Transition Metal-Stabilized Arenium Cations: Protonation of Arenes Dihapto-Coordinated to π-Basic Metal Fragments

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Abstract: A series of metal complexes was synthesized in which arenes were dihapto-coordinated to π-basic metal fragments having the general form {TpM(π-acid)(L)}, where Tp = hydridotris(pyrazolyl)borate, M = rhenium, molybdenum, or tungsten, π-acid = CO or NO$^+$, and L = 1-methylimidazole, 1-butylimidazole, pyridine, or trimethylphosphine. The arene complexes were shown to be significantly more basic than the analogous pentaammineosmium(II) arene complexes and were protonated by moderate acids to give remarkably stable η^2 and η^3 arenium cation complexes. A crystal structure of [TpRe(CO)(MeIm)(5,6-η^2-2*H*-anisolium)](OTf) confirmed the η^2 coordination of the anisolium ligand, but suggests a weak long-range interaction between the metal and C1 of the anisolium.

Introduction

Due to their role as intermediates in electrophilic aromatic substitution reactions, arenium ions represent an important but often transient class of chemical species. In the course of earlier studies involving pentaammineosmium(II), it was demonstrated that the dihapto-coordinated arenes show a dramatic increase in basicity (pK_a for the benzenium complex is −8.9), when compared to their native state.[1] In most cases, ^{1}H and ^{13}C NMR chemical shift data suggest the formation of species most closely resembling η^3-arenium complexes:
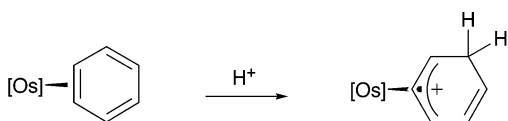
Because of the electron-donation from oxygen, the η^2-anisole complex of pentaammineosmium(II) is even more basic, showing a pK_a value of −6.0.[1] In contrast to that of the benzene or toluene complexes, NMR data of the protonated pentaammineosmium(II) anisole complex indicate that the arenium ligand is η^2 coordinated:
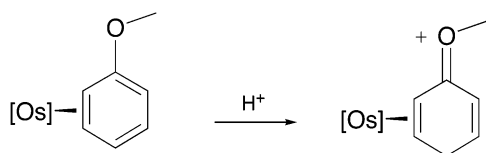
Although stabilized by the metal, these bound arenium ions act as potent electrophiles with carbon nucleophiles such as silyl ketene acetals, enol ethers, aryllithiums, and pyrroles.[2]

While osmium(II) promotes a variety of otherwise inaccessible transformations of arenes,[3−6] the specific requirement for the pentaammine ligand set[7,8] prevents a study examining the correlation between the chemical properties of the metal and ligand reactivity. In addition, the cost and possible toxicity of stoichiometric osmium have limited its synthetic application. However, a new series of thermally stable rhenium,[9−12] molybdenum,[13] and tungsten[14] arene complexes with a diverse array of ligand sets now makes such a study feasible. Initial reports of this second generation of dearomatization agents suggest that these metal complexes can π-back-bond to a greater degree than their pentaammineosmium(II) analogues.[14,15] A greater π-basicity of the dearomatization agent is expected to translate into an enhanced reactivity of the corresponding arene complexes toward electrophiles. In hopes of gauging this reactivity and gaining insight into known and potential elec-

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Table 1. [a]
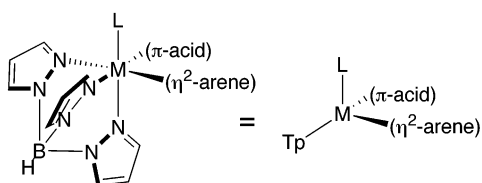
compound	M	L	π-acid	arene	yield (%)
1	Re	MeIm	CO	benzene	59[b]
2	Re	MeIm	CO	anisole	33[b]
3	Re	MeIm	CO	3-methylanisole	87[c,j]
4	Re	MeIm	CO	naphthalene	57[c]
5	Re	BuIm	CO	benzene	56[d]
6	Re	BuIm	CO	toluene	54[e]
7	Re	BuIm	CO	*o*-xylene	37[e]
8	Re	BuIm	CO	*m*-xylene	18[e,j]
9	Re	BuIm	CO	anisole	85[e]
10	Re	BuIm	CO	3-methylanisole	59[e]
11	Re	BuIm	CO	4-methylanisole	79[e]
12	Re	BuIm	CO	naphthalene	83[e,j]
13	Re	Py	CO	naphthalene	46[f]
14	Re	PMe₃	CO	naphthalene	55[g]
15	Mo	MeIm	NO	naphthalene	41[h]
16	W	PMe₃	NO	anisole	40[i]

[a] [M] = TpM(π-acid), MeIm = 1-methylimidazole, BuIm = 1-butylimidazole, Py = pyridine. [b] From TpRe(MeIm)Br₂. [c] From TpRe(CO)(MeIm)(η^2-benzene). [d] From TpRe(BuIm)Br₂. [e] From TpRe(CO)(BuIm)(η^2-benzene). [f] From TpRe(Py)Br₂. [g] From TpRe(CO)(PMe₃)(η^2-cyclohexene). [h] From TpMo(NO)Br₂. [i] From TpW(NO)(PMe₃)Br. [j] Not analytically pure.

trophilic reactions of rhenium, molybdenum, and tungsten η^2-arene complexes, protonations of TpM(π-acid)(L)(η^2-arene) (Tp = hydridotris(pyrazolyl)borate, M = rhenium, molybdenum, or tungsten, π-acid = CO or NO⁺, L = a variable ligand) complexes were investigated.

