Reviews

A New Generation of π-Basic Dearomatization Agents

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A new generation of dearomatizing π-bases having the general form {TpM(L)(π-acid)} (where Tp = hydridotris(pyrazolyl)borate, M = rhenium, molybdenum, tungsten, L = variable ligand, and π-acid = CO, NO^+) has been developed. These fragments show reactivity patterns similar to those of their pentaammineosmium(II) predecessor, binding aromatic molecules across two carbons and subsequently activating these ligands toward electrophilic addition and cycloaddition reactions. In many cases, these second-generation dearomatization agents show a greater degree of π-back-bonding than was observed for the analogous pentaammineosmium(II) complexes. A number of unprecedented reaction pathways have been discovered for these second-generation systems, most notably a broad array of cyclization reactions. In addition, these chiral-at-metal dearomatization agents are readily resolved and have been utilized in reaction sequences to give highly enantioenriched polycyclic molecules from common aromatic precursors.

I. Introduction

Almost 20 years ago, initial reports began to detail the remarkable π-basicity of the pentaammineosmium(II) metal fragment and the resulting affinity for binding aromatic molecules across two carbons (e.g. **1**−**3**; Scheme 1).[1−3] The pentaammineosmium(II) system was found not only to bind a wide range of aromatic molecules in this manner but also to activate them toward hydrogenation, electrophilic addition, and cycloaddition reactions (**4**−**6**).[3−6]

The fundamental interaction that makes such transformations possible is strong π-back-bonding. Donation of π-electron density from a filled d orbital of the octahedral d^6 metal into an antibonding orbital of the aromatic molecule serves to both increase and localize the electron density of the aromatic π-system while protecting the bound carbons from further reaction (Figure 1).

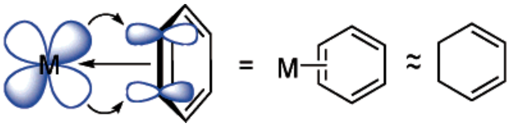

Figure 1. η^2 coordination stabilized through π-donation of electron density.

The true potential of this chemistry lies in the fact that aromatic molecules represent a largely untapped feedstock for the synthesis of alicyclic molecules. The prototypical benzene ring, with its six unsaturated carbons, would be a versatile synthon if the aromatic character of the ring could be reduced in a controlled fashion. Consider the popularity of the Birch reduction, which, despite its limitations, remains a synthetic mainstay because of its ability to dearomatize benzenoid structures. With the realization that the pentaammineosmium(II) metal fragment could serve as another avenue for dearomatization, an intense effort has been made to study the chemistry of its complexes. There are numerous publications detailing novel manipulations of aromatic molecules facilitated by this fragment, some notable examples of which (**12**−**18**) are shown in Scheme 2.[4−6,8−40]

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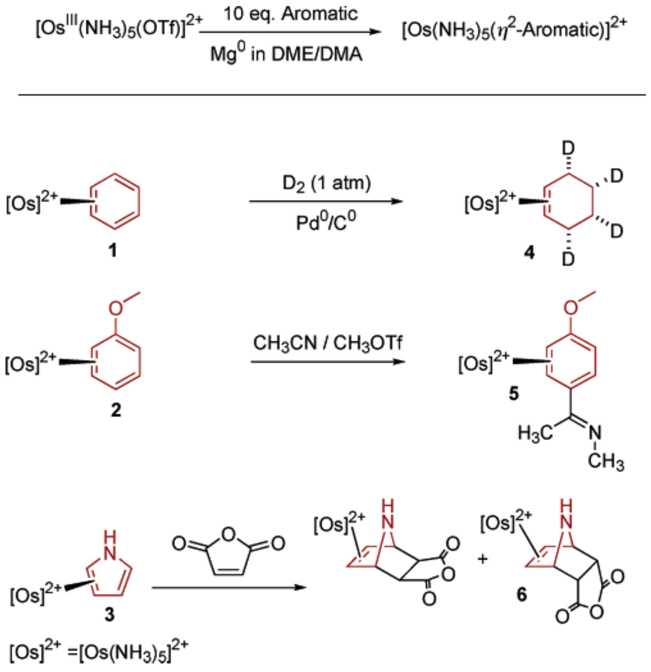
10.1021/om050029h CCC: $30.25

Scheme 1. Early Examples of Hydrogenation, Electrophilic Addition, and Cycloaddition of Aromatic Molecules Mediated by the π-Base Pentaammineosmium(II) ($[Os]^{2+}$)



Further discussion of the chemistry of the pentaammineosmium(II) metal fragment can be found in several reviews which have addressed this landmark system.[41−48]

Despite its remarkable ability to promote a number of otherwise inaccessible organic transformations (see Scheme 2), the pentaammineosmium(II) system has several inherent limitations. The complex is achiral, and thus the transformations that it facilitates either are limited to racemic reactions or require the use of chiral auxiliary strategies.[30,49,50] This aspect of the metal cannot be changed through ligand alterations, as previous studies have shown that substitution of a single ammine ligand renders the metal incapable of η^2 binding of aromatic molecules.[51] In addition, because the $\{Os(NH_3)_5\}^{2+}$ fragment is used stoichiometrically, the cost of osmium is a significant deterrent to its widespread use.

For the above reasons, an intense effort was put forth in our laboratories to develop alternatives to the pentaammineosmium(II) system. This effort has now come to fruition on a number of fronts. Systematic synthetic, spectroscopic, and electrochemical studies of low-valent octahedral d^6 metal complexes have resulted in a series of complexes of the form {TpM(L)(π-acid)} (Tp = hydridotris(pyrazolyl)borate, M = rhenium(I), molybdenum(0), tungsten(0), L = variable ligand, and π-acid = CO, NO^+) that bind and activate a range of aromatic molecules in a manner comparable to that of the pentaammineosmium(II) system. Subsequent studies of these systems have addressed a variety of topics, including conformational arrangements, linkage isomerizations, exploitations of solid-state configurations, and metal-directed asymmetric reactions. In addition, these complexes have been shown to facilitate a wide range of reactions, including a number of cyclization pathways not previously observed for pentaammineosmium(II).

II. Development of the Second Generation Dearomatization Agents

The pentaammineosmium(II) metal fragment is not unique in its ability to bind aromatic molecules in a η^2

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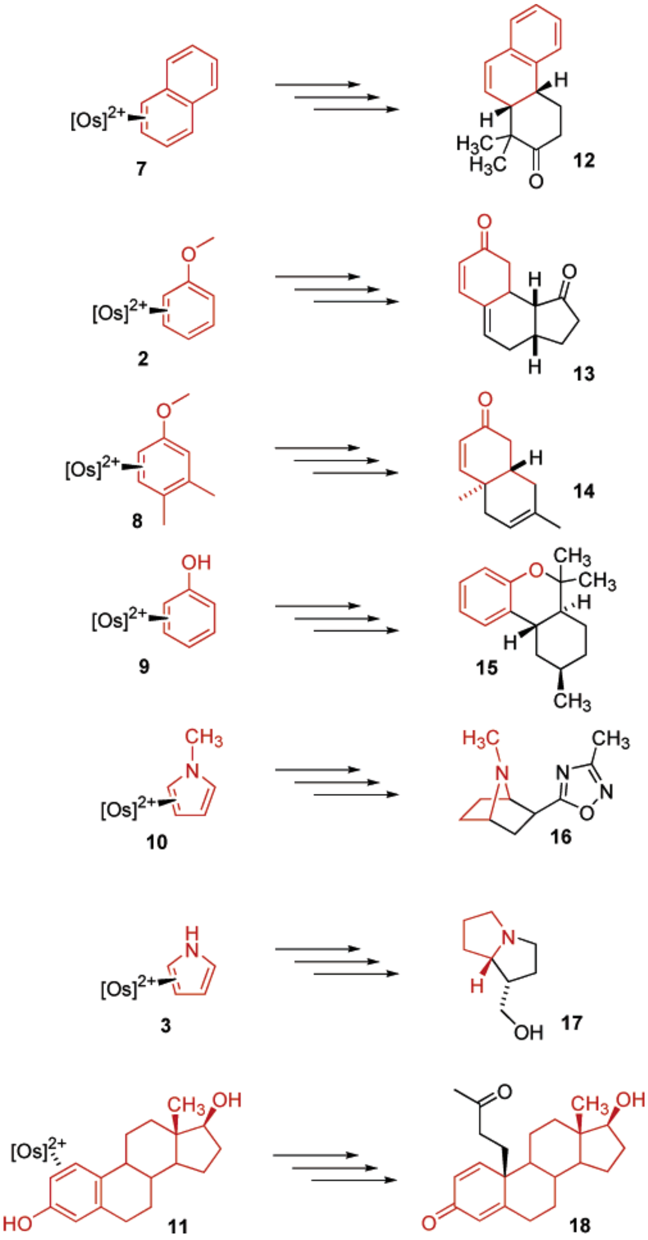
Scheme 2. Notable Manipulations of Aromatic Molecules Facilitated by η^2 Coordination with the Pentaammineosmium(II) Metal Fragment



fashion, with d^{10} Cu(I),[52–56] Ag(I),[57] Pt(0),[58,59] and Ni(0),[60–63] d^2 Ta(III)[64–66] and Nb(III),[67] d^8 Rh(I)[68–71] and Ru(0),[72] and d^6 Ru(II)[73,74] and Re(I)[75–82] complexes having been reported.[83] What distinguishes the pentaammineosmium(II) fragment is its ability to form thermally stable complexes of a wide range of aromatic molecules and to subsequently activate these molecules toward reactions with electrophiles. Unlike many of the above examples, complexes of pentaammineosmium(II) are coordinatively saturated and therefore resist attack of electrophiles at the electron-rich metal center. Given these properties, the first studies directed at the production of surrogates for the pentaammineosmium(II) system focused on the synthesis of low-valent rhenium fragments with various combinations of predominantly σ-donating ligands.[84–89] While these early attempts failed to produce systems that bound aromatic molecules, they demonstrated the delicate electronic balance present in the complexes of pentaammineosmium(II) with aromatic molecules. The metal center is sufficiently electron-rich to overcome the aromatic stability but not so electron-rich as to favor C–H insertion or other oxidative pathways.

