57	H	-3.89142	-1.19318	1.347178
58	C	-4.21057	-1.9939	-2.0793
59	H	-3.78935	-2.77383	-2.72721

60	H	-5.30337	-2.10604	-2.08232
61	H	-3.96714	-1.02657	-2.52947
62	C	-4.01258	-3.54933	-0.11994
63	H	-3.69708	-3.68137	0.924993
64	H	-5.09704	-3.71449	-0.16594
65	H	-3.52131	-4.32786	-0.72069
66	H	-3.56498	1.176794	-1.3658
67	H	-3.42845	3.887515	0.092961
68	W	0.843767	-0.3612	-0.38353
69	P	0.759248	-2.22785	1.485554
70	C	0.92275	-3.98673	0.834178
71	H	0.050619	-4.23201	0.223097
72	H	1.807267	-4.05539	0.194822
73	H	1.007894	-4.69933	1.662943
74	C	2.156432	-2.1549	2.755785
75	H	3.121684	-2.30577	2.268433
76	H	2.156452	-1.16984	3.232724
77	H	2.008183	-2.92853	3.518277
78	C	-0.69252	-2.37499	2.687533
79	H	-0.66568	-1.53221	3.384904
80	H	-1.64219	-2.36737	2.151227
81	H	-0.605	-3.30712	3.257593

MoTp(NO)(DMAP)(κ^1-OTf) (**26**)



In a 50 mL round bottom flask with a stir egg, MoTp(NO)(4-DMAP)(CO) (5.0 g, 10 mmol) was combined with 20 mL THF and stirred until homogenous. To the homogenous solution, $Cu(OTf)_2$ (2.03 g, 5.6 mmol) was added (Caution: CO released during reaction) and allowed to mix until bubbling had ceased. About 20 mL of ether was then added and the solution was transferred to a 60 mL medium porosity fritted disk, about 3/4 full of silica, and a green band was eluted with a 1:1 ET_2O : THF solution (500 mL). The green filtrate was evaporated *in vacuo* to ~ 10 mL and then added to 100 mL stirring pentane. The green solid was collected on a 60 mL medium porosity fritted disk and washed with pentane (3 x 30 mL). The solid was dried and the green product was collected (5.61 g, 9.2 mmol, 90% yield), IR υ_{NO}: 1624 Hz, υ_{BH}: 2517 Hz. CV E_{pa} (I/II): 608 mV, E_{pc} (0/I): -1382 mV.

Compound **26**: Crystal grown by Jeffery T. Myers, Data collected by Diane A. Dickie

