ORGANOMETALLICS

Article

Spatial Recognition Within Terpenes: Redox and H-bond Promoted Linkage Isomerizations and the Selective Binding of Complex Alkenes

Steven J. Dakermanji, Karl S. Westendorff, Emmit K. Pert, Katy B. Wilson, Jeffery T. Myers, Justin H. Wilde, Diane A. Dickie, Kevin D. Welch, and W. Dean Harman*



INTRODUCTION

accompanied by significant decomposition.

Since Zeise's discovery in 1830,¹ the ability of a transition metal to bind an alkene through interactions with 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, their interaction can be substantial, with the complex taking on features of a metallocyclopropane in which the bound carbons has tetrahedral geometry (Dewar–Chatt–Duncanson ; eq 1). Depending on the symmetry of the ligands (L) and alkene substituents (R), the metal and bound alkene carbons can all become independent stereogenic centers:



Our interest in controlling the regio- and stereochemistry of dihapto-coordinated alkenes, as well as for η^2 -polyenes and η^2 -aromatics, stems from our research objective to use these systems as a foundation for the preparation of novel organic compounds.⁴⁻⁶ Our approach 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 multiple isomers. As pioneering work by Gladysz et al. has 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 1).

[M] = WTp(NO)(PMe₃) or MoTp(NO)(DMAP)



Figure 1. Eight isomers resulting from propene complexed to an asymmetric transition metal fragment.

For molecules with more than one alkene unit, the situation becomes more complicated, owing to the possibility of constitutional isomers. Consider, for example, the dienes (*R*)-limonene or taxadiene (Figure 2), where a single enantiomer of these terpenes gives 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 -

 Received:
 March 2, 2020

 Published:
 April 27, 2020





© 2020 American Chemical Society

pubs.acs.org/Organometallics



Figure 2. Examples of a diene, triene, and arene that could form dihapto-coordinated π complexes with a metal.

coordination isomers are possible, respectively, even though these hydrocarbons themselves are achiral.

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 generally facile at ambient temperatures, and binding selectivity usually is governed by thermodynamic factors.⁴ However, for alkenes and nonaromatic polyenes, their coordination often results in complex isomeric mixtures, even in cases where thermodynamic factors favor one isomer over others. Attempts to equilibrate these isomers through heating typically result in ligand displacement or compound decomposition (vide infra), similar to what others have observed.¹⁵

How can one avoid the kinetic traps associated with dihaptocoordination of polyalkenes with π -basic transition metal complexes? We hypothesized (Figure 3) that the complex



Figure 3. Reaction coordinate for the proposed Lewis-acid- or redoxpromoted isomerization of an alkene 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 weakened to the point that isomerization could occur (red curve, Figure 3). The following account demonstrates the promise of such an approach to alkene-complex isomerization.

RESULTS AND DISCUSSION

1. Propene: Mapping Out the Steric Profile of a π -Base. In an earlier study,¹⁶ the complex ReTp(MeIm)(CO)- $(\eta^2$ -propene) was prepared as a racemic mixture of four diastereomers (Figure 4). The {ReTp(CO)(MeIm)} fragment



Figure 4. Four diastereomers of the rhenium propene complex $\operatorname{ReTp}(\operatorname{CO})(\operatorname{MeIm})(\eta^2$ -propene) (energies experimentally determined).¹⁶

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 $d\pi$ orbitals, leaving the HOMO oriented in a plane perpendicular to the Re-CO bond axis. As a result, the alkene orients 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 4). At ambient temperatures, interconversion of rotamers is facile, but an intramolecular face-flip isomerization, such as initially proposed by Gladysz et al., 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 much higher, owing to the greater difference in energy between the HOMO and the other $d\pi$ orbital capable of π bonding with the alkene.⁴

Propene complexes for both the molybdenum (1A-D) and tungsten (2A-D) systems were modeled using DFT calculations at the B3LYP level of theory. The hybrid basis set utilized used LANL2DZ and its associated pseudopotentials for metal atoms and 6-31G* for all other atoms. Of the four diastereomers for each system, the isomer placing the methyl group in the C quadrant, 1C or 2C, is the least stable (Figure 5), owing to steric interactions with the pyrazole ligand trans to the NO ligand. For the tungsten system, steric interactions in the C quadrant are compounded by the PMe₃ group (6.4 kcal/mol calculated for tungsten vs 2.4 kcal/mol calculated for the molybdenum; Gibbs free energy, 298 K). For all three systems (Re, Mo, W), the three remaining isomers are of similar energy, and thus, the synthesis of 1 and 2 were not pursued. Nonetheless, these modeling studies verify the general steric profile for the W and Mo systems as being similar to their {ReTp(CO)(MeIm)} predecessor.¹⁶

2. *trans*-**3**-Hexene: "Face-Flip" Isomerization. The hydrocarbon *trans*-**3**-hexene was chosen as a test case in which only two isomers (face-flip diastereomers) were possible, as rotation about the metal- π bond does not generate a unique isomer. Further, since only one of these isomers avoids placing an ethyl group in the C quadrant, that isomer should be thermodynamically favored. The {MoTp(NO)-(DMAP)} synthon,¹⁸ MoTp(NO)(DMAP)(η^2 - α , α , α -trifluor-



Figure 5. Relative calculated energies (BL3LYP; vacuum) for the four diastereomers of group 6 propene complexes and the methyl steric profiles for $MoTp(NO)(DMAP)(\eta^2\text{-propene})$ and $WTp(NO)-(PMe_3)(\eta^2\text{-propene})$. (Gibbs free energy; 298 K; kcal/mol).

otoluene), was dissolved in THF along with an excess of 3hexene and stirred overnight. An ¹H NMR spectrum taken of the crude reaction mixture reveals the kinetic ratio is close to 1:1. After chromatography, the resulting hexene complex **3** was isolated by precipitation into pentane (55%) as a mixture of diastereomers. The ratio of **3A:3B** varied from 1:1 to 2:1 over several trials, depending on the extent of precipitation. A similar process was used to prepare the tungsten complex **4**, this time using the {WTp(NO)(PMe₃)} synthon, WTp(NO)-(PMe₃)(η^2 -benzene).¹⁹ A ³¹P NMR spectrum indicated that **4A** and **4B** were formed in a 1:1 ratio, but in contrast to its molybdenum congener, initial precipitation (pentane) from the reaction solution yielded only isomer **4B**. Isolation of the bulk of the mixture was accomplished by adding additional pentane to the filtrate.