To gauge the amount of electron density available for π-back-bonding from various metal fragments, dinitrogen stretching frequencies and d^5/d^6 reduction potentials for a number of rhenium dinitrogen complexes were compared with those of the $[Os(NH_3)_5N_2]^{2+}$ complex (Figure 2).[90]

It was determined that most of the metal fragments that had previously been investigated as potential pentaammineosmium(II) alternatives were poor electronic surrogates for the osmium system. In fact, counter to expectation, most were far too electron-rich.

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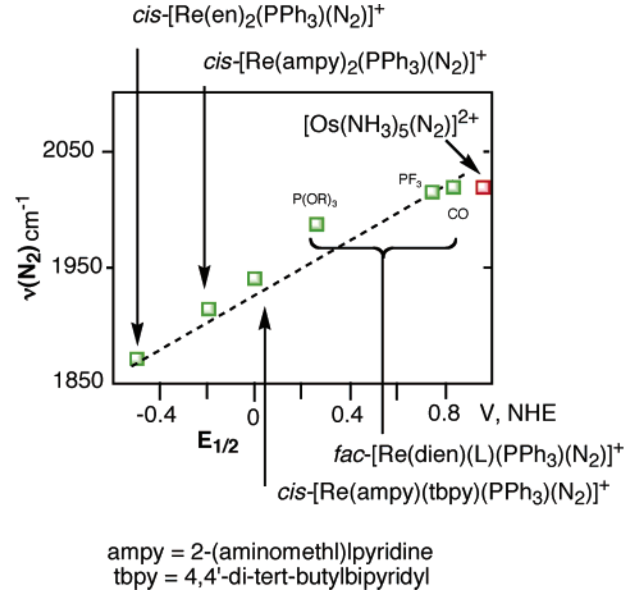
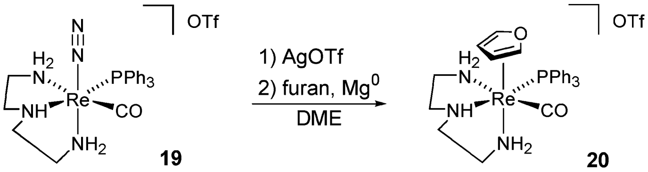


Figure 2. Dinitrogen IR stretching frequencies and electrochemical data for various rhenium systems and the $[Os(NH_3)_5N_2]^{2+}$ complex.

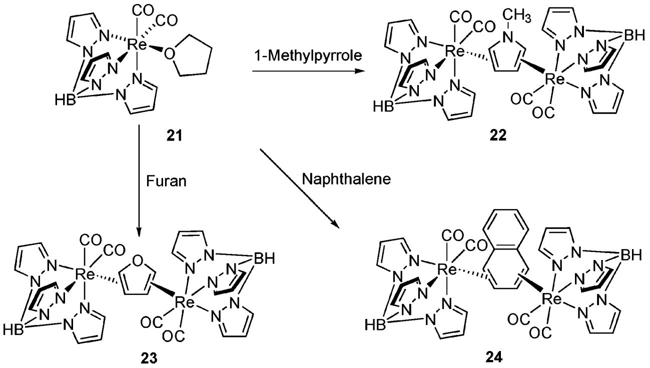
Scheme 3. Synthesis of *fac*-[Re(dien)(PPh$_3$)(CO)(η^2-furan)](OTf)



Studies involving the introduction of a single strongly π-acidic ligand into the ligand set eventually led to the synthesis of the η^2-coordinate furan complex [Re(dien)(PPh$_3$)(CO)(η^2-furan)]$^+$ (Scheme 3; **20**),[90] which at the time was the only other example of a furan complex with this coordination geometry other than that formed by pentaammineosmium(II).

While the *fac*-{Re(dien)(PPh$_3$)(CO)}$^+$ fragment failed to bind a range of aromatic ligands or activate furan toward novel reactions, this complex is significant in that it validated a strategy by which other such fragments could be designed. IR and electrochemical data suggest that unlike previously investigated rhenium systems, such as {Re(en)$_2$(PPh$_3$)}$^+$ and {Re(ampy)$_2$(PPh$_3$)}$^+$, the {Re(dien)(PPh$_3$)(CO)}$^+$ fragment is a close electronic match to the pentaammineosmium(II) system. Unfortunately, the steric profile of {Re(dien)(PPh$_3$)(CO)}$^+$ is considerable, and this aspect is thought to be responsible for the narrow range of aromatic molecules that it could bind. Subsequent studies focused on the production of a fragment with electronic properties similar to those of pentaammineosmium(II) and a steric profile significantly smaller than that of {Re(dien)(PPh$_3$)(CO)}$^+$. In their design, insight was drawn from various reports that compared the properties of Cp and Tp.[91] The benzene complex Cp*Re(CO)$_2$(η^2-C$_6$H$_6$) was proposed to be an intermediate in the synthesis of Cp*(CO)$_2$Re(μ-1,2-η^2-3,4-η^2-C$_6$H$_6$)Re(CO)$_2$Cp* by photolysis of Cp*Re(CO)$_3$ in benzene.[75] A number of reports have described the electronic similarities of six-coordinate complexes of Tp and Cp, while also noting the decreased tendency of the former to support oxidative addition.[92-96] Therefore, complexes of the form TpRe(CO)$_2$(η^2-aromatic) were considered as potential targets for investigation. Stirring the previously reported complex TpRe(CO)$_2$(THF)[97] (**21**) in solutions of various aromatic molecules yielded stable binuclear complexes of various aromatic molecules (**22**−**24**), as shown in Scheme 4.

Scheme 4. Formation of Binuclear η^2 Complexes from TpRe(CO)$_2$(THF)



The {TpRe(CO)$_2$} fragment, like {Re(dien)(PPh$_3$)(CO)} before it, failed altogether to bind benzenes. Furthermore, the aromatic molecules that bridged the two rhenium complexes in the binuclear species **22**−**24** were completely shielded from participation in organic reactions. However, the investigation of {TpRe(CO)$_2$} with aromatic molecules was valuable in that it determined a lower limit of the π-basicity required to form stable mononuclear complexes with aromatic molecules. Presumably, formation of **22**−**24** proceeded through such an intermediate, but a single {TpRe(CO)$_2$} fragment was not sufficiently electron-rich to prevent its disproportionation. These studies led to the pursuit of complexes of the type {TpRe(L)(CO)}, where L is a variable ligand more σ-donating and less π-withdrawing than CO. Modifications of a procedure reported by Mayer and Brown gave the complex TpRe(PMe$_3$)Cl$_2$.[98,99] Reduction of TpRe(PMe$_3$)Cl$_2$ (**25**) in the presence of an excess of both CO gas and cyclohexene gave the η^2 olefin complex TpRe(PMe$_3$)(CO)(η^2-cyclohexene) (**26**). Exposure of this complex to silver triflate provided the corresponding Re(II) species, which loses cyclohexene to form TpRe(PMe$_3$)(CO)(OTf) (**27**). Subsequent reduction of this complex in the presence of an aromatic molecule afforded η^2 complexes of the form TpRe(PMe$_3$)(CO)(η^2-aromatic) (where aromatic = furan (**28**), thiophene (**29**), naphthalene (**30**); Scheme 5).[100,101]

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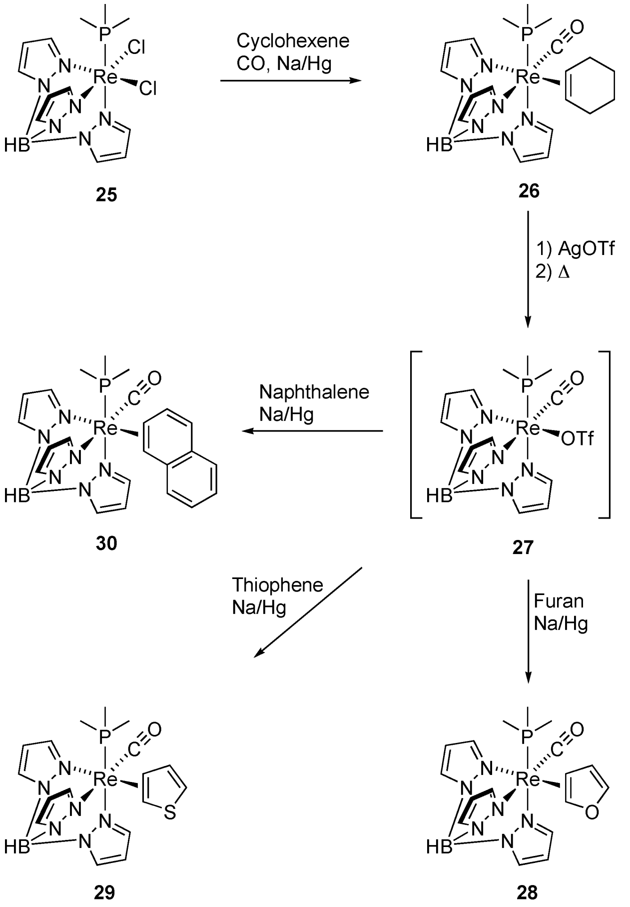
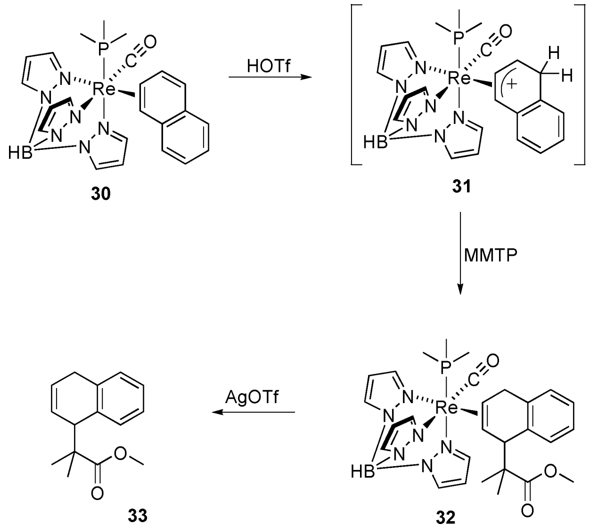
Scheme 5. Synthesis of TpRe(PMe$_3$)(CO)(η^2-furan), TpRe(PMe$_3$)(CO)(η^2-thiophene), and TpRe(PMe$_3$)(CO)(η^2-naphthalene) Complexes