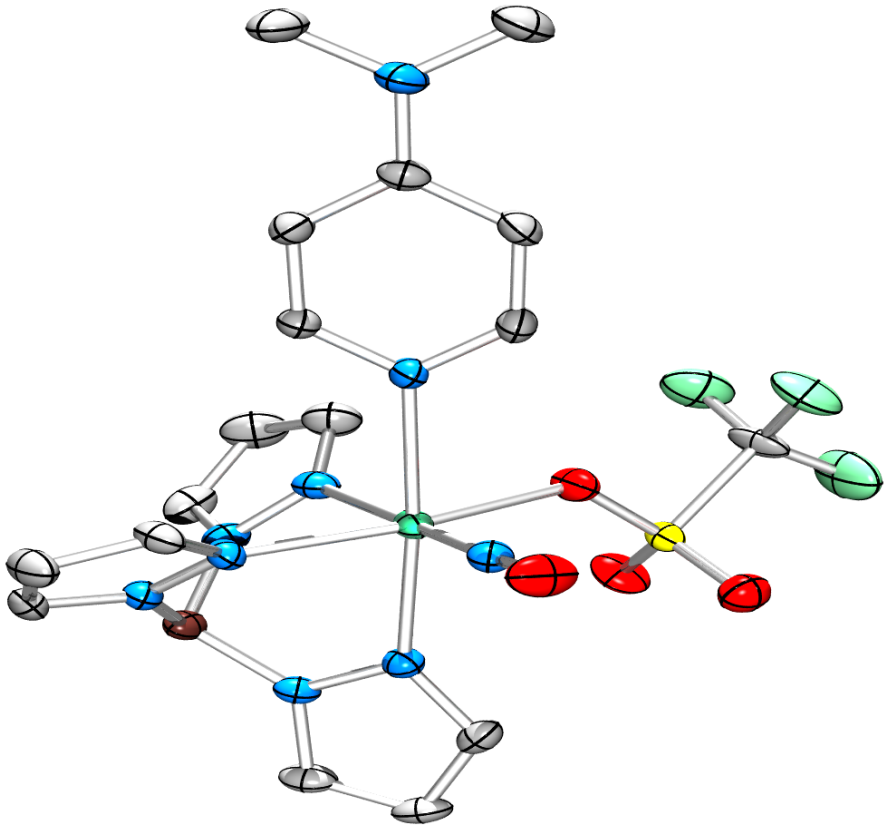


Table 1. Sample and crystal data for $C_{17}H_{20}BF_3MoN_9O_4S$.

Identification code	Harman_20JTM299
Chemical formula	$C_{17}H_{20}BF_3MoN_9O_4S$
Formula weight	610.23 g/mol
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal size	0.131 x 0.131 x 0.509 mm
Crystal habit	green rod
Crystal system	monoclinic
Space group	P 2_1/n

Unit cell dimensions	a = 15.4891(13) Å	α = 90°
	b = 8.9300(8) Å	β = 107.675(2)°
	c = 18.1362(16) Å	γ = 90°
Volume	2390.1(4) $Å^3$	
Z	4	
Density (calculated)	1.696 g/cm^3	
Absorption coefficient	0.704 mm^{-1}	
F(000)	1228	

Table 2. Data collection and structure refinement for $C_{17}H_{20}BF_3MoN_9O_4S$.

Diffractometer	Bruker Kappa APEXII Duo
Radiation source	fine-focus sealed tube (Mo K_α, λ = 0.71073 Å)
Theta range for data collection	1.52 to 27.14°
Index ranges	-18<=h<=19, -10<=k<=11, -23<=l<=23
Reflections collected	24474
Independent reflections	5284 [R(int) = 0.0433]
Coverage of independent reflections	99.8%
Absorption correction	Multi-Scan
Max. and min. transmission	0.9130 and 0.7160
Structure solution technique	direct methods
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2017/1 (Sheldrick, 2017)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$

Data / restraints / parameters	5284 / 0 / 362	
Goodness-of-fit on F^2	1.058	
Δ/σ_{max}	0.001	
Final R indices	3950 data; $I>2\sigma(I)$	R1 = 0.0434, wR2 = 0.0874
	all data	R1 = 0.0694, wR2 = 0.0974
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0324P)^2+5.1049P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	1.753 and -0.805 eÅ^{-3}	
R.M.S. deviation from mean	0.094 eÅ^{-3}	

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for $C_{17}H_{20}BF_3MoN_9O_4S$.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
Mo1	0.52033(2)	0.74491(4)	0.23095(2)	0.02044(9)
F1	0.23906(17)	0.0302(3)	0.14639(15)	0.0515(7)
F2	0.17889(16)	0.9670(4)	0.02718(15)	0.0643(9)
O1	0.6167(2)	0.0382(3)	0.25938(17)	0.0447(8)
O2	0.38596(16)	0.8228(3)	0.16875(13)	0.0337(7)
O4	0.32013(18)	0.7397(3)	0.03602(15)	0.0377(7)
N1	0.45404(19)	0.5229(4)	0.21780(16)	0.0251(7)
N2	0.4948(2)	0.4016(3)	0.19735(16)	0.0258(7)
N3	0.63843(18)	0.6216(3)	0.29048(15)	0.0216(6)