Structural assignments for 3A, 3B, 4A, and 4B were made on the basis of NOESY and COSY data, as well as the characteristic upfield shift of the bound alkene proton in quadrant B, (~1.8 ppm), which resides in a pocket flanked by two pyrazole rings (Figure 6).

As a control, a 2:1 mixture (3A:3B) of the molybdenum hexene complex was dissolved in acetone- d_6 and allowed to stand. Over the course of several days, ¹H NMR spectra reveal a gradual loss in the signals corresponding to 3 ($t_{1/2} \sim 4$ days). This was accompanied by the formation of a significant amount of the acetone complex 5. Repeating this reaction in an acetone- d_6 /DMF- d_7 mixture, using the DMF- d_6 impurity as an integration standard, confirmed that there was virtually no



Figure 6. Relative calculated energies (BL3LYP; vacuum) for the two diastereomers of the *trans*-3-hexene complexes 3 and 4, which are shown from different perspectives (used herein). (Gibbs free energy; 298 K; kcal/mol).

change in the ratio of isomers after 72 h at 25 °C. The hypothesis that we aimed to validate was that treatment of **3** with an additive could decrease electron density at the metal and therefore hasten the isomerization from one face of the hexene ligand to the other face. We envisioned this could be accomplished either by interaction of the Lewis-basic nitrosyl ligand or by transient oxidation of the metal (Figure 7).

The oxidant was chosen in order to avoid stoichiometric oxidation of the Mo(0). A cyclic voltammogram of the 3A/3Bmixture in DMA shows a single anodic wave at 0.03 V (vs NHE). Upon return scan, the only cathodic peak present is one at -1.20 V, corresponding to the DMA complex $[MoTp(NO)(DMAP)(\kappa^{1} - O-DMA)]^{+}$. This compound was verified by its independent synthesis and crystal structure.²⁰ Decamethylferricenium tetrakis [3,5-bis(trifluoromethyl)phenyl]borate, $(Fe(Cp^*)_2)(BArF)$ ($E^\circ = 0.04$ V, NHE) has a potential near 3 and $(CoCp_2)(BArF)$ ($E^{\circ} = -0.78$ V, NHE) has a potential considerably negative of 3. We found that both were capable of promoting the isomerization, but the more oxidizing ferrocenium ion provided the faster oxidation, even at reduced concentration (cf. $t_{1/2}$ FeCp₂^{*+} ~ 40 min (25 °C, 11 mM, 0.25 equiv); $t_{1/2}$ CoCp₂⁺ ~ 4 h (25 °C, 85 mM, 0.43 equiv)). As shown in Figure 7, addition of 0.25 equiv of decamethylferricenium ion allows for >95% conversion of the mixture of 3A to 3B in less than 3 h (TON > 4). Previously reported examples of redox-promoted linkage-isomerizations have involved sigma-bound heteroatoms.²¹⁻

Addition of a Lewis acid or strong H-donor solvent was found to accelerate the isomerization of the hexene coordination diastereomers (**3A** to **3B**; Figure 7). For example, a 0.28 M solution of the fluorinated alcohol 1,1,1,3,3,3hexafluoro-2-propanol (HFIP) in trifluorotoluene allows for conversion of a 2:1 mixture of **3A**:**3B** to **3B** exclusively, with a half-life of about 40 min, with only minimal formation (5%) of the acetone complex **5**. Similar behavior was seen with nonafluoro-*t*-butanol. Meanwhile, Lewis acids, such as BF₃. Et₂O and Zn(OTf)₂ (0.1 equiv), also promoted the isomerization on a similar time scale. However, these isomerization



Figure 7. ¹H NMR spectra of a starting mixture of 3A/3B and after addition of $[FeCp*_2](BArF)$ (only 3B remains).

reactions were accompanied by formation of large amounts of free *trans*-3-hexene as observed by ¹H NMR, indicating decomposition of the alkene complex **3**. 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 CH₃OTf was added to a solution of **3A** and **3B** in a deuterated solvent. Within minutes, an ¹H 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 singlet at 4.11 ppm integrating to three protons and a full set of hexene signals shifted downfield support the formation of **3B**·CH₃ (Figure 7).^{24,25} While there is decomposition associated with methyl triflate addition, the methylated analogue **3B·CH₃** was formed in roughly 65% yield.

The mechanism for the face-flip isomerization on Mo(0) is postulated to occur via a complex weakly coordinated at hydrogen (Figure 8), where rotation can easily occur. While a transition state leading to this intermediate was elusive, we were able to capture a κ -H *intermediate* (**3** κ H) roughly 26 kcal/mol above the ground state (Figure 8), which can be treated as a lower limit for the transition state. This species is about 2 kcal lower in enthalpy than complete dissociation.



Figure 8. Reaction coordinate diagram for an uncatalyzed face-flip isomerization of Mo(0)-*trans*-hexene complex, **3A** to **3B**. The κ -H complex is an intermediate (**3\kappaH**) roughly 26 kcal/mol above ground state. For an *R* configuration of the metal, isomerization from the *Si* face to the *Re* face of the *trans*-hexene is spontaneous (calculated enthalpies; BL3LYP; vacuum).

When one electron is removed from 3A, the reaction energy barrier drops to about 12 kcal/mol (Figure 9). The purported Mo(I) species derived from 3A is not in the ground state



Figure 9. Reaction coordinate diagram for the face-flip isomerization of purported transient Mo(I)-trans-hexene complex ($3A^+$ to $3B^+$). The κ -H complex is a transition state roughly 12 kcal/mol above ground state.

geometry and must undergo a 90° rotation to form $3A^+$. To get to the transition state, the hexene π -bond is released and a κ -H complex now becomes the transition state according to DFT calculations (Figure 9). After rotation, collapse of the κ -H complex leads to the isomer $3B^+$. Effectively, the Mo(I) barrier to isomerization has dropped roughly by half (from 26 to 12 kcal/mol). The decrease in calculated activation energy is supported by a markedly decreased half-life of isomerization (vide supra) in the presence of a redox catalyst.

Regarding the Lewis-acid and H-donor accelerated face-flip reactions, it is unclear whether this is simply a result of electron-withdrawal from the π basic metal via the nitrosyl ligand, which would weaken the M-alkene bond, or whether a small amount of oxidation is occurring at the metal, opening up a Mo(I) reaction pathway (vide supra).