The dearomatization agent {TpRe(PMe$_3$)(CO)} is notable both for the significant range of aromatic molecules with which it forms stable complexes and for the fact that it was the first fragment after pentaamminеosmium(II) that was shown to activate aromatic molecules toward electrophilic addition reactions through η^2 coordination. The complex TpRe(PMe$_3$)(CO)(η^2-naphthalene) (**30**) smoothly undergoes a 1,4 -tandem electrophilic/nucleophilic addition with triflic acid and a silylketene acetal (**32**; Scheme 6).

While the {TpRe(PMe$_3$)(CO)} fragment forms a greater range of η^2 complexes than {Re(dien)(PPh$_3$)(CO)}, it is not capable of binding the broad range of species that has been manipulated through complexation with the pentaammineosmium(II) fragment. Most notably, {TpRe(PMe$_3$)(CO)} fails to form stable π-complexes with benzenes and nitrogenous heterocycles, such as pyrrole and pyridine. However, this complex signaled a turning point, as a general synthetic strategy to rhenium(I) dearomatization agents had been forged. Through methods similar to those utilized in the synthesis of the {TpRe(PMe$_3$)(CO)} fragment, several other {TpRe(L)(CO)} fragments were eventually synthesized, with the intent of varying the degree of electron donation from the variable ligand L and consequently varying the amount of electron density available for π-donation to a bound aromatic molecule.[102] Most such fragments, including those having L = *tert*-butyl isocyanide and L = pyridine, were found to be similar to L = PMe$_3$ in their binding ability. However, the 1-methylimidazole variant {TpRe(MeIm)(CO)} was found to bind a much larger range of aromatic molecules, including benzenes (**35**, **40**), 2,6-lutidine (**39**), and *N*-methylpyrrole (**42**). The benzene complex TpRe(MeIm)(CO)(η^2-benzene) (**35**) served as a valuable precursor to the other aromatic complexes, as shown in Scheme 7. The dearomatization fragment {TpRe(NH$_3$)(CO)}, a compound that is more electron-rich than the imidazole variant, has also been investigated to a limited degree, but exploration of this fragment has been hampered by synthetic difficulties.[102]

Scheme 6. Activation of Naphthalene through η^2 Coordination to the Second-Generation {TpRe(PMe$_3$)(CO)} π-Basic Metal Fragment



Lessons learned in the development of {TpRe(CO)L} systems were applied to group 6 transition metals. A comparison of Re(CO)$_2$(dmpe)$_2^+$ and Mo(CO)$_2$(dmpe)$_2$ reduction potentials (1.66 and 0.22 V, respectively)[103,104] suggested that moving from rhenium(I) to molybdenum(0) effects a decrease of approximately 1.4 V. Furthermore, studies of [TpMo(CO)$_3$]$^-$ and TpMo(CO)$_2$(NO) d^5/d^6 reduction potentials (0.00 V and $E_{p,a}$ = 1.12 V, respectively)[105] indicated that replacement of CO with NO$^+$ results in an increase of nearly equivalent magnitude. It was therefore hypothesized that, as a rhenium analogue to the pentaammineosmium(II) system was developed through the replacement of an ammine with a carbonyl ligand, a molybdenum analogue could likewise be produced through the replacement of the carbonyl ligand with the stronger π-acid NO$^+$ (Figure 3).

Reduction of the reported compound TpMo(NO)(Br)$_2$ in the presence of 1-methylimidazole and various aromatic molecules effected the formation of stable TpMo(MeIm)(NO)(η^2-aromatic) compounds (aromatic = naphthalene, furan, thiophene).[105,106] A tandem addition sequence of protonation followed by addition of an ester enolate (delivered in the form of a silylketene acetal) was successfully performed on TpMo(MeIm)(NO)(η^2-

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[102] Meiere, S. H.; Brooks, B. C.; Gunnoe, T. B.; Carrig, E. H.; Sabat, M.; Harman, W. D. *Organometallics* **2001**, *20*, 3661.

[103] Pombeiro, A. J. L. *Inorg. Chim. Acta* **1985**, *103*, 95.

[104] Morris, R. H.; Earl, K. A.; Luck, R. L.; Laaarowych, N. J.; Sella, A. *Inorg. Chem.* **1987**, *26*, 2674.

[105] Meiere, S. H.; Keane, J. M.; Gunnoe, T. B.; Sabat, M.; Harman, W. D. *J. Am. Chem. Soc.* **2003**, *125*, 2024.

[106] McCleverty, J. A.; Seddon, D.; Bailey, N. A.; Walker, N. W. J. *J. Chem. Soc., Dalton Trans.* **1975**, 898.

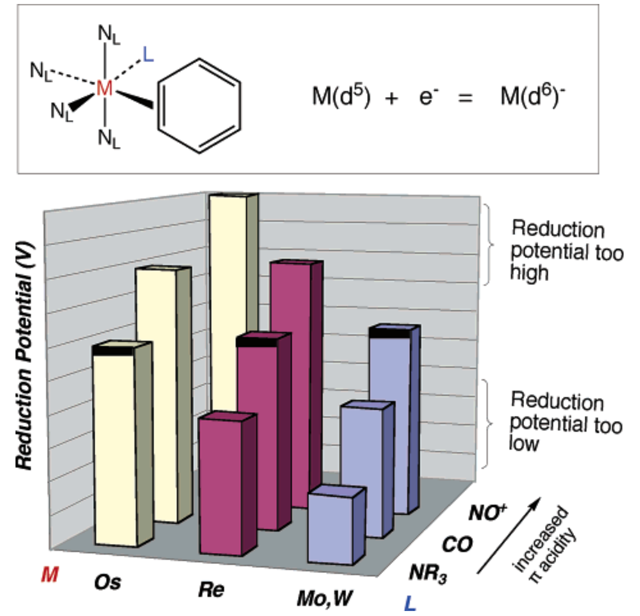
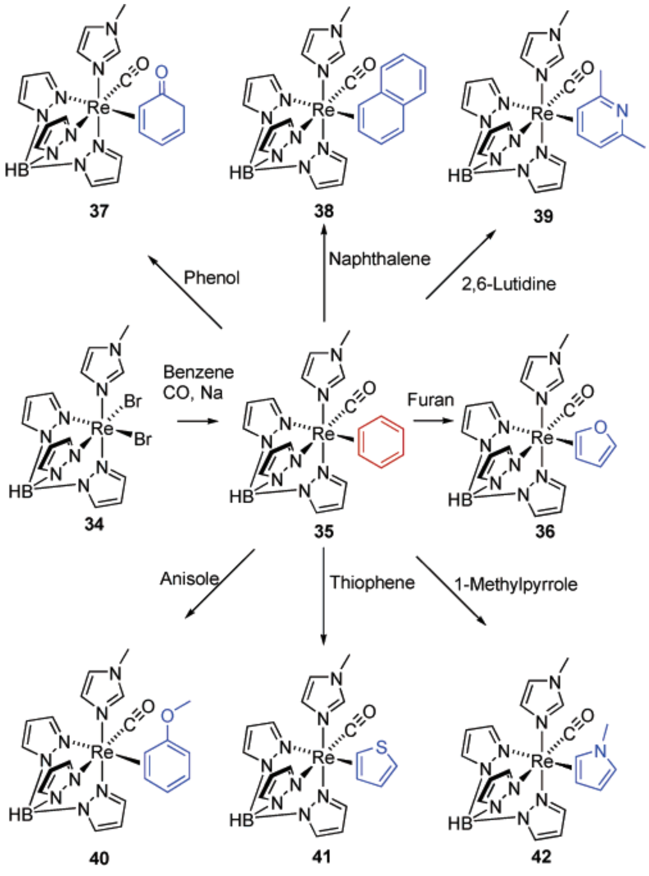