Results

Complexes **1**−**16** (Table 1) were produced according to literature procedures or modifications thereof.[9−15] Noteworthy changes to the reported procedures include the substitution of sodium dispersion for sodium amalgam in the reduction of TpRe(RIm)Br₂ to generate TpRe(CO)(RIm)(η^2-benzene) complexes in a mercury-free process, and the use of 1-butylimidazole in place of 1-methylimidazole to provide variants having greater solubilities in organic media. The complex TpRe(CO)(BuIm)-(N₂) was observed as a trace product in the synthesis of the arene complexes, and its characterization is provided in the Supporting Information. Spectroscopic properties of novel complexes **3**, **5**−**12**, and **16** are generally analogous to those of the previously reported TpM(π-acid)(L)(η^2-arene) complexes. The stereochemical assignments of complexes **2**, **4**, **5**, **9**, **10**, **11**, and **16** were confirmed by single-crystal X-ray structural analysis. The majority of the initial studies of rhenium-based η^2 arene complexes, including many protonation experiments, were performed using the {TpRe(CO)(MeIm)} fragment. However, the low solubilities of the corresponding anisole complexes prompted us to prepare a {TpRe(CO)(BuIm)} variant in several cases (see Table 1). Attempts to generate complexes of 2-methyl-, or 3,5-dimethylanisole, or *p*-xylene resulted instead in a dimeric species featuring two bridging η^1:η^2 imidazole ligands. The ORTEP diagram from a crystal structure determination of {TpRe(CO)}₂(μ-η^1:η^2-BuIm)₂ (**1D**), a representative compound, is shown in Figure 1.
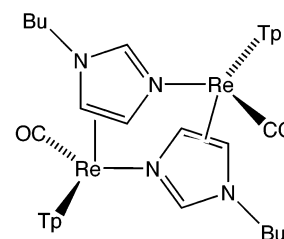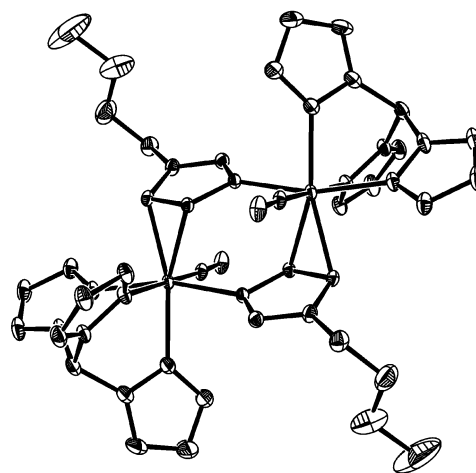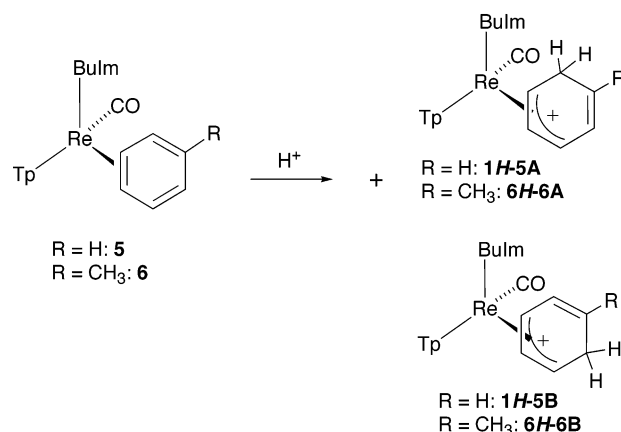

Figure 1. ORTEP diagram (30% ellipsoids) for {TpRe(CO)}₂(μ-η^1:η^2-BuIm)₂ (**1D**).

Scheme 1

Initial attempts to observe the conjugate acids of TpRe(CO)-(MeIm)(η^2-benzene) (**1**) and TpRe(CO)(MeIm)(5,6-η^2-anisole) (**2**) under conditions similar to those employed with the corresponding pentaammineosmium(II) complexes were unsuccessful, with exposure of these complexes to triflic acid in acetonitrile resulting in rapid decomposition (-40 °C). However, when TpRe(CO)(BuIm)(η^2-benzene) (**5**) was exposed to the comparatively weaker methanesulfonic acid ($pK_a = -2.6$) in CDCl₃ at -20 °C, ¹H NMR and correlation spectroscopy experiments showed the following spin systems (δ, ppm; -20 °C): 5.45−4.73−3.53−6.29−5.36, 5.39−4.64−4.38−6.32−5.39, 3.19−3.43, and 3.24−3.51.