The tungsten variation of the 3-hexene complex (4) acts differently than its molybdenum analogue. In contrast to the single $E_{p,a}$ for the **3A** and **3B** mixture, the two isomers are wellseparated electrochemically, with an $E_{p,a}$ corresponding to 4A at $E_{p,a}$ = 0.18 V (100 mV/s), and a reversible couple for 4B at $E_{1/2}$ = 0.29 V. In addition, when 4A is oxidized during the course of a cyclic voltammogram, the reversible couple at 0.29 V is generated, corresponding to formation of 4B. An anodic sweep of isolated 4B, in contrast, does not lead to any features corresponding to $4A^+$ or 4A. The generation of 4B from 4A in the cyclic voltammogram experiment provides supporting evidence for an oxidant-catalyzed isomerization reaction, but attempts to catalyze this reaction chemically were unsuccessful. Use of 0.1 equiv of $[Fe(Cp^*)_2](BArF)$ or $[Co(Cp)_2](BArF)$, was ineffective in converting 4A to 4B, as were multiple equivalents of fluorinated alcohols, (~5 equiv). Even methyl triflate led to the same 1:1 mixture of isomers, resulting in only nitrosyl methylation (4A·CH₃; 4B·CH₃). Meanwhile, treatment with a full equivalent of the stronger oxidant $[Fe(Cp)_2]$ -(BArF) fully oxidizes 4. Interestingly, we found that using a stoichiometric amount of $[Fe(Cp^*)_2](BARF)$ (1:1, relative to 4A) allows for full conversion of 4A to 4B within 30 s of oxidant addition (Figure 10) with little decomposition (<5%). It appears that this isomerization is accompanied by loss of the $[Fe(Cp^*)_2]^+$, and thus is not catalytic, but the isomerization can still be promoted by this oxidant.

3. 1,3-Cyclohexadiene: Constitutional Isomerization for Conjugated Dienes. In principle, 1,3-cyclohexadiene can



Figure 10. Initial 1:1 mixture of the diastereomers of 4 (a) and the resolution of only 4B by decamethylferricenium (b).

react with either $\{MoTp(NO)(DMAP)\}$ or $\{WTp(NO)-(PMe_3)\}$ to form eight different stereoisomers (four pairs of enantiomers). DFT calculations shown in Figure 11 find that



Figure 11. Cyclohexadiene complex diastereomers of molybdenum (6) and tungsten (7) showing various isomerization mechanisms. W = $WTp(NO)(PMe_3)$ and Mo = MoTp(NO)(DMAP) (Gibbs free energy; 298 K; kcal/mol).

only three isomers are energetically competitive for either metal. Previously, we have reported that both {MoTp(NO)-(MeIm)} and {WTp(NO)(PMe_3)} react with 1,3-cyclo-hexadiene to form diastereomers A and D.^{26,27} We envisioned a process in which a "ring-slip" (intrafacial isomerization) from **D** to **A** could be accomplished via a redox-catalyzed mechanism similar to the face-flip (interfacial isomerization) described above. This would be particularly valuable in cases where the two alkene binding sites were chemically distinguishable (vide infra). For the tungsten system, DFT calculations identify an η^4 -diene transition state (7^{+*}; Figure 12) on the reaction coordinate between the two η^2 -diene isomers for the W(I) complex [WTp(NO)(PMe_3)(η^2 -1,3-cyclohexadiene)]⁺ (7A⁺ and 7B⁺) that is 11.6 kcal above the η^2 -alkene 7A⁺.

Given that DFT studies find the two diastereomers A and D to be virtually isoergic for both the $\{MoTp(NO)(DMAP)\}$ and $\{WTp(NO)(PMe_3)\}$ systems, 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 face-flip (interfacial isomerization) rather than the "ring-slip", we intended to probe (Figure 11). Thus, we opted instead to investigate the substituted cyclohexadiene complex 8 (Figure 13), which could be prepared solely as its kinetic isomer (8A) from benzene.²⁵ The 3,4- η^2 -diene complex 8A was determined to be roughly 0.8 kcal/mol more stable than its $1,2-\eta^2$ isomer **8B** via DFT calculations (Gibbs free energy; 298 K kcal/mol). Yet this linkage isomerization shown in Figure 13 was accomplished in 87% isolated yield with 0.1 equiv of the mild oxidant ([Fe(Cp*)₂] (Tf₂N)). Complex 8A has an $E_{p,a} = 0.54$ V, whereas the decamethylferricenium cation has a Fe(III)/Fe(II)couple with an $E_{1/2}$ = +0.04 V (DMA). X-ray molecular structure determinations of single crystals of both 8A and 8B



Figure 12. Energy barriers for intrafacial isomerization of a 1,3-cyclohexadiene complex of $\{WTp(NO)(PMe_3)\}$ and the transition state 7^{+*}.



Figure 13. Redox-catalyzed intrafacial isomerization of a 1,5-disubstituted 1,3-cyclohexadiene tungsten complex. $[O]^+ = [FeCp*_2] - (Tf_2N); [R] = FeCp*_2.$

provided confirmation of the purported isomerization.²⁵ The addition of cobaltocenium bistriflimide did not have a noticeable effect on the isomerization, nor did the use of HFIP. A molybdenum analogue of **8A** has been prepared from trifluorotoluene,²⁸ but in this case, the CF₃ substituent on C1 destabilizes the purported analogue of **8B**, and thus this

reaction was not further pursued. Of note, aside from these group 6 complexes, dihapto-coordinated 1,3-cyclohexadiene complexes remain uncommon.^{29,30}

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 14). Of these, 10 can be



Figure 14. Sixteen possible isomers shown for the limonene complexes (9: $WTp(NO)(PMe_3)$, 10: MoTp(NO)(DMAP)). (Gibbs free energy; 298 K; kcal/mol).

considered thermodynamically unstable for either MoTp-(NO)(DMAP) or WTp $(NO)(PMe_3)$, as they have a carbon extending into the C quadrant (red, Figure 14). On the basis of DFT calculations, another three isomers (in orange) are between 1 and 6 kcal/mol destabilized compared to the three most stable isomers (in green). All three low-energy isomers are bound through the propenyl group and have a hydrogen extending into quadrant C. Correspondingly, their energies differ by less than 1 kcal/mol for either metal.