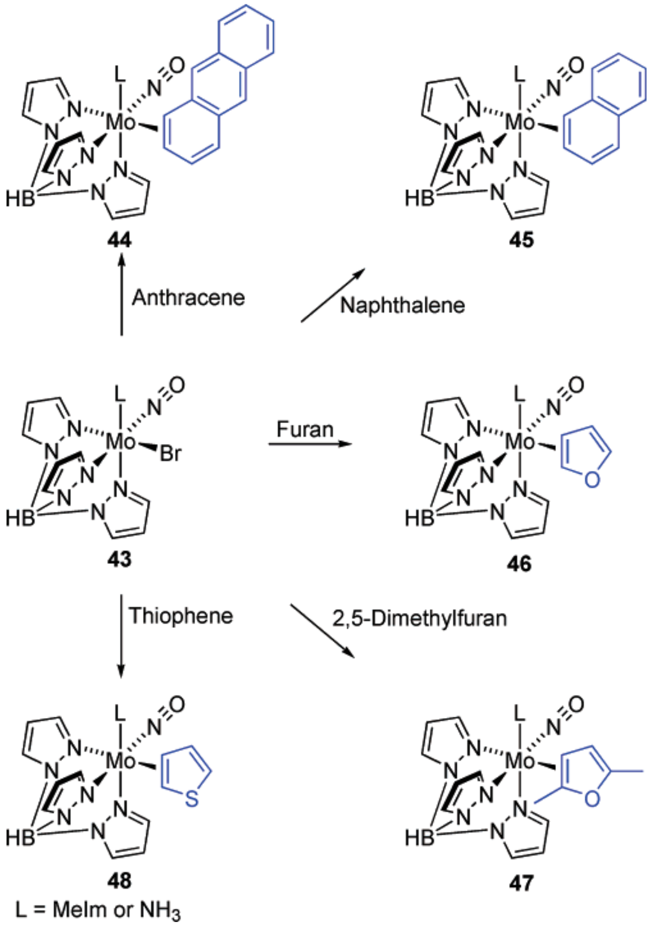
Figure 3. Reduction potentials of d^6 metal complexes as a function of ligand identity.

Scheme 7 . η^2 Complexation of Aromatic Molecules by the Metal Fragment {TpRe(MeIm)(CO)}.



naphthalene), and the resulting 1,2-dihydronaphthalene was readily demetalated with exposure to air. These observations validated the {TpMo(MeIm)(NO)} fragment as an effective group 6 dearomatization agent. Further studies have explored alternative synthetic pathways for the {TpMo(MeIm)(NO)} fragment, the synthesis and properties of a more electron-rich {TpMo(NH_3)(NO)} fragment, and the range of unsaturated ligands that can be bound to these fragments (Scheme 8; **44**−**48**).[107] Unfortunately, like {TpRe(PMe_3)(CO)}, both {TpMo(MeIm)(NO)} and {TpMo(NH_3)(NO)} fail to form stable η^2 complexes with benzenes and nitrogenous heterocycles.

Scheme 8. Range of Aromatic Ligands That Have Been Bound to {TpMo(L)(NO)} Fragments



It is likely that the failure of {TpMo(L)(NO)} fragments to form stable complexes with monocyclic arenes may be related less to the ability of these fragments to donate π-electron density and more to greater substitution rates observed generally for second-row transition metals when compared to their third-row analogues.[105,108] Studies directed at the synthesis of analogous {TpW(L)(NO)} fragments were therefore undertaken. The TpW(NO)Br_2 complex was prepared according to reports by Deane and McCleverty.[109,110] Reduction of this complex in the presence of PMe_3 yields the isolable 17-electron W(I) species TpW(PMe_3)(NO)Br. The trimethyl phosphite and pyridine analogues have been prepared by analogous methods.[111] Further reduction of the phosphine derivative in the presence of benzene affords the complex TpW(PMe_3)(NO)(η^2-benzene). The benzene ligand in this complex is readily substituted by other

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[107] Mocella, C. J.; Delafuente, D. A.; Keane, J. M.; Warner, G. R.; Friedman, L. A.; Sabat, M.; Harman, W. D. *Organometallics* **2004**, *23*, 3772.

[108] Spessard, G. O.; Miessler, G. L. *Organometallic Chemistry*; Prentice-Hall: Upper Saddle River, NJ, 1997.

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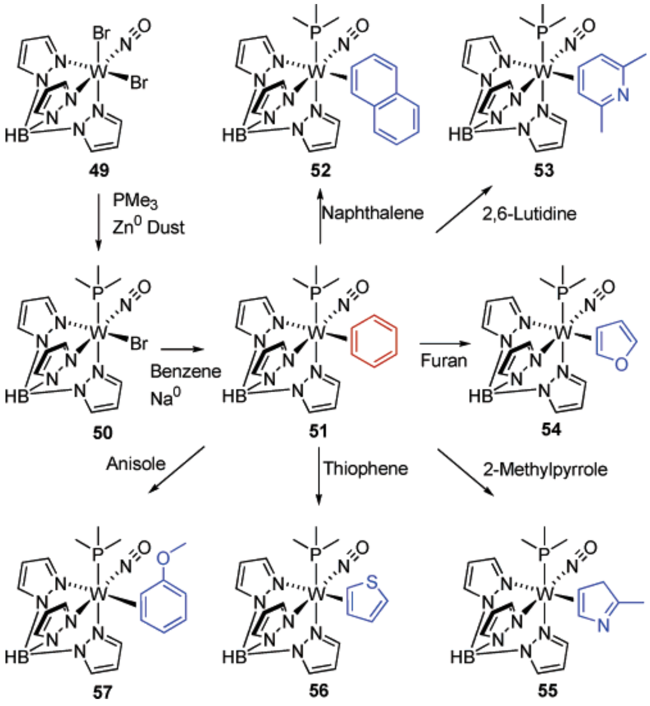
[110] McCleverty, J. A.; Rae, A. E.; Wolochowicz, I.; Bailey, N. A.; Smith, J. M. A. *J. Chem. Soc., Dalton Trans.* **1982**, 429.

[111] Unpublished results.

Scheme 9. Synthesis of TpW(PMe$_3$)(NO)(η^2-aromatic) Complexes



arenes, furans, and thiophenes, as well as certain pyrroles and pyridines (Scheme 9; **49**–**57**).[112]

III. Aspects of TpM(L)(π-acid)(η^2-aromatic) Complexes

A. Coordination Diastereomers. One of the more significant practical differences between the pentaammineosmium(II) metal fragment and the second generation {TpM(L)(π-acid)} fragments is that the latter involve a stereogenic metal center. These systems therefore form diastereomeric mixtures with prostereogenic unsaturated molecules. In principle, an enantioenriched form of these asymmetric metal fragments could be utilized in dearomatization sequences to provide enantioenriched organic products. However, the successful implementation of this strategy generally requires controlling the ratio of coordination diastereomers, as shown in Scheme 10 for naphthalene. Given that the specific rates of chemical transformation of a bound arene are similar for the two coordination diastereomers, the enantiomer ratio for the products should directly reflect that of the coordination diastereomers.

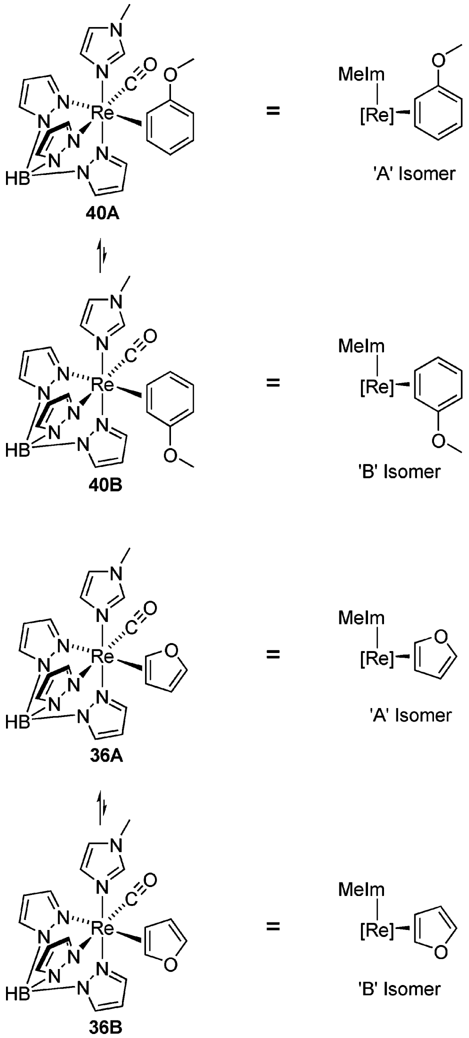
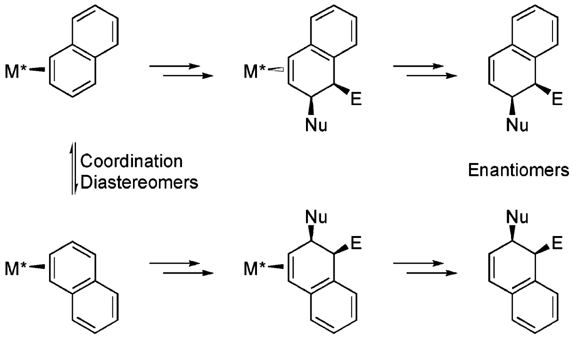


Figure 4. Coordination diastereomers of TpRe(MeIm)(CO)(5,6-η^2-anisole) and TpRe(MeIm)(CO)(3,4-η^2-furan).