Comparison of these data with those observed for pentaammineosmium(II)[1] indicates the formation of two isomers of an η^3 benzenium complex (**1H-5A** and **1H-5B**; Scheme 1), with the first three signals in each set of five corresponding to protons at π-bound allylic positions, the remaining two corresponding to protons on an unbound olefinic group, and the two sets of

upfield resonances corresponding to the geminal protons of methylene groups.

In contrast, when TpRe(CO)(BuIm)(η^2-benzene) (**5**) was exposed to 1 equiv of the weaker Brønsted acid, diphenyl-ammonium triflate (DPAT, pK_a = 0.8), addition of the reaction solution into hexanes gave a mixture of products, including a compound (**17**) that is assigned to be the allyl complex [TpRe(CO)(BuIm)(η^3-C$_6$H$_9$)](OTf):[16]
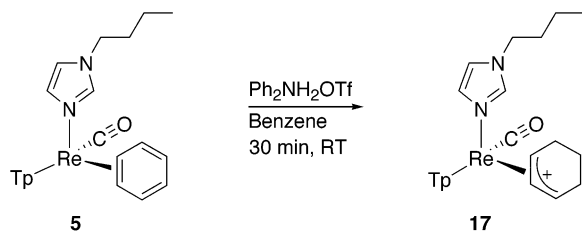
Apparently, a portion of the Re(I) acts as the electron source in the reduction of the benzene ligand of **5** (eq 1), but neither the fate of the rhenium nor the nature of the reaction mechanism were uncovered due to the complexity of the product mixture.
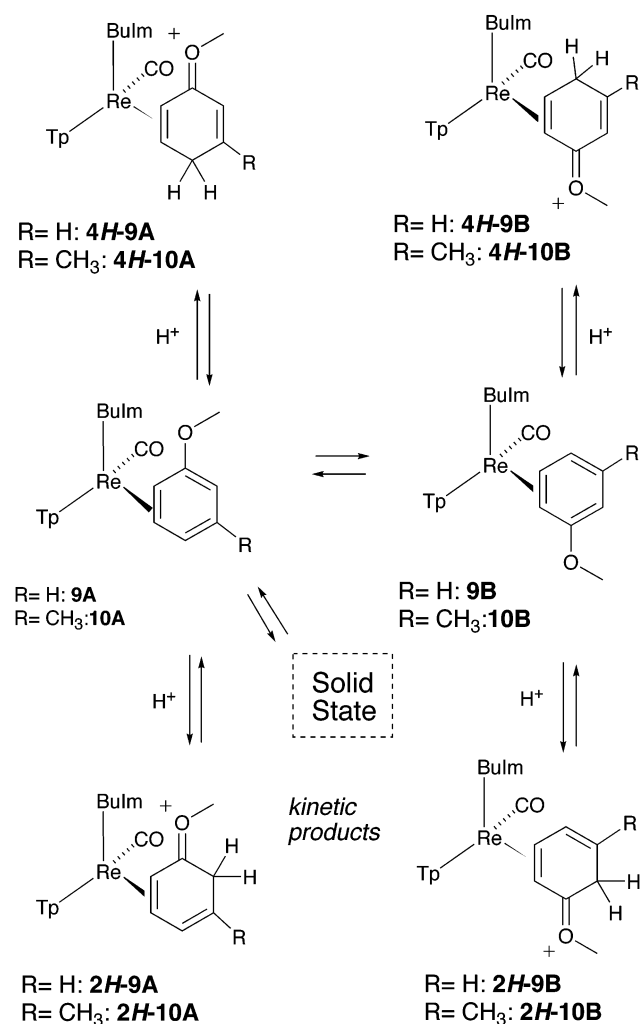
$$\text{TpRe(CO)(BuIm)}(\eta^2\text{-C}_6\text{H}_6) + 2e^- + 3H^+ \rightarrow$$
$$[\text{TpRe(CO)(BuIm)}(\eta^3\text{-C}_6\text{H}_9)]^+ \quad (1)$$
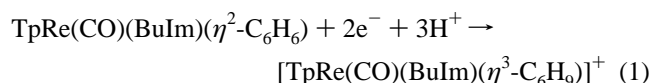
Exposure of TpRe(CO)(BuIm)(η^2-toluene) (**6**) to methanesulfonic acid in CDCl$_3$ generated the complex [TpRe(CO)-(BuIm)(η^3-2*H*-toluenium)]$^+$ in the form of two diastereomers (**2*H*-6A** and **2*H*-6B**), with NMR data closely correlating to that observed for the benzene derivative. However, attempts to protonate TpRe(CO)(BuIm)(η^2-(*o*-xylene)) (**7**), even at −20 °C, resulted in rapid decomposition.