When the molybdenum limonene complex was synthesized from a racemic metal source such as $MoTp(NO)(DMAP)(\eta^2$ -TFT = α,α,α -trifluorotoluene) or by reduction of MoTp-(NO)(DMAP)(I), multiple pairs of diamagnetic complexes were formed according to the ¹H NMR spectrum of the isolated product mixture (Figure 15, a). We found the Pz4 region of the NMR spectrum (5.9–6.4 ppm) to be relatively free of other signals, and thus, it proved to be a valuable window for determining the number of diamagnetic complexes present in solution. Remarkably, treatment with 0.1 equiv of cobaltocenium ion resulted in a simplification of the NMR spectrum but not without significant decomposition of the complex. However, when the complex mixture was treated



Figure 15. NMR data for the Mo-limonene complex **9** showing Tp H4 and DMAP protons for: (a) initial mixture of isomers, (b) 1:1 mixture of (S_{Mo},S) -**9** and (R_{Mo},R) -**9** after redox catalyst addition, (c) (S_{Mo},R) -**9A**, prepared from (R_{Mo},S) -**11** d) (R_{Mo},R) -**9A**, prepared from (R_{Mo},R) -**11**.

with ~5 equiv of HFIP in trifluorotoluene, the many isomers of the Mo complex converged into just two within 45 min (Figure 13, b). In an earlier report,²⁸ the terpene α -pinene was used to prepare enantioenriched versions of {MoTp(NO)-(DMAP)}. When either MoTp(NO)(DMAP)(η^2 -(R)- α pinene) ((R_{Mo} ,R)-11) or MoTp(NO)(DMAP)(η^2 -(S)- α pinene) ((S_{Mo} ,S)-11) was added to (R)-limonene with HFIP present, *a single major compound* (Figure 15, c, d) was synthesized, with only minor amounts (~10:1) of the other metal diastereomer present. An unknown side product (~20%) also appeared in solution.

Crystals from the diastereomeric mixture of (R_{Mo},R) -9A and $(S_{Mot}R)$ -9A (as prepared from (racemic) MoTp(NO)- $(DMAP)(\eta^2 - \alpha, \alpha, \alpha - trifluorotoluene)$ were grown and analyzed. The analysis confirmed the postulated structure (Figure 16), but showed significant disorder in the limonene ring, owing to this complex packing in the P-1 space group. Because this space group requires an inversion center, it also requires both enantiomers of the limonene ligand to be present, which calls into question the validity of the P-1 symmetry. Attempts to solve the structure in lower symmetry (P1), required to conserve the *R* stereocenter of the limonene, resolved the disorder issue in the limonene ring, but nonhydrogen atoms were refined anisotropically with EADP constraints on most of the pseudosymmetrically related atoms. Our efforts to grow crystals from enantioenriched versions of 9A via α -pinene complexes (S_{Mo},S) -9 or (R_{Mo},R) -9 resulted in the same unit cell with pseudo P-1 symmetry as that prepared from a racemic source of $\{MoTp(NO)(DMAP)\}$.

Combining WTp(NO)(PMe₃)(η^2 -benzene) with (*R*)-limonene in DME again results in the formation of multiple isomers (~10; estimated from ³¹P NMR spectra). Initial attempts to isolate a solid from the reaction solution caused a selective precipitation of a single diastereomer (3% mass recovered). According to a comparison of ¹H NMR data with the molybdenum analogues, the isomer is thought to be (S_W,R)-**10A** (Figure 14). Further precipitation from the reaction mixture provided most of the mass, which was shown to be a mixture of ~10 isomers. Attempts to converge this mixture into just two isomers using 0.1 equiv of a redox catalyst or 5 equiv of HFIP failed. Use of a half equivalent of



Figure 16. (S_{Mo},R) -**9A** prepared from (S_{Mo},S) - α -pinene, and (R_{Mo},R) -**9A**, prepared from (S_{Mo},R) - α -pinene, and a solid-state structure (solved in P1) of a diastereomeric mixture of **9A**. Note the pseudo inversion center.

decamethylferricenium ion causes some simplification, but nothing approaching the results seen with the Mo analogue (9). Interestingly, small crystals formed from a dilute pentane solution of **10** were shown to be a 1:1 mixture of (R_W, R) -**10A** and (S_W, R) -**10A**. Few limonene complexes with transition metals have been reported,^{31–34} and in only one case was the limonene bound in a dihapto fashion.³¹ For the complex MoCp*(NO)(CO)(limonene), a mixture of isomers was reported.³¹

5. Humulene: Constitutional Isomerization of an Unconjugated Triene. The achiral sesquiterpene α -humulene can bind in a dihapto fashion to a metal complex forming up to 12 enantiomeric pairs of isomers (12, 13). These are shown for the R form of the {MoTp(NO)(DMAP)} and {WTp(NO)(PMe_3)} fragments in Figure 17. Of the 12 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 17. For both the molybdenum and tungsten systems, isomers A and B were found to be the lowest energy (green), with the *trisubstituted* isomer A being the lowest energy for both.

As expected, when humulene was combined with either MoTp(NO)(DMAP)(η^2 -trifluorotoluene) or WTp(NO)-(PMe₃)(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 (decamethylferrice-nium BArF, 0.25 equiv) or a fluorinated alcohol (HFIP, > 2



Figure 17. Twelve possible isomers possible when humulene binds to the R configuration of either $\{MoTp(NO)(DMAP)\}$ (12) or $\{WTp(NO)(PMe_3)\}$ (13). DFT calculations (Gibbs free energy; 298 K; kcal/mol) were carried out on the four lowest energy isomers (isomers with no substituent projecting into the C quadrant).

equiv), ¹H NMR data shows that the number of isomers in solution *converges to just one major product* (**12A**, Figure 18, 19; vide infra). Two minor complexes were detected (\sim 5%), as well as a moderate amount of oxidation (\sim 30%). Unambiguous assignment of all of the ring protons, even from a full 2D NMR analysis that included COSY, NOESY, HSQC, and



Figure 18. Formation of a mixture of isomers of the form $MoTp(NO)(DMAP)(\eta^2$ -humulene) (12) (a) and their conversion to one major isomer (12A) (b).