Scheme 10. Prochiral Aromatic Molecules Forming Coordination Diastereomers Yield Enantiomeric Products from Dearomatization Sequences



M* = a π-basic metal fragment with a stereogenic metal center

NMR studies have established the fluxional nature of η^2 pentaammineosmium(II) complexes, which typically undergo rapid intrafacial and interfacial isomerizations at ambient temperature.[2,3] However, due to the high degree of symmetry of the pentaammineosmium(II) fragment, only constitutional isomers and their enantiomers are possible for complexes of this fragment and prochiral aromatic molecules. Similar isomerizations occur in TpM(L)(π-acid)(η^2-aromatic) complexes, but in this case migrations to the opposite face of a prochiral aromatic ligand result in different coordination diastereomers. Initial NMR studies of TpRe(PMe$_3$)(CO)(η^2-aromatic) complexes established that the bound aromatic molecule is oriented parallel to the Re–P bond axis, with the uncoordinated portion extending toward the CO (e.g., Figure 4). This orientation provides the strongest possible π-back-bonding interaction between a π^* orbital of the aromatic molecule and the metal-centered HOMO.[100,101] This orientation, which also serves to minimize steric interactions between the bound aromatic molecule and the Tp pyrazolyl groups,

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[112] Graham, P.; Meiere, S. H.; Sabat, M.; Harman, W. D. *Organometallics* **2003**, *22*, 4364.

Table 1. Diastereomeric Ratios and Isomerization Data for TpM(L)(π-acid)(η^2-aromatic) Complexes

	interfacial isomerizn[a]		intrafacial isomerizn[a]	
compd	T_{inter} (K)	$\Delta G_{\text{inter}}^{\ddagger}$ (kcal/mol)[b]	T_{intra} (K)	$\Delta G_{\text{intra}}^{\ddagger}$ (kcal/mol)[b]
TpRe(CO)(^{t}BuNC)(η^2-furan)	273	16.2	273	18.0
TpRe(CO)(^{t}BuNC)(η^2-2-methylfuran)	298	17.4		
TpRe(CO)(^{t}BuNC)(η^2-thiophene)[c]	273	16.9	273	16.9
TpRe(CO)(^{t}BuNC)(η^2-naphthalene)		>18.4	273	15.4
TpRe(CO)(^{t}BuNC)(η^2-2-methoxynaphthalene)		>20.8		
TpRe(CO)(^{t}BuNC)(η^2-1,8-dimethylnaphthalene)	293	17.5		
TpRe(CO)(PMe_3)(η^2-furan)	323	19.0	323	21.7
TpRe(CO)(PMe_3)(η^2-thiophene)[d]	323	19.0	323	20.0
TpRe(CO)(PMe_3)(η^2-naphthalene)	n/a	n/a	n/a	n/a
TpRe(CO)(py)(η^2-furan)	323	20.9		>21.9
TpRe(CO)(py)(η^2-thiophene)	323	21.0	323	21.9
TpRe(CO)(py)(η^2-naphthalene)		>21.9	323	20.3
TpRe(CO)(MeIm)(η^2-furan)	343	22.8		>23.3
TpRe(CO)(MeIm)(η^2-thiophene)	343	23.0		>23.3
TpRe(CO)(MeIm)(η^2-naphthalene)		>23.3	343	22.5
TpRe(CO)(MeIm)(η^2-benzene)[e]			233	14.5
TpRe(CO)(MeIm)(η^2-anisole)[f]	293	18.1	293	17.2
TpRe(CO)(MeIm)(η^2-1-methylpyrrole)[g]			213	10.6
TpMo(NO)(MeIm)(η^2-thiophene)	323	21.0	323	21.4
TpMo(NO)(MeIm)(η^2-naphthalene)	323	20.7	323	20.7
TpW(NO)(PMe_3)(η^2-benzene)			298	~17

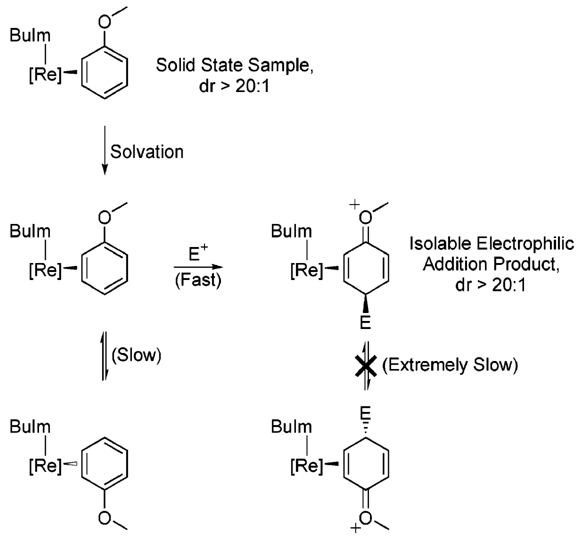
[a] Defined in text. [b] Errors in $\Delta G^{\ddagger}$ are estimated to be ±0.3 kcal/mol. [c] Observed spin saturation exchange with S-bound isomer. [d] Observed no spin saturation exchange with S-bound isomer. [e] Refers to migration from 1,2-η^2 to 2,3-η^2 isomer. [f] Refers to migration from 2,3-η^2 to 5,6-η^2 isomer. [g] Measured using coalescence data of bound protons.

is general among TpM(L)(π-acid)(η^2-aromatic) complexes and has been confirmed by numerous crystal structures.[100,101,105,107,112−114] Most of these complexes are observed as ratios of two facial diastereomers. These linkage isomers are designated as A and B, on the basis of the orientation of heteroatoms and substituent groups (**36** and **40**; see Figure 4).

Equilibrium diastereomeric ratios of TpM(L)(π-acid)(η^2-aromatic) complexes vary considerably, with complexes having smaller L ligands favoring the A diastereomer and complexes having larger L ligands favoring the B diastereomer. Complexes having smaller bound aromatic ligands show lower A:B ratios, and complexes having larger bound aromatic ligands show higher A:B ratios. Through spin-saturation experiments, isomerization rates and mechanisms were determined for a number of TpM(L)(π-acid)(η^2-aromatic) complexes, and these data are summarized in Table 1.[115]

B. Solid State Control of Diastereomers. Extensive protonation and low-temperature NMR studies have demonstrated that, in contrast to the low solution-state diastereomer ratios typically observed for TpM(L)(π-acid)(η^2-aromatic) complexes, solid-state diastereomeric ratios of these complexes are uniformly high (>20:1).[116] Remarkably, these highly diastereomerically enriched samples are consistently arrived at by simple precipitation of solution-state samples using pentane or hexanes. In a number of instances, this solid-state control of kinetically unstable diastereomers has been exploited to achieve highly diastereoselective electrophilic addition reactions. Under certain conditions, TpM(L)(π-acid)(η^2-aromatic) complexes have been solvated and made to react with electrophiles at rates significantly faster than the corresponding linkage isomerization rates.[114,116,117] The resulting cationic complexes do not easily undergo linkage isomerization and can subsequently be manipulated and isolated in high diastereomeric purity (Scheme 11).

Scheme 11. Highly Diastereoselective Additions to TpRe(BuIm)(CO)(η^2-anisole) Complexes Based on Diastereoselectivity Present in Solid-State Samples



C. Resolution and Enantiocontrol. A strategy was developed for resolving the enantiomeric forms of the {TpRe(MeIm)(CO)} fragment.[118] The steric environment of this system was evaluated through extensive binding

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(113) Friedman, L. A. Sabat, M.; Harman, W. D. *J. Am. Chem. Soc.* **2002**, *124*, 7395.

(114) Ding, F.; Valahovic, M. T.; Keane, J. M.; Anstey, M. R.; Sabat, M.; Trindle, C. O.; Harman, W. D. *J. Org. Chem.* **2004**, 69, 2257.

(115) Brooks, B. C.; Meiere, S. H.; Friedman, L. A.; Carrig, E. H.; Gunnoe, T. B.; Harman, W. D. *J. Am. Chem. Soc.* **2001**, *123*, 3541.

(116) Keane, J. M.; Ding, F.; Sabat, M.; Harman, W. D. *J. Am. Chem. Soc.* **2003**, *126*, 785.

(117) Keane, J. M.; Chordia, M. D.; Mocella, C. J.; Sabat, M.; Trindle, C. O.; Harman, W. D. *J. Am. Chem. Soc.* **2004**, *126*, 6806.