	x/a	y/b	z/c	U(eq)
N4	0.65351(19)	0.4840(3)	0.26377(15)	0.0224(6)
N5	0.55514(18)	0.6816(3)	0.12909(15)	0.0216(6)
N6	0.58363(19)	0.5383(3)	0.12290(15)	0.0220(6)
N7	0.5770(2)	0.9205(4)	0.24541(16)	0.0268(7)
N8	0.47525(18)	0.7775(3)	0.33327(15)	0.0221(7)
N9	0.3972(2)	0.8529(4)	0.53218(17)	0.0310(7)
C1	0.3744(3)	0.4767(5)	0.2220(2)	0.0359(10)
C2	0.3632(3)	0.3256(5)	0.2048(2)	0.0425(11)
C3	0.4410(3)	0.2825(4)	0.1893(2)	0.0343(10)
C4	0.7062(2)	0.6444(5)	0.35629(19)	0.0262(8)
C5	0.7642(2)	0.5250(5)	0.3718(2)	0.0354(10)
C6	0.7295(2)	0.4263(5)	0.3124(2)	0.0298(9)
C7	0.5622(2)	0.7555(5)	0.06702(18)	0.0260(8)
C8	0.5959(2)	0.6627(5)	0.02146(19)	0.0301(9)
C9	0.6087(2)	0.5267(5)	0.05828(19)	0.0282(8)
C10	0.4265(2)	0.8987(4)	0.3405(2)	0.0275(8)
C11	0.3982(2)	0.9266(4)	0.4040(2)	0.0287(8)
C12	0.4222(2)	0.8283(4)	0.4680(2)	0.0253(8)
C13	0.4749(2)	0.7052(4)	0.4608(2)	0.0263(8)
C14	0.4979(2)	0.6829(4)	0.39443(19)	0.0241(8)
C15	0.3384(3)	0.9780(5)	0.5353(2)	0.0411(10)
C16	0.4282(3)	0.7538(5)	0.5990(2)	0.0395(10)
B1	0.5898(3)	0.4202(5)	0.1870(2)	0.0235(9)
S1	0.34163(9)	0.86259(15)	0.08793(6)	0.0202(4)

	x/a	y/b	z/c	U(eq)
F3	0.1894(2)	0.8088(4)	0.1174(2)	0.0507(10)
O3	0.3792(2)	0.9929(4)	0.06438(18)	0.0349(8)
C17	0.2308(3)	0.9198(7)	0.0958(3)	0.0338(13)
S1A	0.3024(10)	0.8013(18)	0.1055(6)	0.050(5)
F3A	0.307(2)	0.065(3)	0.0586(14)	0.083(12)
O3A	0.235(2)	0.729(3)	0.1418(17)	0.056(9)
C17A	0.260(3)	0.941(7)	0.085(3)	0.0338(13)

Table 4. Bond lengths (Å) for $C_{17}H_{20}BF_3MoN_9O_4S$.

Mo1-N7	1.777(3)	Mo1-N3	2.127(3)
Mo1-N5	2.151(3)	Mo1-O2	2.159(2)
Mo1-N8	2.191(3)	Mo1-N1	2.212(3)
F1-C17	1.325(6)	F1-C17A	1.48(5)
F2-C17	1.329(6)	F2-C17A	1.39(4)
O1-N7	1.205(4)	O2-S1A	1.458(11)
O2-S1	1.461(2)	O4-S1	1.418(3)
O4-S1A	1.476(12)	N1-C1	1.325(5)
N1-N2	1.361(4)	N2-C3	1.333(5)
N2-B1	1.548(5)	N3-C4	1.344(4)
N3-N4	1.366(4)	N4-C6	1.341(4)
N4-B1	1.550(5)	N5-C7	1.338(4)
N5-N6	1.369(4)	N6-C9	1.346(4)
N6-B1	1.551(5)	N8-C10	1.349(5)
N8-C14	1.353(4)	N9-C12	1.352(4)