Figure 19. Conversion of **12A** MoTp(NO)(DMAP)(η^2 -humulene) to its methylated form **12** A·CH₃. DFT simulation of **12A** shows a humulene ring conformation consistent with NOESY interactions for **12A·CH**₃ (red).

HMBC spectra, proved to be difficult. To aid in the characterization of 12, the initial mixture of the humulene complexes was methylated, analogous to the procedure used for the hexene complex $(3B \cdot CH_3)$. Since the methylation of the nitrosyl oxygen creates a triflate salt, the complex 12A·CH₃ is easier to isolate via precipitation with ether and pentane $(\sim 75\%)$. The additional 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 19). A concentration dependence for the rate of isomerization of the humulene complex was not rigorously determined. However, studies²⁰ of a large number of substitution reactions with these MoTp(NO) and WTp(NO) systems has established that ligand displacement reactions are generally dissociative in nature and independent of concentration. Even when the experiment was repeated in acetone, a ligand known to form thermally stable complexes with {MoTp(NO)-(DMAP)},²⁰ isomerization occurs with minimal formation of the acetone complex.

The tungsten humulene analogue 13 is also formed as a mixture of ~10 isomers, according to 31 P NMR spectra. Precipitation from solution provides an isolated solid that, according to 31 P NMR data, still contains approximately the same ratio of isomers. Letting the compound mixture 13 sit in trifluorotoluene for a week does not change the isomer ratio. As with the hexene and limonene complexes, attempts to converge the mixture of isomers into a single major form were unsuccessful for the heavy metal. However, the addition of 0.5 equiv of decamethylferricenium ion allows for resolution to one major compound (Figure 20). The single isomer (13A) matches the most stable molybdenum structure (12A), as shown in Figure 19. Unfortunately, there is a significant



Figure 20. Tp triplet region of 13 (a) before and (b) after addition of decamethylferricenium 13A.

amount of free humulene in the reaction mixture, and while it is possible that some isomerization occurred, it appears that the simplification of the NMR spectrum is due to the selective oxidation of the least stable isomers in the case of the tungsten analogue.

6. Alkene-to-Alkene Ligand Exchange. In addition to intramolecular isomerization, it was noted that intermolecular alkene-to-alkene exchange can be promoted with a fluorinated alcohol. Conversion of the Mo-pinene complex 11 to other alkene complexes in homogeneous solution normally takes several days to reach equilibrium. Consider the exchange of pinene for cyclopentene with the addition of THF as a cosolvent. Substitution proceeds with a $t_{1/2} \sim 15$ h at 25 °C. However, upon treating a suspension of 11 in cyclopentene with 0.2 M HFIP, the solution becomes homogeneous, and the substitution is complete (>99%) in less than 15 min. 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 21).

Earlier work in our group found that the pinene complex **11** is a good synthon for {MoTp(NO)(DMAP)}, providing access to a broad range of compounds through substitution.³⁵ However, this substitution is accompanied by complete loss of stereochemical retention. The earlier finding (vide supra) that the α -pinene complex **11** reacted with limonene in the presence of HFIP to provide mostly one diastereomer of the limonene complex (**9A**, Figure 16) 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.²⁸



Figure 21. HFIP-promoted substitution of pinene for cyclopentene. The inset NMR is of the myrtenal test³⁵ done to the enantioenriched **14**.

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 11 to prepare cyclopentene complex 14 (solid-state molecular structure determination reported in Supporting Information). 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 (>30:1 R_{Mo},1R: 1 S_{Mo},1R, stating from (R_{Mo},R) -11. Unfortunately, a considerable amount of oxidation of the molybdenum was observed, and recovered yields for this sequence were 10-25%. While we do not fully understand the reason for increased retention of the molybdenum stereocenter, the ligand exchange is thought to be dissociative,^{4,28} and the barrier to isomerization of the purported squarepyramidal intermediate²⁸ is presumably being raised by action of the HFIP (Figure 21).

Although an exhaustive mechanistic study is beyond the scope of this study, three pathways are worth mentioning. The first two, described earlier involve the metallocene oxidant or fluorinated alcohol solvent playing the role of *reversibly* activating the alkene complex, either through oxidation or hydrogen-bonding. A third mechanism should be considered in which either the alcohol or the metallocene acts as a sacrificial initiator for an electron-transfer chain (ETC) catalysis process.²⁰ In Figure 22, this mechanism is shown for a constitutional isomerization, but it could apply to any of the processes described herein. The initiation step can occur either through a direct one-electron redox process or more complicated chemical oxidation that results in a small amount of the initial alkene (A) being oxidized to form B. Once oxidized, this 17e intermediate (B) undergoes rapid isomer-



[M] = WTp(NO)(PMe₃) or MoTp(NO)(DMAP)

Figure 22. Proposed electron-transfer chain catalysis mechanism for alkene-complex isomerization.

ization to C, which then undergoes electron transfer with the initial species (A) to generate the product D and propagate the reaction via B. A similar process was recently investigated in considerable detail for the redox-promoted ligand exchange for alkene and carbonyl complexes.²⁰ This process could be considered as a tool for isomerization or substitution of alkene ligands as part of any 18e system that has ready access to its 17e conjugate. While electron transfer chain catalyzed substitution reactions have been well-documented,^{36–38} most of these studies have focused on κ^1 -bound ligands. This study demonstrates the intriguing possibility of this mechanism in alkene-complex isomerizations. Examples of ETC processes with alkenes are uncommon and tend to be initiated by reduction to a 19e intermediate, rather than initiated by oxidation.^{39–41}

CONCLUSIONS

The group 6 transition metal π bases {WTp(NO)(PMe₃)} and {MoTp(NO)(DMAP)} form stable complexes with a number of polyene hydrocarbons owing to a strong π backbonding interaction. These complexes are generally formed as a complex kinetically trapped mixture of isomers. This study demonstrates how the addition of a substoichiometric amount of a mild one-electron oxidant or an excess of a strong hydrogen donor can promote an isomerization at room temperature reducing the half-life from days or weeks to minutes. This redox-promoted isomerization has been demonstrated for face-flip of an alkene, linkage isomerization of a conjugated or unconjugated diene or polyene, and in the case of molybdenum, even intermolecular alkene-complex isomerization with retention of the metal stereocenter.