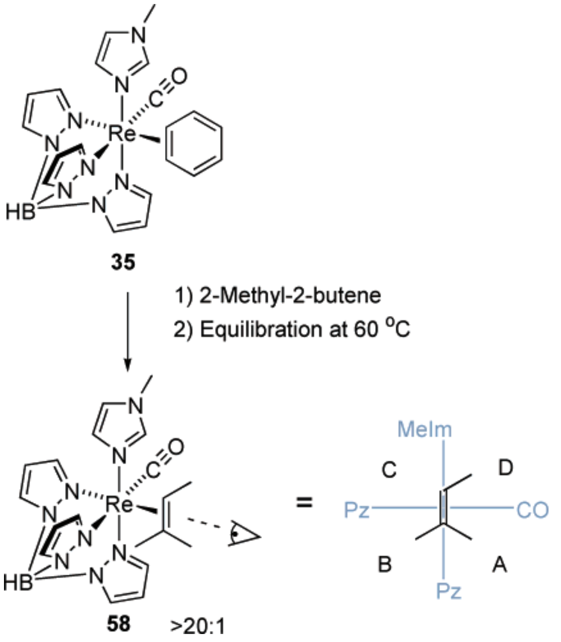


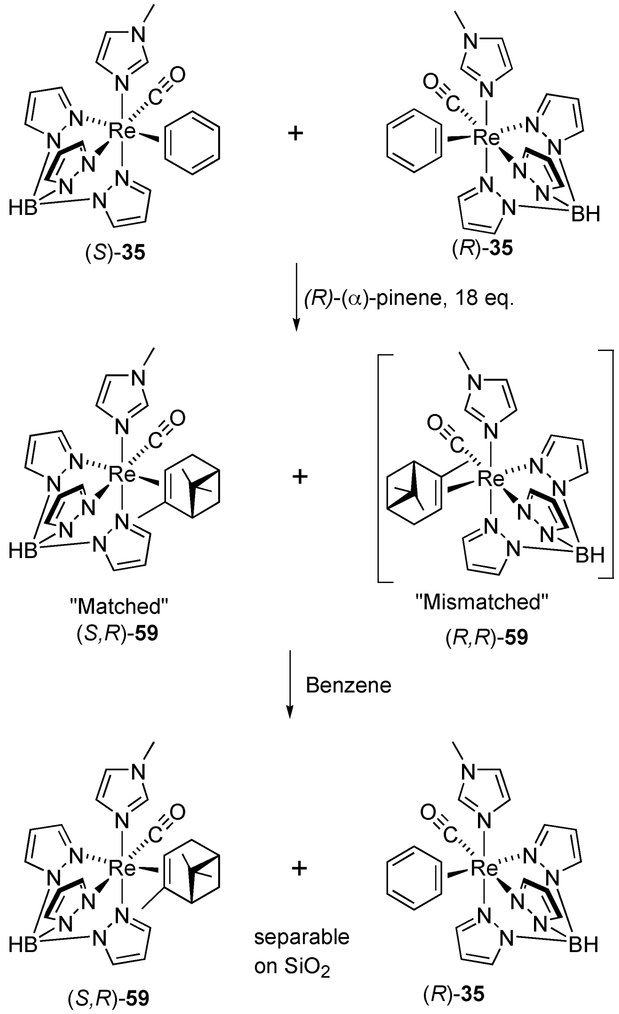
Figure 5. Thermodynamically favored orientation of the alkene in TpRe(MeIm)(CO)(η^2-2-methyl-2-butene) and the corresponding quadrant representation.

studies, the results of which are described using a quadrant system adapted from the work of Gladysz et al.[119,120] For example, the observation that 2-methyl-2-butene thermodynamically favors a single conformation with methyl groups in all quadrants except for C shows that this quadrant is the most sterically hindered (**58**; Figure 5).

A series of similar studies demonstrated that the steric hindrance in the quadrants increases in the order D < A < B < C. On the basis of this analysis, α-pinene was chosen as a source of asymmetry. Stirring a sample of TpRe(MeIm)(CO)(η^2-benzene) with an excess of (*R*)-α-pinene yields two diastereomeric complexes. A more stable "matched" TpRe(MeIm)(CO)(η^2-α-pinene) isomer has the α-pinene bridge directed away from the metal center and the olefinic methyl group directed into quadrant B, placing no substituents into the sterically disfavorable C quadrant (**59**; Scheme 12). A significantly less stable "mismatched" TpRe(MeIm)(CO)(η^2-α-pinene) isomer has not been fully characterized but is thought to likewise have the α-pinene bridge directed away from the metal center, now with the olefinic methyl group oriented directly into the congested C quadrant. When a combination of the matched and mismatched forms is stirred in excess benzene, the mismatched form exchanges α-pinene for benzene, and the resulting mixture of matched-TpRe(MeIm)(CO)(η^2-α-pinene) (**59**) and TpRe(MeIm)(CO)(η^2-benzene) (**35**) can be separated by column chromatography, effecting the resolution of the enantiomeric forms of the {TpRe(MeIm)(CO)} fragment (Scheme 12).

TpRe(MeIm)(CO)(η^2-benzene) can be regenerated from matched-TpRe(MeIm)(CO)(η^2-α-pinene) through an oxidation/reduction sequence, and resolved samples of other aromatic ligands can be obtained through typical ligand exchange procedures. Using this and similar sequences, resolved samples of TpM(L)(π-acid)(η^2-aromatic) complexes have been produced and utilized in highly diastereoselective addition reactions to give dearomatized products (**60**−**62**) in high enantiomeric excess (Scheme 13).[114,118,121]

Scheme 12. α-Pinene-Based Resolution of the {TpRe(MeIm)(CO)} Fragment



IV. New Reaction Pathways

Investigations of the chemistry of TpM(L)(π-acid)(η^2-aromatic) complexes have revealed a vast array of useful reaction pathways. Some of these, such as tandem additions to naphthalenes and benzenes and additions of Michael acceptors to anisoles, are comparable in principle to reactions previously demonstrated for complexes of aromatic molecules and pentaammineosmium(II).[23,31,37,114,122,123] Other transformations of TpM(L)(π-acid)(η^2-aromatic) complexes represent manifolds not formerly observed for the corresponding pentaammineosmium(II) analogues. Among these are a series of novel cyclization pathways, including Diels−Alder type

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[118] Meiere, S. H.; Valahovic, M. T.; Harman, W. D. *J. Am. Chem. Soc.* **2002**, *124*, 15099.

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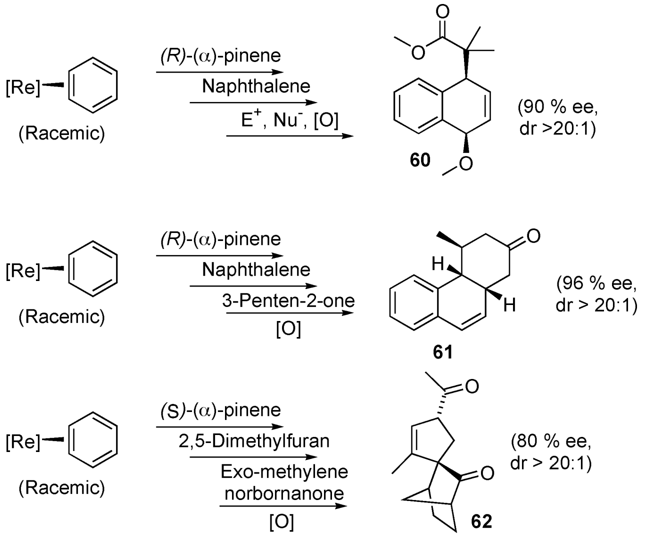
[120] Gladysz, J. A.; Boone, B. J. *Angew. Chem., Int. Ed.* **1997**, *36*, 550.

[121] Friedman, L. A.; You, F.; Sabat, M.; Harman, W. D. *J. Am. Chem. Soc.* **2003**, *125*, 14980.

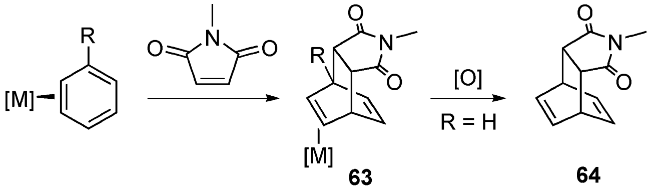
[122] Valahovic, M. T.; Gunnoe, T. B.; Sabat, M.; Harman, W. D. *J. Am. Chem. Soc.* **2002**, *124*, 3309.

[123] Smith, P. L.; Keane, J. M.; Shankman, S. E.; Chordia, M. D.; Harman, W. D. *J. Am. Chem. Soc.* **2004**, *126*, 15543.

Scheme 13. Examples of Highly Enantioselective Dearomatization Reactions Promoted by a Resolved π-Basic Metal Fragment



Scheme 14. Synthesis of Functionalized Bicyclo[2.2.2]octenes from Simple Arenes



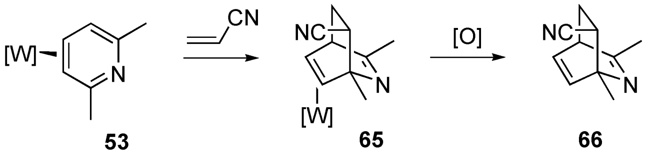
R = H or OCH_3

[M] = {TpRe(MeIm)(CO)} or {TpW(PMe_3)(NO)}

reactions of {TpM(L)(π-acid)} bound arenes and heterocycles, Michael−aldol and Michael−Michael ring closure sequences of TpRe(MeIm)(CO)(η^2-naphthalene), and cycloaddition and cyclopentannulation reactions of furan complexes. In addition, {TpM(L)(π-acid)} metal fragments have shown a significant propensity to form stable η^2 complexes with amides. While not directly germane to the topic of dearomatization, these deamidization reactions are noteworthy in that they speak to the extremely π-basic nature of these second-generation systems.

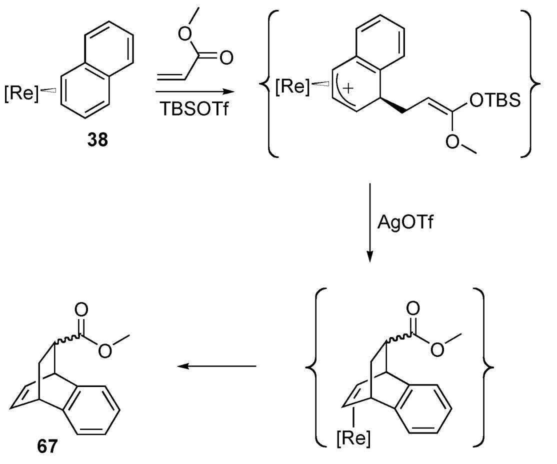
Arenes bound to {TpM(L)(π-acid)} metal fragments have been found to undergo Diels−Alder cycloadditions under remarkably mild conditions. When complexed to {TpRe(MeIm)(CO)} or {TpW(PMe_3)(NO)}, benzene cyclizes with *N*-methylmaleimide at a rate greater than that of the analogous reaction with cyclohexadiene.[112,124] The complex TpRe(MeIm)(CO)(η^2-anisole) undergoes analogous reactions with *N*-methylmaleimide (**63**) and dimethyl acetylenedicarboxylate (DMAD).[123,124] Oxidative decomplexation of the addition products of these reactions (where R = H) yields the functionalized bicyclo[2.2.2]octene **64** (Scheme 14).