Protonation of anisole bound to rhenium occurs under significantly milder conditions than was seen with the benzene analogue, and the conjugate acid products of the former are more stable. Solutions of complexes of the form [TpRe(CO)-(RIm)(η^2-anisolium)]$^+$ (where RIm = 1-butylimidazole or 1-methylimidazole) can be observed for several hours at 20 °C. Acids ranging in strength from pK_a −2.6 (methanesulfonic acid) to pK_a 2.1 (phosphoric acid) give products identified as either 2*H*- or 4*H*-anisolium complexes (Scheme 2). In a typical experiment, TpRe(CO)(BuIm)(5,6-η^2-anisole) (**9**) and 1 equiv of the acid were dissolved in d_6-acetone, and ^{1}H NMR spectra revealed various ratios of four isomers (**2*H*-9A**, **2*H*-9B**, **4*H*-9A**, **4*H*-9B**; see Scheme 2). Regiochemical assignments were made through extensive use of correlation spectroscopy, and stereochemical assignments were made using established chemical shift trends related to anisotropic effects associated with the pyrazolyl groups of the hydridotris(pyrazolyl)borate ligand.[12,17]

The regioselectivity of TpRe(CO)(BuIm)(5,6-η^2-anisole) (**9**) protonations varied considerably with changes in reaction conditions. For example, the C2/C4 protonation ratio was found to be 3:1 when 1 equiv of diphenylammonium triflate was used at 20 °C; however, this ratio improved with either an increase in the amount of acid or a decrease in reaction temperature, reaching a ratio of >20:1 when over 2 equiv of the acid were used at −60 °C. Attempts to equilibrate this reaction mixture

Scheme 2

R= H: **4*H*-9A**
R= CH$_3$: **4*H*-10A**

R= H: **4*H*-9B**
R= CH$_3$: **4*H*-10B**

R= H: **9A**
R= CH$_3$: **10A**

R= H: **9B**
R= CH$_3$: **10B**

Solid State

kinetic products

R= H: **2*H*-9A**
R= CH$_3$: **2*H*-10A**

R= H: **2*H*-9B**
R= CH$_3$: **2*H*-10B**

resulted in significant decomposition.[18] However, the addition of CD$_3$OD to isolated samples of the protonated complex (**2*H*-9A**) at 20 °C resulted in the exchange of one geminal proton, indicating that protonation is reversible. A stereoselective H/D exchange is consistent with those results obtained for the isoelectronic pentaammineosmium(II) system, where protonation was shown to occur exclusively exo to the metal.[1,19] Complex **9** could be regenerated by deprotonation of ***H*-9** with pyridine, but not without partial decomposition.

The stereoselectivity of protonation is also dependent on reaction conditions. Whereas treating **9** with 1 equiv of an acid at 20 °C resulted in a **2*H*-9A**:**2*H*-9B** ratio approaching 1:1, when TpRe(CO)(BuIm)(5,6-η^2-anisole) (**9**) was added to an acidic solution containing either multiple equivalents of acid at 20 °C or 1 equiv of acid at −60 °C, a **2*H*-9A**:**2*H*-9B** ratio of >20:1 was observed. A control experiment was performed in which solutions of **9** were prepared at 20 °C and then combined with the acid at −60 °C. The resulting **2*H*-9A**:**2*H*-9B** ratio was again close to 1:1. Together, these experiments indicate that **9A** is the only isomer present in the solid state (Scheme 2), even though **9A** and **9B** rapidly equilibrate in solution,[20] and that
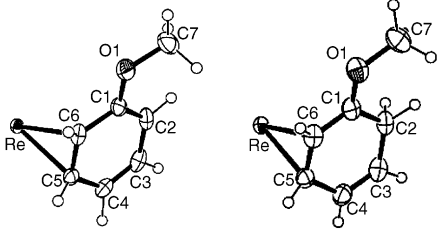
(16) ^{1}H NMR signals include 4.97, 4.85, and 4.22 ppm, respectively, and six upfield ^{1}H NMR signals between 1.26 and 3.32 ppm.
(17) Meiere, S. H.; Harman, W. D. *Organometallics* **2001**, *20*, 3876.

(18) As the possibility of differences in rates of decomposition among the isomers could not be excluded, a thermodynamic ratio could not be obtained.
(19) Valahovic, M. T.; Gunnoe, T. B.; Sabat, M.; Harman, W. D. *J. Am. Chem. Soc.* **2002**, *124*, 3309.
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Table 2. [a]

atom pair	**2A** (select atoms)	**2H-2A** (select atoms)	**2H-2A** (calcd)
O1−C7	1.43	1.47	1.42
O1−C1	1.36	1.30	1.32
C1−C2	1.36	1.49	1.48
C2−C3	1.43	1.47	1.48
C3−C4	1.35	1.33	1.34
C4−C5	1.45	1.47	1.46
C5−C6	1.44	1.44	1.43
C6−C1	1.45	1.39	1.40
Re−C1	3.17	2.95	2.75
Re−C4	3.22	3.15	
Re−C5	2.24	2.17	2.17
Re−C6	2.20	2.22	2.19

[a] Distances in angstroms.

the selective formation of **2H-9A** was achieved by protonating **9A** more rapidly than it could isomerize to **9B**.