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 ¹H or ¹³C 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 standards. The peak-to-peak separation was approximately 100 mV for all reversible couples. Unless otherwise noted, all synthetic reactions were performed in a glovebox 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 $2(\pm 0.2)$ Hz. BH peaks (around 4–5 ppm) are not identified because of their quadrupole broadening; IR data are used to confirm the presence of a BH group (around 2500 cm^{-1}).

Compounds $5^{18}_{,,18} 6^{42}_{,,27} 7^{26}_{,28} 8^{25}_{,11} 11^{35}_{,15} 15^{35}_{,35}$ and the complex MoTp(NO)(DMAP)(trifluorotoluene)¹⁸ have been previously reported.

 $MoTp(NO)(DMAP)(\eta^2$ -trans-3-Hexene) (3). A 4 dram vial was charged with a stir bar, MoTp(NO)(DMAP)(η^2 trifluorotoluene) (1.0 g, 0.0017 mol), trans-3-hexene (1.6 g, 0.019 mol, 12 equiv) and 12 mL of THF. The vial was capped and the solution stirred for 4 h (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 \sim 200 mL of ether. The filtrate was then evaporated to dryness under vacuum, and the residue was dissolved in ~5 mL of THF. The THF solution was added to 75 mL of stirring cold pentane to precipitate a yellow solid. The yellow solid was collected on a 30 mL fine porosity fritted disk and washed with pentane $(3 \times 20 \text{ mL})$. The yellow solid was dried and collected (0.43 g, 0.00079 mol, 48% yield, Diastereomer ratio 1:1.5). IR $v_{\rm NO}$: 1557 cm⁻¹ $v_{\rm BH}$: 2476 cm⁻¹. CV E_{na} : 0.12 V. ¹H NMR (d_6 -Acetone, δ): diastereomer A: 7.91 (2H, d, TpA3 and Tp3/5), 7.88 (1H, d, Tp3/5), 7.78 (1H, b, 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). ¹H 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). ¹³C NMR (d_6 -Acetone, δ): Isolated diastereomer 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). ¹³C 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. Anal. (mixture of isomers) Calcd for C₂₂H₃₂BMON₉O·1/4CH₂Cl₂: C, 47.17; H, 5.78; N, 22.25. Found: C, 47.54; H, 5.97; N, 22.07

 $(MoTp(NO-Me)(DMAP)(\eta^2-3-trans-Hexene))(OTf)$ (3·CH₃). A 4 dram vial was loaded with MoTp(NO)(DMAP)(η^2 trans-3-hexene) (0.10g, 0.18 mmol) and DCM (1 mL), and an excess of methyl triflate (~10 drops) was added. The reaction was then mixed with a clean pipet for about 10 s 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 $(3 \times 10 \text{ mL})$. The solid was dried and collected (0.032 g, 0.000046 mol, 15% mass recovered, ~12% yield of product). IR v_{NO} : 1540 cm⁻¹, v_{BH} : 2490 cm⁻¹. CV $E_{p,a}$: 0.95 V, E_{pc} –1.39 V. ¹H 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). ¹³C 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).

 $WTp(NO)(PMe_3)(\eta^2$ -trans-3-Hexene) (4). A 4 dram vial was charged with a stir bar, WTp(NO)(PMe₃)(η^2 -anisole) (0.50 g, 0.82 mmol), trans-3-hexene (2 mL, 16 mmol), and DME (4 mL, anhydrous). The reaction vial was then capped, and the solution was stirred for 3 days. At this time, the solution was doubled in volume with ether and added to a 15 mL medium porosity fritted disk filled $\sim 3/4$ full with silica, and then a yellow band was eluted with ~30 mL of 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 of 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 $(3 \times 10 \text{ mL})$. This solid was dried and collected (0.11 g, 0.20 mmol, 25% yield, 1:10 ratio, diastereomer A: diastereomer 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, 0.044 g, 0.081 mmol ~10% yield). Alternative synthesis of 4: To a 4 dram vial charged with a stir bar, $WTp(NO)(PMe_3)(\eta^2 -$

benzene) (0.25 g, 0.00041 mol) was combined with trans-3hexene (1 mL, 16.1 mmol) and DME (3 mL, anhydrous). The vial was capped and stirred 18 h. To the solution, 4 mL of ether was added and the solution was loaded on a 15 mL medium porosity fritted disk, $\sim 3/4$ full of silica. A yellow band was eluted with ~ 20 mL of ether. The filtrate was then evaporated to dryness in vacuo. The resulting solid was dissolved in 1 mL of DCM and added to 75 mL of 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: diastereomer A: $v_{\rm NO}$: 1540 cm⁻¹, $v_{\rm BH}$: 2480 cm⁻¹, diastereomer **B**: $v_{\rm NO}$: 1537 cm⁻ $v_{\rm BH}$: 2478 cm⁻¹. CV $E_{\rm pa}$: A: $E_{\rm pa}$: 180 mV, B: $E_{1/2}$: 294 mV. ¹H NMR $(d_6$ -Acetone, $\delta)$: 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, toward PzC3), 2.44 (1H, m, H5), 2.00 (1H, m, H4), 1.77 (1H, m, H2y toward NO), 1.36 (9 H, d, J = 8.0, PMe₃), 1.36 (3H, t, J = 7.3, H6), 1.21 (4 H, (t, J = 7.3, H1), m H5), 1.17 (1H, m, H3). ¹H 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 PMe₃), 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, PMe₃), 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). ¹³C 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, PMe₃). ¹³C 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, PMe₃). ³¹P NMR (THF, δ): A: 14.04 ($J_{WP} =$ 288 Hz), **B**: 12.40 (J_{WP} = 286 Hz). Calcd for C₁₈H₃₂BN₇OPW: C, 36.76; H, 5.48; N, 16.67. Found C, 36.22; H, 5.14; N, 16.48.

 $MoTp(NO)(DMAP)(\eta^2-R-Limonene)$ (9). In a 250 mL roundbottom flask charged with a stir bar, sodium dispersion in paraffin wax (\sim 35% Na⁰ by weight, 3 g, 0.050 mol) and \sim 250 mL of hexanes were combined. The mixture was capped and stirred vigorously for 18 h. The hexanes were then decanted, and the remaining Na⁰ 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 MoTp(NO)-(DMAP)(I) (3.0 g, 5.1 mmol). The flask was recapped and stirred for 2 h. At this time, 200 mL of ether was added to the dark solution and stirred for about 30 s. 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 of stirring hexanes. The solution of hexanes 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 $(3 \times 30 \text{ mL})$. Desiccating the solid yielded a fluffy orange solid (0.64 g, 1.1 mmol, 20% yield). IR $v_{\rm NO}$: 1555 cm⁻¹, $v_{\rm BH}$: 2475 cm⁻¹. CV E_{pa} : -0.090 V. Anal. Calcd for C₂₆H₃₆BMoN9O·1/2Et₂O: C, 53.01; H, 6.51; N, 19.87. Found: C, 53.59; H, 6.46; N, 20.09.