N9-C15	1.453(5)	N9-C16	1.459(5)
C1-C2	1.385(6)	C1-H1	0.95
C2-C3	1.372(6)	C2-H2	0.95
C3-H3	0.95	C4-C5	1.368(5)
C4-H4	0.95	C5-C6	1.369(6)
C5-H5	0.95	C6-H6	0.95
C7-C8	1.379(5)	C7-H7	0.95
C8-C9	1.370(6)	C8-H8	0.95
C9-H9	0.95	C10-C11	1.372(5)
C10-H10	0.95	C11-C12	1.413(5)
C11-H11	0.95	C12-C13	1.398(5)
C13-C14	1.370(5)	C13-H13	0.95
C14-H14	0.95	C15-H15A	0.98
C15-H15B	0.98	C15-H15C	0.98
C16-H16A	0.98	C16-H16B	0.98
C16-H16C	0.98	B1-H1A	1.04(4)
S1-O3	1.424(4)	S1-C17	1.838(5)
F3-C17	1.304(7)	S1A-C17A	1.41(6)
S1A-O3A	1.53(4)	F3A-C17A	1.47(6)

Table 5. Anisotropic atomic displacement parameters (Å^2) for $C_{17}H_{20}BF_3MoN_9O_4S$.

The anisotropic atomic displacement factor exponent takes the form: -
$2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mo1	0.02171(15)	0.02422(16)	0.01510(13)	-0.00123(13)	0.00513(10)	0.00429(14)
F1	0.0473(14)	0.0523(17)	0.0599(16)	-0.0275(14)	0.0235(13)	0.0047(13)
F2	0.0362(14)	0.105(3)	0.0434(15)	0.0055(16)	0.0001(12)	0.0299(15)
O1	0.066(2)	0.0260(17)	0.0535(18)	-0.0110(14)	0.0355(16)	-0.0130(15)
O2	0.0274(13)	0.0534(19)	0.0189(12)	0.0038(12)	0.0049(10)	0.0140(13)
O4	0.0384(15)	0.0375(17)	0.0364(14)	-0.0203(13)	0.0100(12)	-0.0003(13)
N1	0.0244(15)	0.0330(18)	0.0203(14)	-0.0021(13)	0.0102(12)	0.0002(14)
N2	0.0322(16)	0.0256(17)	0.0211(14)	-0.0025(12)	0.0101(13)	-0.0049(14)
N3	0.0222(14)	0.0236(16)	0.0191(13)	-0.0004(12)	0.0067(11)	0.0054(12)
N4	0.0250(15)	0.0236(16)	0.0202(13)	0.0008(12)	0.0092(12)	0.0053(13)
N5	0.0225(14)	0.0245(16)	0.0178(13)	-0.0007(12)	0.0059(11)	0.0005(12)
N6	0.0230(14)	0.0251(17)	0.0202(13)	-0.0049(12)	0.0099(12)	-0.0015(13)
N7	0.0336(17)	0.0272(18)	0.0221(14)	0.0005(13)	0.0125(13)	0.0056(14)
N8	0.0234(14)	0.0244(18)	0.0186(13)	0.0014(11)	0.0064(11)	0.0052(12)
N9	0.0367(18)	0.0322(19)	0.0292(16)	-0.0042(14)	0.0179(14)	0.0036(15)
C1	0.031(2)	0.044(3)	0.036(2)	-0.0041(18)	0.0145(17)	-0.0063(19)
C2	0.037(2)	0.051(3)	0.044(2)	-0.006(2)	0.0178(19)	-0.018(2)
C3	0.048(2)	0.027(2)	0.0272(18)	-0.0029(15)	0.0112(17)	-0.0098(18)
C4	0.0191(16)	0.039(2)	0.0204(16)	-0.0062(15)	0.0054(13)	0.0040(16)
C5	0.0239(19)	0.056(3)	0.0235(18)	0.0014(18)	0.0036(15)	0.0122(19)
C6	0.0277(19)	0.037(2)	0.0277(18)	0.0069(16)	0.0129(15)	0.0151(17)
C7	0.0234(16)	0.031(2)	0.0217(15)	0.0069(16)	0.0039(13)	-0.0041(17)
C8	0.0291(19)	0.046(3)	0.0182(16)	-0.0027(16)	0.0119(15)	-0.0086(18)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C9	0.0265(18)	0.041(2)	0.0195(16)	-0.0097(16)	0.0098(14)	-0.0047(17)
C10	0.033(2)	0.026(2)	0.0237(17)	0.0044(15)	0.0076(15)	0.0071(16)
C11	0.0296(19)	0.027(2)	0.0306(19)	-0.0023(16)	0.0115(16)	0.0082(16)
C12	0.0219(17)	0.029(2)	0.0263(17)	-0.0057(15)	0.0095(14)	-0.0040(16)
C13	0.0312(19)	0.026(2)	0.0230(16)	0.0024(14)	0.0097(15)	0.0007(15)
C14	0.0265(18)	0.0252(19)	0.0219(16)	-0.0001(14)	0.0093(14)	0.0040(15)
C15	0.044(2)	0.041(3)	0.045(2)	-0.009(2)	0.024(2)	0.006(2)
C16	0.057(3)	0.038(2)	0.0307(18)	-0.0011(19)	0.0254(18)	0.002(2)
B1	0.030(2)	0.020(2)	0.0230(19)	-0.0029(16)	0.0124(17)	0.0007(17)
S1	0.0172(6)	0.0257(7)	0.0162(5)	-0.0029(4)	0.0026(4)	0.0029(5)
F3	0.0363(17)	0.058(2)	0.067(2)	-0.0113(18)	0.0284(16)	-0.0142(18)
O3	0.0382(19)	0.0324(19)	0.0358(17)	0.0020(14)	0.0140(15)	-0.0032(16)
C17	0.014(3)	0.057(4)	0.030(2)	-0.012(2)	0.0072(19)	0.005(3)
S1A	0.048(7)	0.067(9)	0.032(5)	-0.004(5)	0.004(5)	0.006(7)
F3A	0.14(3)	0.054(18)	0.043(14)	0.002(12)	0.006(16)	-0.028(19)
O3A	0.047(16)	0.026(16)	0.073(19)	0.020(13)	-0.014(15)	-0.018(13)
C17A	0.014(3)	0.057(4)	0.030(2)	-0.012(2)	0.0072(19)	0.005(3)