X-ray quality crystals of [TpRe(CO)(MeIm)(5,6-η^2-(2H-anisolium))](OTf) (**2H-2A**) were obtained by chilling to −40 °C a solution of TpRe(CO)(MeIm)(5,6-η^2-anisole) (**2**) in acidic methanol prepared at 20 °C. Select atomic distances for **2H-2A** are shown in Table 2 along with corresponding atomic distances for **2A**. The following structural changes are among those revealed by the solved X-ray structures of **2** and **2H-2A**. Upon protonation of **2**, the lengths of the C1−C2, C2−C3, and C4−C5 bonds increase by 0.13, 0.04, and 0.02 Å, respectively, while the length of the C1−O bond decreases by 0.06 Å and the C5−C6 bond length shows no detectable change. Of particular note, the Re−C1 distance decreases by 0.22 to 2.95 Å, suggesting a weak interaction between the ipso carbon and the metal.

As originally observed for osmium(II), the 3-methylanisole complex TpRe(CO)(BuIm)(5,6-η^2-(3-methylanisole)) (**10**) is significantly more basic than the parent complex TpRe(CO)-(BuIm)(5,6-η^2-anisole) (**9**). When **10** was combined with a stoichiometric quantity of protonated TpRe(CO)(BuIm)-(5,6-η^2-anisole) (**H-9**), the initial anisolium was completely (>95%) consumed to give [TpRe(CO)(BuIm)(5,6-η^2-(3-methyl-anisolium))](OTf) (**H-10**) and **9**.[21] Like the protonations of TpRe(CO)(RIm)(5,6-η^2-anisole) complexes, the protonations of methylanisole complexes yield up to four isomeric products (Scheme 2). For example, treating a solution of TpRe(CO)-(BuIm)(5,6-η^2-(3-methylanisole)) (**10**) with 1 equiv of DPAT in acetone-d_6 at 20°C produced a 12:3:3:1 ratio of complexes **4H-10A**, **2H-10A**, **4H-10B**, and **2H-10B**, respectively, with ^{1}H NMR chemical shifts analogous to those of the parent anisolium analogues (**H-9**). As with the anisole derivative, lower temperatures and higher concentrations of acid tended to give better selectivity for the 2H-anisolium species **2H-10A**, while longer
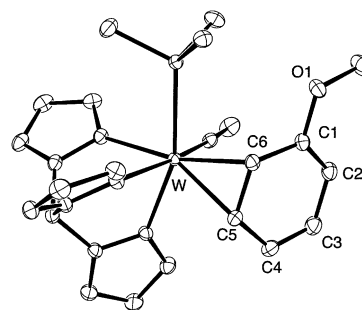
reaction times gave higher proportions of the 4H-anisolium isomer, **4H-10A**. Similar to the parent anisolium analogues (**H-9**), a thermodynamic ratio could not be obtained because of concurrent decomposition.

In a surprising result, the R = methyl and butyl variants of TpRe(CO)(RIm)(5,6-η^2-(3-methylanisole)) reacted with acid to give complementary stereochemistries. Whereas the protonation of **10** under kinetic control yielded predominantly **2H-10A** and **4H-10A**, the analogous reaction with **3** delivered only **2H-3B** and **4H-3B**. As with the parent anisole complex TpRe(CO)-(BuIm)(5,6-η^2-anisole) (**9**), coordination stereoselectivity in the protonation of **3** and **10** was ultimately traced to the solid state.[20] The 3-methyl and 4-methylanisole complexes TpRe(CO)-(BuIm)(5,6-η^2-(methylanisole)) (**10** and **11**) also show complimentary stereochemistries in the solid state and for their kinetically controlled protonations. In contrast to **10** (vide supra), solutions of **11** at ambient temperature show a **11A:11B** ratio of ~1:2, and protonation of **11** at −40 °C forms a 1:6 ratio of **2H-11A** to **2H-11B** (−40 °C). 4H-Arenium complexes were not detected for **H-11**.

The ORTEP diagram for the tungsten anisole complex TpW(NO)(PMe₃)(5,6-η^2-anisole) (**16**) [14] is shown in Figure 2. Its protonation was effected using DPAT and gave exclusively the 2H regioisomer [TpW(NO)(PMe₃)(5,6-η^2-(2H-anisolium))]-(OTf) (**2H-16**). The diastereomer **2H-16A** has diagnostic ^{1}H NMR signals for protons at the bound positions appearing at 2.78 (H5) and 4.80 (H6) ppm, while the other diastereomer, having the methoxy group directed away from the PMe₃ ligand (**2H-16B**), has diagnostic ^{1}H NMR signals for protons at the bound positions appearing at 4.61 (H5) and 3.46 (H6) ppm. Protonation of TpW(NO)(PMe₃)(5,6-η^2-anisole) (**16**) immediately as it enters the solution state[22] (excess acid at −78 °C) gave >20:1 **2H-16A**, a result suggesting that solid-state samples of **16** contained exclusively isomer **16A**. Alternatively, when **16** was protonated only after it was first fully dissolved, and then treated with acid at 20 °C (or protonated at low temperature and then allowed to warm to ambient temperature), <1:20 **2H-16A:2H-16B** was observed.