 $WTp(NO)(PMe_3)(\eta^2-R-Limonene)$ (R,R)- **10A** and (S,R)-**10A.** To a 4 dram vial charged with a stir pea, WTp(NO)- $(PMe_3)(\eta^2$ -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 stirred 18 h. About 4 mL of ether was added to the reaction solution and then loaded onto a 15 mL medium porosity fritted disk, $\sim 3/4$ full of silica. An orange band was eluted with ~25 mL of ether. The filtrate was evaporated to dryness under vacuum, and the residue was dissolved in about 2 mL of DCM and added to 75 mL of stirring pentane. The pentane solution was concentrated to about 10 mL, and the solid precipitate was collected on a 15 mL fine porosity fritted disk. The solid was dried to yield a yellow solid (0.065 g, 0.10 mmol, 24% yield). IR: v_{NO} : 1544 cm⁻¹ v_{BH} : 2483 cm⁻¹ (mix of diastereomers). CV: E_{pa} : 23 mV. ¹H NMR (d_6 -acetone, δ): diastereomer Ws: 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, PMe₃), 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). ¹H NMR (d_6 -acetone, δ): diastereomer 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, PMe₃), 0.80 (1H, m, H4), -0.05 (1H, m, H3y). ¹³C 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, PMe₃). 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, PMe₃). ³¹P 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.Attempts to purify this material were unsuccessful.

 $MoTp(NO)(DMAP)(\eta^2 - \alpha - Humulene)$ (12). To a 4 dram vial charged with a stir bar, 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 stirred 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 of 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 $(3 \times 20 \text{ mL})$, desiccated, and collected (0.15 g, 0.23 mmol, 14%). IR $v_{\rm NO}$: 1557 cm⁻¹, $v_{\rm BH}$: 2466 cm⁻¹. CV: E_{pa} : 12: b, 0.05 V, diastereomer 12A: 0.00 V. ¹H NMR (d_6 -Acetone, δ) 12A: 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).¹³C NMR (d_6 -Acetone, δ) 12A: 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 C₃₁HBMoN₉O: C, 55.95; H, 6.66; N, 18.94. Found: C, 55.92; H, 6.83; N, 18.54.

 $(MoTp(NO-Me)(DMAP)(\eta^2 - \alpha - Humulene))(OTf)$ (**12A**·CH₃). In a 4 dram vial, MoTp(NO)(DMAP)(η^2 - 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 pipet) was then added. Immediately the solution was added to 100 mL of ether. The solution was reduced in vacuo to about 25 mL. Then 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 $(3 \times 10 \text{ mL})$. The solid was desiccated and collected (0.093 g, 0.11 mmol, 77% mass recovered, ~70% yield). IR $v_{\rm NO}$: 1623 cm⁻¹ $v_{\rm BH}$: 2497 cm⁻¹. CV E_{pc} : -1.40 V E_{pa} : -0.38 V. 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). ¹³C 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).

 $WTp(NO)(PMe_3)(\eta^2-\alpha$ -Humulene) (13). To a four-dram vial charged with a stir bar, $WTp(NO)(PMe_3)(\eta^2$ -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 stirred 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 of ether. The filtrate was evaporated *in vacuo* to dryness and then dissolved with about 2 mL of DCM and added to 75 mL of stirring pentane. The pentane solution was concentrated to about 10 mL and the resulting precipitate was collected on a 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 decamethylferricenium impurity). IR: v_{NO} : 1540 cm⁻¹ $v_{\rm BH}$: 2486 cm⁻¹. CV: $E_{\rm pa}$: + 0.030 V.¹H NMR-(d_6 -Acetone, δ) diastereomer 13A: 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 orH11x 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, PMe₃), 0.97 (3H, s, 6x methyl syn), 1.02 (3H, s, 6y methyl anti), 0.93 (1H, m, H3y syn). ¹³C NMR- $(d_6$ -Acetone, δ) **13A**: 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, PMe₃). ³¹P NMR-(THF, δ) 13A: -13.14. Attempts to purify this material were unsuccessful.

 $MoTp(NO)(DMAP)(\eta^2-Cyclopentene)$ (14). In a 100 mL round-bottom charged with a stir egg, sodium dispersion in paraffin wax (3 g, ~35% Na⁰ by weight, ~1.1 g Na⁰, 0.049 mol) and 100 mL of hexanes were combined. The mixture was capped and stirred vigorously for 18 h. The hexanes were then decanted, and the remaining Na⁰ 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 stirred 1 h. At this time, 50 mL of ether was added to the dark solution and stirred for about 30 s. 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 $(3 \times 30 \text{ mL})$. Desiccating for 2 h yielded a fluffy yellow solid (1.1 g, 2.1 mmol, 42% yield). IR: v_{NO} : 1550 cm⁻¹, v_{BH} : 2478 cm⁻¹. CV: E_{pa} : 0.010 V. ¹H 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). ¹³C 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. Calcd: 2(C₂₁H₂₈BMoN₉O)·CH₂Cl₂: 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.

 $MoTp(NO)(DMAP)(\eta^2$ -Cyclopentene) (14) Alternative Synthesis. To a 4 dram vial charged with a stir pea, magnesium powder (1.0 g, 325 mesh) was combined with I₂ (0.033 g, 0.13 mmol) dissolved in 2 mL of 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 Mg⁰. 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 of THF. Then $[MoTp(NO)(DMAP)(\kappa^{1}-$ DMA)](OTf) (0.25 g, 0.36 mmol) was added to the magnesium suspension, and the vial was capped. The solution was stirred for 2 days. After this duration, the solution was added to a 15 mL medium porosity fritted disk, $\sim 3/4$ 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 (3×10) mL). The solid was desiccated, and the product was then collected (0.13 g, 0.24 mmol, ~62% yield, ~5% starting material impurity).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00151.