Scheme 15. Diels−Alder Cycloaddition of Acrylonitrile to TpW(PMe₃)(NO)(η²-2,5-lutidine) Followed by Oxidative Demetalation



[w] = {TpW(PMe_3)(NO)}

Scheme 16. Stepwise 1,4-Cycloaddition of Methyl Acrylate and TpRe(L)(CO)(η²-naphthalene) Complexes



[Re] = {TpRe(MeIm)(CO)} or {TpRe(Py)(CO)}

A similar reactivity pattern has also been observed for substituted pyridines bound to the {TpW(PMe_3)(NO)} fragment. These complexes undergo Diels−Alder cycloadditions with electron-poor olefins (e.g., **65**), and the resulting 2-azabicyclo[2.2.2]octanes (e.g., **66**) can be liberated by oxidative demetalation (Scheme 15).[125]

A similar outcome is observed for the naphthalene complexes TpRe(L)(CO)(η^2-naphthalene) (L = py, MeIm) and methyl acrylate, which undergo net [4 + 2] cyclization, but in a stepwise fashion. When TpRe(L)(CO)(η^2-naphthalene) is combined with methyl acrylate and TBSOTf, the resulting material does not show evidence of methyl acrylate addition. However, if after 2 h silver triflate and pyridine are added, free 1,4-dihydro-1,4-(1-methoxycarbonylethano)naphthalene is isolated. The reaction is thought to proceed through two unobserved intermediates wherein the bound naphthalene first adds to the activated acrylate and the resulting silyl enolate and naphthalenium react only upon oxidation of the metal fragment (Scheme 16).[114] This type of reaction was never observed with pentaammineosmium(II).

Methyl acrylate was also found to give a novel cyclization product in a reaction with TpRe(L)(CO)(η^2-2-methoxynaphthalene) (**68**).[114] Investigations of this complex are complicated by the fact that it is present in solution as a mixture of many linkage isomers. However, when this mixture was treated with methyl acrylate and TBSOTf, followed 18 h later by AgOTf, a tetrahydrophenanthrene was isolated as the major product. This compound is thought to form through a series of two Michael additions, the product of which cyclizes and eliminates methanol upon oxidation (Scheme 17).

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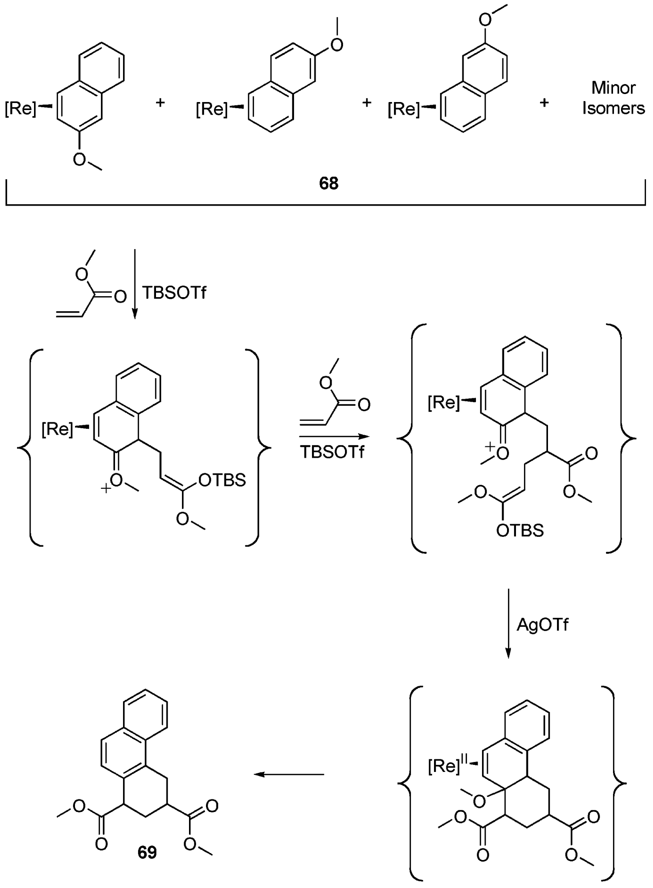
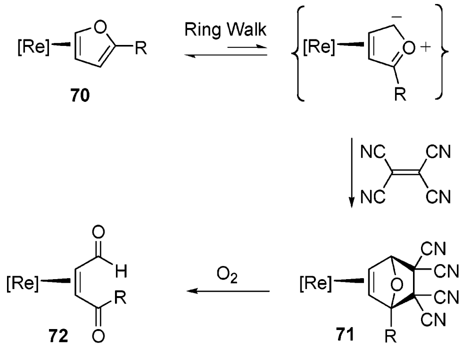
Scheme 17. Synthesis of a Tetrahydrophenanthrene from TpRe(L)(CO)(η^2-2-methoxynaphthalene) Isomers via a Michael−Michael Ring Closure Sequence (69)

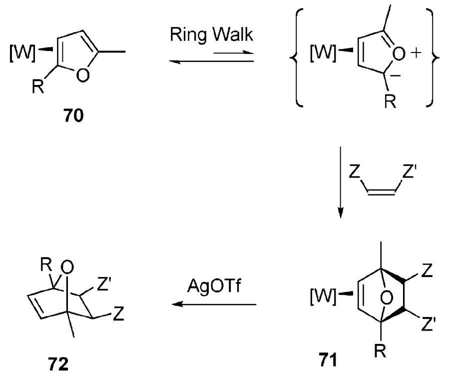


Scheme 18. [3 + 2] Cycloaddition of TpRe(^{t}BuNC)(CO)(4,5-η^2-furan) and TpRe(PMe$_3$)(CO)(4,5-η^2-furan) with Subsequent Atmospheric Oxidation

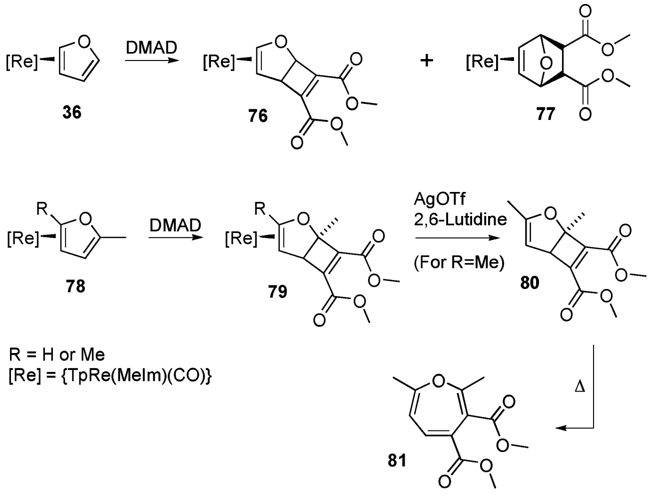


R = H or Me
[Re] = {TpRe(^{t}BuNC)(CO)} or {TpRe(PMe$_3$)(CO)}

Scheme 19. Synthesis of 7-Oxabicylo[2.2.1]heptenes (72) by [3 + 2] Cycloadditions of TpW(PMe$_3$)(NO)(4,5-η^2-2-methylfuran) and TpW(PMe$_3$)(NO)(2,3-η^2-2,5-methylfuran)



Scheme 20. Cycloadditions of TpRe(MeIm)(CO)(2,3-η^2-furan), TpRe(MeIm)(CO)(4,5-η^2-2-methylfuran), and TpRe(MeIm)(CO)(4,5-η^2-2,5-dimethylfuran) Complexes with Dimethyl Acetylenedicarboxylate (DMAD)



R = H or Me
[Re] = {TpRe(MeIm)(CO)}

Novel cycloaddition reactions have also been observed for furans complexed to {TpM(L)(π-acid)} fragments. Furan and 2-methylfuran complexes of {TpRe(L)(CO)} (L = ^{t}BuNC, PMe$_3$) undergo rapid [3 + 2] cyclizations with tetracyanoethylene (TCNE), generating 7-oxabicycloheptene complexes.[113] These addition reactions are thought to proceed through an intermediate ylide isomer of the furan complex (**70**) in a manner similar to that observed for pyrrole complexes of pentaammineosmium(II).[5,17] Exposure to air of the resulting oxabicycloheptene complexes (e.g., **71**) yields the corresponding *C*,*C*-η^2-(*Z*)-2-butenedial or *C*,*C*-η^2-(*Z*)-4-oxo-2-pentenal complexes (**72**; Scheme 18).

Comparable [3 + 2] cycloaddition reactions have been observed for the furan complex of {TpRe(MeIm)(CO)} and the 2-methylfuran and 2,5-dimethylfuran complexes of {TpW(PMe$_3$)(NO)}. TpRe(MeIm)(CO)(2,3-η^2-furan) cyclizes with dimethyl acetylenedicarboxylate (DMAD) under mild heating to give the [3 + 2] cycloaddition product together with a [2 + 2] product (vide infra),[113] while TpW(PMe$_3$)(NO)(4,5-η^2-2-methylfuran) and TpW(PMe$_3$)(NO)(2,3-η^2-2,5-methylfuran) complexes react in a [3 + 2] fashion with a range of dipolarophiles, including *N*-methylmaleimide, *N*-phenylmaleimide, and acrylonitrile, at reaction rates significantly faster than for the organic reaction analogues.[126] The products of these {TpW(PMe$_3$)(NO)}-promoted cycloadditions (**71**) can be oxidized to liberate 7-oxabicylo[2.2.1]heptenes (**72**) in moderate to high yields (Scheme 19).