The relative basicity of **16** was investigated by exposing **2H-16B** to equivalent portions of TpRe(CO)(BuIm)(5,6-η^2-anisole) (**9**) and TpW(NO)(PMe₃)(5,6-η^2-(3-methylanisole)) (**10**). Rigorous analysis of the resulting mixtures was hampered by the large number of species involved. However, when **2H-16B** was combined with **9**, approximately 10% of the **2H-16B** sample was deprotonated. When **2H-16B** was combined with **10**, approximately 50% of the **2H-16B** sample was deprotonated.

Figure 2. ORTEP diagram of the complex TpW(NO)(PMe₃)(5,6-η^2-anisole) (**16**).

(21) The conversion was not quantitative, as a significant portion of free anisole was also observed.

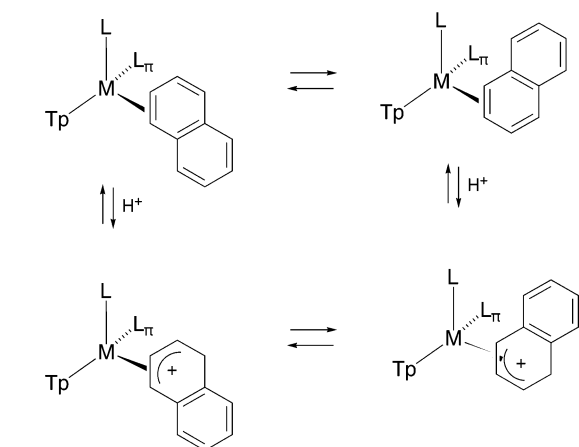(22) Solid samples of these arene complexes were obtained by precipitation from a THF solution using hexanes.

Scheme 3

L = BuIm, L_π = CO, M = Re: **1*H*-12A** **1*H*-12B**

L = MeIm, L_π = CO, M = Re: **1*H*-4A** **1*H*-4B**

L = py, $L_{\pi'}$ = CO, M = Re: **1*H*-13A** **1*H*-13B**

L = PMe₃, $L_{\pi'}$ = CO, M = Re: **1*H*-14A** **1*H*-14B**

L = MeIm, L_π = NO, M = Mo: **1*H*-15A** **1*H*-15B**

To compare the weaker π-base{TpMo(NO)(MeIm)} with the heavy-metal complexes described earlier, we needed to change the aromatic ligand to one for which the corresponding molybdenum complex could be isolated. Thus, the protonation of η^2-bound naphthalene complexes was explored. Previous studies reported that TpRe(CO)(MeIm)(3,4-η^2-naphthalene) (**4**), TpRe(CO)(Py)(3,4-η^2-naphthalene) (**13**), TpRe(CO)(PMe₃)(3,4-η^2-naphthalene) (**14**), and TpMo(NO)(MeIm)(3,4-η^2-naphthalene) (**15**),[13,19] as well as the pentaammineosmium(II) analogue,[1] could be protonated by triflic acid in acetonitrile to give 1*H*-naphthalenium complexes (Scheme 3). However, much weaker acids could be used for rhenium than were needed to protonate the arene bound to osmium.[1] Complexes **4**, **13**−**15**, and TpRe(CO)(BuIm)(3,4-η^2-naphthalene) (**12**) were found to be only slightly less basic than the {TpRe(CO)(BuIm)} anisole complexes, protonating completely (>95%) in the presence of diphenylammonium triflate (pK_a 0.8), while showing no reactivity with phosphoric acid (pK_a 2.12). Contrary to our original beliefs,[19] the conjugate acids of TpRe(CO)(MeIm)(3,4-η^2-naphthalene) (**4**) could be observed in solution at 20 °C for hours. Isolated samples of [TpRe(CO)(BuIm)(2,3,4-η^3-(1*H*-naphthalenium))](OTf) (**1*H*-12**) showed low diastereoselectivity (2:1 or less) with respect to the orientation of the unbound portion of the naphthalene ring (**1*H*-12A**:**1*H*-12B**), if prepared from an equilibrated solution. However, when care was taken to protonate immediately after dissolving the solid, only diastereomer **1*H*-12A** was observed (Scheme 3). Similarly, [TpRe(CO)(py)(2,3,4-η^3-(1*H*-naphthalenium))](OTf) could be formed in a high dr (10:1:trace), where the favored isomer has the unbound naphthalene ring directed toward the pyridine ligand (**1*H*-13A**).

Studies of TpMo(NO)(MeIm)(3,4-η^2-naphthalene) (**15**) and its conjugate acid (**1*H*-15**) were generally comparable to those of the {TpRe(CO)(RIm)} analogues. Protonation of **15** was accomplished using a solution of triflic acid in acetonitrile. Solvation and subsequent observation by NMR spectroscopy at −40 °C indicated the presence of a 20:1 ratio of two

diastereomers, **1*H*-15A** and **1*H*-15B** (Scheme 3). However, complex **15** showed no reaction with phosphoric acid. Unlike the rhenium analogue (*H*-12), *H*-15 was not stable to isolation as a solid. It also showed a shorter half-life toward decomposition (hours at −20 °C) than that of *H*-12. To compare the effects of different metals, equivalent portions of [TpRe(CO)(BuIm)-(2,3,4-η^3-(1*H*-naphthalenium))](OTf) (**1*H*-12B**) and TpMo(NO)-(MeIm)(3,4-η^2-naphthalene) (**15**) were combined. After 0.5 h, no proton transfer was observed at −20 °C (¹H NMR), indicating that the molybdenum-bound naphthalene was less basic than that bound to rhenium.