¹HNMR and ¹³CNMR spectra, infrared spectra, and cyclic voltammetric data (PDF)

Cartesian coordinates for terpenes (XYZ)

Accession Codes

CCDC 1971582–1971584 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

Authors

- Steven J. Dakermanji University of Virginia, Department of Chemistry, Charlottesville, Virginia 22904, United States
- Karl S. Westendorff University of Virginia, Department of Chemistry, Charlottesville, Virginia 22904, United States
- **Emmit K. Pert** University of Virginia, Department of Chemistry, Charlottesville, Virginia 22904, United States
- Katy B. Wilson University of Virginia, Department of Chemistry, Charlottesville, Virginia 22904, United States
- Jeffery T. Myers University of Virginia, Department of Chemistry, Charlottesville, Virginia 22904, United States
- Justin H. Wilde University of Virginia, Department of Chemistry, Charlottesville, Virginia 22904, United States
- Diane A. Dickie University of Virginia, Department of Chemistry, Charlottesville, Virginia 22904, United States; orcid.org/0000-0003-0939-3309
- Kevin D. Welch University of Virginia, Department of Chemistry, Charlottesville, Virginia 22904, United States

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.organomet.0c00151

W. Dean Harman – University of Virginia, Department of Chemistry, Charlottesville, Virginia 22904, United States; orcid.org/0000-0003-0939-6980; Email: wdh5z@ virginia.edu

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Acknowledgement is made to the National Science Foundation (CHE-1800051) and the National Institutes of Health (1R01GM132205-01) for supporting this work.

REFERENCES

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

(2) Hartwig, J. F. Organotransition Metal Chemistry: from Bonding to Catalysis; University Science Books: Herndon, VA, 2010.

(3) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; John Wiley & Sons, Inc.: New York, 2001.

(4) Liebov, B. K.; Harman, W. D. Group 6 Dihapto-Coordinate Dearomatization agents for Organic Synthesis. *Chem. Rev.* 2017, 117, 13721–13755.

(5) Keane, J. M.; Harman, W. D. A New Generation of Pi-Basic Dearomatization Agents. *Organometallics* **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. J. Am. Chem. Soc. **2008**, 130, 7449–7458.

(8) Amouri, H. Chirality in Transition Metal Chemistry: Molecules, Supramolecular Assemblies and Materials; Wiley, Chichester, U.K., 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 Enantio-selective Reactions with an Aldehyde. *Organometallics* **1993**, *12*, 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. *Chem. Soc. Rev.* 2012, 41, 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. 2011, 133, 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. Chem., Int. Ed. Engl.* **1997**, *36*, 550–583.

(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 $[(\eta^5-C_5H_5)Re(NO)(PPh_3)]^+$. *J. Am. Chem. Soc.* **1988**, *110*, 4082–4084.

(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 $[(h^5-C_5H_5)Re(NO)(PPh_3)(H_2C = CHR)]^+X^-$. Organometallics **1990**, *9*, 1191–1205.

(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, 3876–3883.

(17) Peng, T.-S.; Gladysz, J. A. Mechansim of Equilibration of Diastereomeric Chiral Rhenium Alkene Complexes of the Formula $[(\eta^5-C_5H_5)Re(NO)(PPh_3)(H_2C=CHR)]^+BF_4^-$. The Metal Traverses between Alkene Enantiofaces without Dissociation! *J. Am. Chem. Soc.* **1992**, *114*, 4174–4181.

(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 CF_3 Group. J. Am. Chem. Soc. 2017, 139, 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 $\{TpW(NO)(PMe_3)\}$ and Convenient Spectroscopic Tools for Product Analysis. *Organometallics* **2007**, *26*, 2791–2794.

(20) Dakermanji, S. J.; Smith, J. A.; Westendorff, K. S.; Pert, E. K.; Chung, A. D.; Myers, J. T.; Welch, K. D.; Dickie, D. A.; Harman, W. D. Electron-Transfer Chain Catalysis of η^2 -Arene, η^2 -Alkene, and η^2 -Ketone Exchange on Molybdenum. ACS Catal. **2019**, *9*, 11274– 11287.

(21) Tomita, A.; Sano, M. Linkage Isomerizations of (Sulfoxide)ammineruthenium Complexes Induced by Electrochemical Processes. *Inorg. Chem.* **1994**, *33*, 5825–5830.

(22) Sano, M.; Taube, H. Molecular hysteresis. J. Am. Chem. Soc. 1991, 113, 2327–2328.

(23) Harman, W. D.; Sekine, M.; Taube, H. Redox-promoted linkage isomerizations of aldehydes and ketones on pentaammineosmium. J. Am. Chem. Soc. **1988**, 110, 2439–2445.

(24) 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*, 5051–5058.

(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. *J. Org. Chem.* **2019**, *84*, 6094–6116.

(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*, 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, 1426–1427. (28) 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, 4446–4456.

(29) 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*, 4535–4544.

(30) 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– 5449.

(31) 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, 117–24.

(32) 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**, 1054–8.

(33) Ullah, S. S.; Molla, M. E.; Begum, N. Synthesis and reactions of limonenetricarbonyliron. *Indian J. Chem., Sect. A* **1984**, *23A*, 992–994. (34) de 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(η 4-

[p-mentha-1,8{9}-diene])platinum(II). Russ. J. Gen. Chem. 2006, 76, 1288-1294.

(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**, *37*, 4446–4456.

(36) Hershberger, J. W.; Klingler, R. J.; Kochi, J. K. Electron-transfer catalysis. Radical chain mechanism for the ligand substitution of metal carbonyls. *J. Am. Chem. Soc.* **1982**, *104*, 3034–3043.

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

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

(39) Astruc, D. Electron Transfer and Radical Processes in Transition-Metal Chemistry; John Wiley & Sons, 1995.

(40) Bezems, G. J.; Rieger, P. H.; Visco, S. Electron-induced nucleophilic substitution reactions in organometallic systems. *J. Chem. Soc., Chem. Commun.* **1981**, 265–266.

(41) Karpinski, Z. J.; Kochi, J. K. Electron-transfer chain catalysis in the electrochemical deligation of bis(arene)iron(II) dications. Application of pulse voltammetric techniques as a mechanistic tool. *Inorg. Chem.* **1992**, *31*, 2762–2767.

(42) 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*, 3772–3779.