When furan, 2-methylfuran, and 2,5-dimethylfuran complexes of {TpRe(MeIm)(CO)} are exposed to electron-

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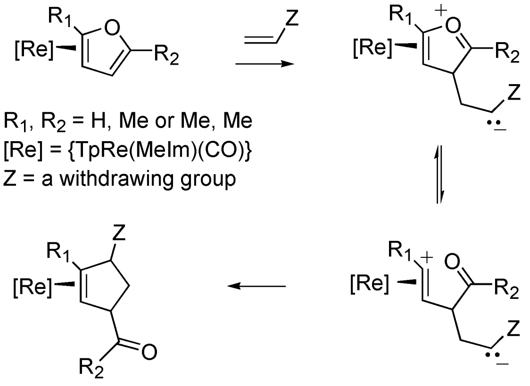
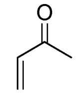
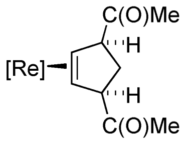
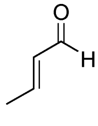
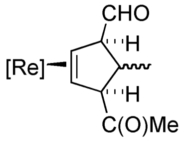
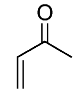
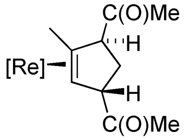
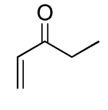
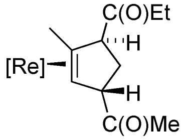
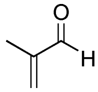
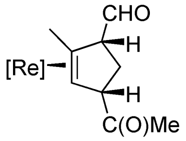
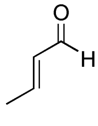
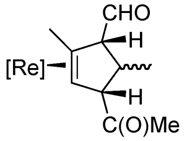
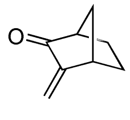
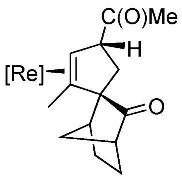
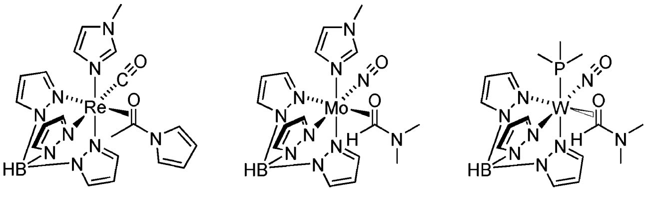
(126) Manuscript in preparation.

Scheme 21. Cyclopentannulation Reactions of {TpRe(MeIm)(CO)} 2-Methylfuran and 2,5-Dimethylfuran Complexes



Electrophile	R_1	R_2	Product	
	H	Me		**82**
	H	Me		**83**
	Me	Me		**84**
	Me	Me		**85**
	Me	Me		**86**
	Me	Me		**87**
	Me	Me		**88**



91 **92** **93**

Figure 6. The only reported examples of η^2-amide complexes.

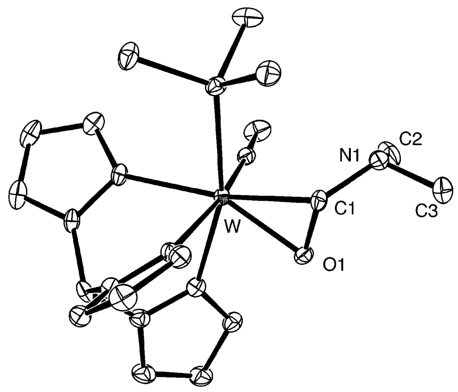
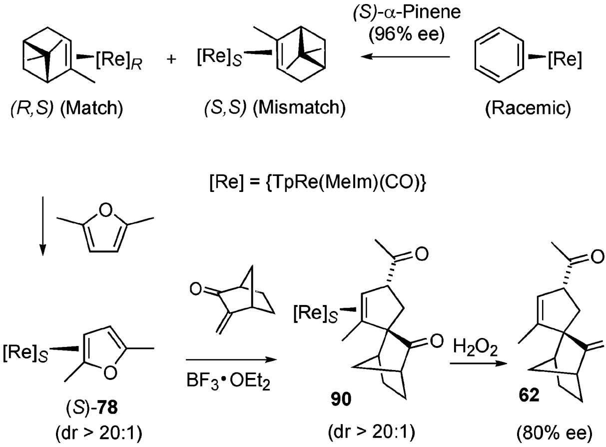


Figure 7. ORTEP diagram (30% ellipsoids) of TpW(PMe$_3$)(NO)(η^2-*N,N*-dimethylformamide) (**93**).

Scheme 22. Enantioselective Synthesis of Tricyclic Enedione from TpRe(MeIm)(CO)(4,5-η^2-2,5-dimethylfuran)[127]



poor olefins, alternative cyclization pathways are typically observed. TpRe(MeIm)(CO)(4,5-η^2-2-methylfuran) and TpRe(MeIm)(CO)(2,3-η^2-2,5-dimethylfuran) undergo [2 + 2] cycloadditions with dimethyl acetylenedicarboxylate (DMAD), generating 2-oxabicyclo[3.2.0]-hepta-3,6-diene complexes (**76** and **79**).[113] Under comparable conditions, the parent TpRe(MeIm)(CO)(2,3-η^2-dimethylfuran) complex gives both [2 + 2] and [3 + 2] cyclization products (vide supra). Oxidative decomplexation of the 2,5-dimethylfuran [2 + 2] adduct liberates the 2-oxabicyclo[3.2.0]hepta-3,6-diene **80** in 43% yield. While this compound is stable at ambient temperature, NMR studies show that it can be isomerized upon heating to give the oxepin **81** in modest yield (Scheme 20).

Unsymmetrical electron-poor olefins were found to follow an alternative reaction pathway with 2-methylfuran and 2,5-dimethylfuran complexes of {TpRe(MeIm)(CO)}. In the presence of BF$_3$·OEt$_2$, these electrophiles add to the 3-position of the complexed furan. It is thought that the labile O−C5 bond then cleaves, forming a stabilized vinyl cation which is subsequently attacked by the pendant nucleophile, generating a highly functionalized bound cyclopentene, often with a very high degree of stereocontrol (**82**−**88**; Scheme 21).[121]

When resolved (*S*)-TpRe(MeIm)(CO)(4,5-η^2-2,5-dimethylfuran) ((*S*)-**78**; vide supra) is utilized with *exo*-

methylenenorbornanone in this reaction, subsequent oxidative decomplexation of **90** gives a spirotricyclic enedione (**62**) in 40% yield and 80% ee (Scheme 22).

While the major focus of studies involving {TpM(L)-(π-acid)} fragments has been dearomatization pathways, a brief discussion of η^2-amide complexes of these fragments is warranted. Although there are many reported examples of η^2-coordinated aldehydes and ketones,[1,101,105,107,119,120,128–132] η^2 complexes of esters, anhydrides, and imides are far less common, owing to the significantly reduced capacity of these functional groups to accept electron density through π-backbonding.[133–135] To date, the only reported examples of η^2-coordinated amide complexes are those involving the second-generation {TpM(L)(π-acid)} metal fragments (**91**–**93**; Figure 6).[112]

While the {TpRe(MeIm)(CO)} fragment is sufficiently π-basic to form the stable η^2-ester complex TpRe(MeIm)-(CO)(η^2-EtOAc), attempts to complex unconjugated amides such as *N,N*-dimethylformamide were not successful. An isolable π-complex can be formed by stirring TpRe(MeIm)(CO)(η^2-benzene) in a THF solution of the pseudo-amide 1-acetylpyrrole. It is thought that in this example the pyrrole-ring conjugation is largely responsible for the stability of the deamidized complex. The {TpMo(MeIm)(NO)} and {TpW(PMe$_3$)(NO)} examples are more significant, with isolable η^2-*N,N*-dimethylformamide complexes being formed from reduction of TpMo(NO)(MeIm)Br in the presence of *N,N*-dimethylformamide and ligand exchange of TpW(PMe$_3$)(NO)(η^2-benzene), respectively. η^2-Amide complexation has been shown to have a profound effect on the nature of this functional group. A crystal structure of TpW(PMe$_3$)-(NO)(η^2-*N,N*-dimethylformamide) shows that the former amide nitrogen has adopted a pyramidal geometry, consistent with disruption of the nitrogen–carbonyl interaction and formation of a more amine-like structure (Figure 7).[112]

This analysis is supported by the observed N-protonation of TpW(PMe$_3$)(NO)(η^2-*N,N*-dimethylformamide) using the weak acid pyridinium triflate (p$K_a \approx 5$), which likewise suggests a more amine-like character of the former amide nitrogen.

V. Conclusion

By carefully tuning the ligand set for a given d^6 transition metal, one can rationally design complexes that have a thermodynamic preference for binding aromatic ligands across a π bond rather than inserting into a C–H bond. The complex acts like a protecting group for the double bond and isolates it from the remainder of the π system, thereby allowing new reaction patterns for the aromatic molecule. The stereochemistry of these ligand-centered reactions can be controlled in many cases by controlling the stereochemistry of coordination.

OM050029H

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(127) The corresponding figure in the original report showed incorrect stereochemistry.

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