Discussion

Cooper et al. have demonstrated that η^4 coordination of arenes to anionic Cr(CO)₃²⁻ and Mn(CO)₃¹⁻ fragments results in activation of the arene ligand toward electrophiles. Benzene,[23] anisole,[24] toluene,[24] naphthalene,[25] and anthracene[26] bound to these fragments have been protonated with a moderate acid. Several examples of reactions of η^4 arene complexes and carbon electrophiles have also been reported.[27−30] Vigalok et al. have shown that dihapto coordination to tethered metal centers is sufficient to stabilize a series of methylene arenium complexes.[31−33] NMR and X-ray crystal data confirm that the reported structures are more characteristic of arenium ions than benzyl cations and that the degree of arenium character is directly related to the π-donating ability of the metal fragment.

The extent of π-back-bonding in the above examples and in the complexes described in the current work makes the involved metal fragments fundamentally different from the vast majority which have been reported to bind arenes. The η^2 and η^4 arene complexes are among the few examples of arene−metal complexes that undergo electrophilic additions to give thermally stable arenium complexes. In addition, the extreme π-basicity of the Cr(CO)₃²⁻, Mn(CO)₃¹⁻, pentaammineosmium(II), and {TpM(π-acid)(L)} metal fragments allows them to bind and stabilize a wide range of species without the aid of a tether. This basic character is highlighted in the current work by both the high degree of basicity of the bound arenes and the robust nature of many of the resulting arenium complexes.

In comparison to that of the pentaammineosmium(II) metal fragment, the greater π-basicity of the {TpM(π-acid)(L)} fragments both enhances the nucleophilic character of bound arenes and makes the fragments more susceptible to decomposition by oxidative pathways. Strong acids quickly oxidize both the pentaammineosmium(II) and the {TpM(π-acid)(L)} systems at 20 °C. However, for these rhenium and tungsten complexes, the basicity of the bound anisole increases by 7 orders of

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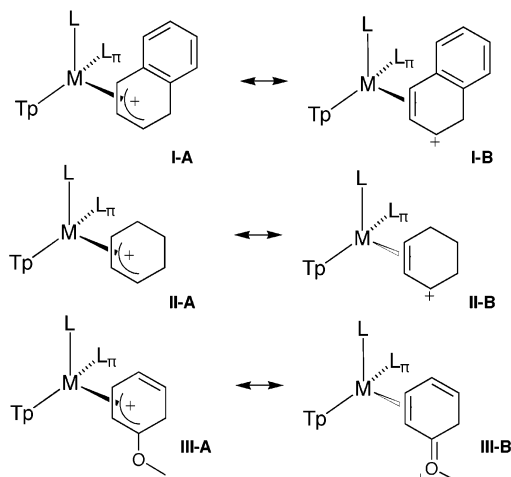(33) Vigalok, A.; Milstein, D. *Acc. Chem. Res.* **2001**, *34*, 798.

Figure 3. Resonance contributors for arenium complexes showing η^2 and η^3 forms.

magnitude, and that of naphthalene increased by about 10^9, making the arenium complexes accessible under very mild reaction conditions.

The arenium complexes described herein can be classified as severely distorted π allyl complexes, lying on the $\eta^2-\eta^3$ continuum (Figure 3).

In the case of the anisolium complexes, the dominant resonance contributor is one in which the carbocycle is bound η^2 with the oxygen stabilizing the positive charge of the carbocycle through π donation. However, both the crystallographic and the NMR data indicate that a weak interaction exists between the metal and the ipso carbon. As compared to its conjugate base, the Re$-$C$_{ipso}$ bond length is significantly shorter. In addition, the methoxy resonance shifts modestly upfield in the conjugate acids of **2B** and **9B**. While the **2A** and **9A** isomers experience a slight downfield shift, in no case does the methoxy resonance approach the values typically associated with methyloxonium ions.[34] DFT calculations (vide infra) faithfully reproduce most of the associated bond lengths of the anisolium complex **2H-2A** (see Table 2), including the weak interaction between Re and the ipso carbon (2.75 Å).

Although the benzenium complex could not be isolated, DFT calculations were carried out, modeling the benzenium complex **H-1**. Our experience in calculating energies and structures for pentaammineosmium(II) systems[35] and TpRe(CO)(L) systems[36] has been that geometries are well represented by schemes using a local density functional with a pseudopotential representation of the heavy metal and a mixed basis including the pseudopotentials associated basis on the metal and a 6-31G* Gaussian basis on other atoms. More realistic binding energies of aromatic species with pentaammineosmium(II) and the Re agent are obtained with the gradient-corrected B3LYP functional. Because it seems plausible that either functional would describe the energy differences at issue here, we chose the less costly local functional.[37,38] The lowest energy stereoisomer is shown in Figure 4. In addition to the distinctly localized C2$-$C3 bond (1.34 Å), the Re$-$C6 distance is 0.17 Å longer than the other Re$-$C bonds, indicating partial η^2 bond character (vide infra).