Table 6. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for $C_{17}H_{20}BF_3MoN_9O_4S$.

	x/a	y/b	z/c	U(eq)
H1	0.3311	0.5384	0.2350	0.043
H2	0.3126	0.2647	0.2039	0.051
H3	0.4541	0.1845	0.1753	0.041

	x/a	y/b	z/c	U(eq)
H4	0.7128	0.7314	0.3877	0.031
H5	0.8173	0.5130	0.4147	0.043
H6	0.7552	0.3321	0.3066	0.036
H7	0.5464	0.8576	0.0559	0.031
H8	0.6076	0.6877	-0.0255	0.036
H9	0.6315	0.4390	0.0411	0.034
H10	0.4108	0.9690	0.2992	0.033
H11	0.3624	1.0124	0.4048	0.034
H13	0.4950	0.6363	0.5024	0.032
H14	0.5318	0.5958	0.3911	0.029
H15A	0.3705	1.0722	0.5346	0.062
H15B	0.3213	0.9720	0.5830	0.062
H15C	0.2838	0.9740	0.4905	0.062
H16A	0.3968	0.6574	0.5871	0.059
H16B	0.4151	0.7994	0.6435	0.059
H16C	0.4937	0.7379	0.6112	0.059
H1A	0.614(2)	0.320(5)	0.172(2)	0.030(10)