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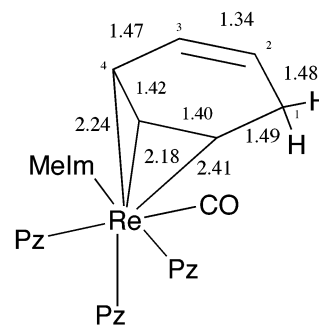(36) Harman, W. D.; Trindle, C. O., submitted for publication.

Figure 4. Calculated bond lengths for the complex **H-1** (distances in angstroms).

NMR data indicate that, like that of **H-1**, the structure of the naphthalenium complexes most closely resembles η^3 allyl complexes. However, the ^{13}C NMR allyl position signals of the Mo$-$naphthalene complex **1H-15A** appear at 143.4 (C2), 101.7 (C3), and 88.1 (C4) ppm, suggesting marked distortion from a symmetrical η^3 interaction. These assignments are heavily based on two-dimensional correlation experiments. A gDQCOSY spectrum shows a spin system consisting of ^{1}H signals at 7.05, 5.80, and 5.27 ppm that is respectively assigned to H2, H3, and H4. A gHSQC spectrum correlates these proton signals to C2, C3, and C4. When compared to the corresponding signals of **1H-12A** at 99.6, 79.0, and 73.0 ppm, respectively, those of **1H-15A** suggest a structure that involves less stabilization of the arenium positive charge by the metal center. Although the molybdenum$-$naphthalenium complex is not sufficiently stable to isolate and analyze by X-ray diffraction, simple diene complexes have been made in our laboratories for this system, such as TpMo(NO)(MeIm)(1,3-cyclohexadiene) (**18**), and they are readily protonated (HOTf/MeOH) to form thermally stable π-allyl complexes. A crystal structure of [TpMo(NO)(MeIm)-(η^3-C$_6$H$_9$)](OTf) (**19**; Figure 5) reveals an exceptionally long Mo$-$C1 bond (average 2.63 Å, cf. Mo$-$C5 bond average 2.32 Å), consistent with a significant component of the resonance contributor II-B (Figure 3). Liebeskind et al. have observed similar behavior in both the solid state and solution in the complexes of the type [TpMo(CO)(NO)(allyl)]$^+$,[39] and distorted allyl interactions were also invoked for pentaammineosmium(II) benzenium complexes.[1]

The available data reveal a discrepancy in the regiochemistries of protonation for the pentaammineosmium(II)(5,6-η^2-anisole)

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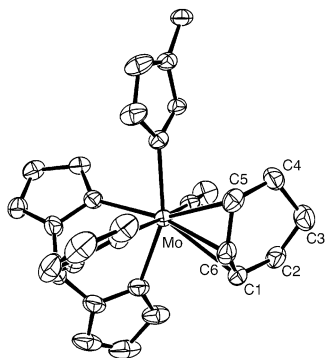
Figure 5. ORTEP diagram (30% ellipsoids) for the compound [TpMo-(NO)(MeIm)(η^3-C_6H_9)](OTf) (**19**). Distances in angstroms are the average of two independent molecules: Mo$-$C1, 2.63, Mo$-$C6, 2.32, Mo$-$C5, 2.33, Mo$-$N(O) 1.77.

and TpM(L$_\pi$)(L)(5,6-η^2-anisole) (**9**) complexes. While the osmium anisole complex underwent deuterium exchange at the ortho position, the 4*H*-anisolium product was the only compound that could be isolated from a protonation reaction.[1] The direct conjugation of the oxonium group with the remaining unbound olefin was invoked as a thermodynamic factor supporting protonation at the 4-position. In contrast, the rhenium analogue **9** was isolated predominantly in the form of 2*H*-anisolium complexes, where exclusive (>20:1) ortho protonation results when multiple acid equivalents were used at low temperatures. For the pentaammineosmium(II)$-$anisole complex, DFT calculations (B3LYP/HYBRID) indicate that C2 (unbound ortho) has a greater buildup of electron density (-0.36) than at C4 (-0.29).[35] Assuming this holds for the other dearomatization agents as well, it is likely that ortho protonation is the kinetic product for W, Re, and Os arene complexes. Presumably, the only difference between the observed regiochemistry of protonation for osmium (at C4) as compared to rhenium or tungsten (at C2) is the rate at which equilibration can occur under the reaction conditions used. Whereas the rhenium and tungsten systems are sufficiently basic that protonation at C2 is rapid and irreversible in the absence of a base (e.g., methanol), the 2*H*-anisolium complex of Os(II) is so acidic that it has access to the 4*H*-anisolium species (via deprotonation and reprotonation).

The fact that [TpW(NO)(PMe₃)(5,6-η^2-(2*H*-anisolium)](OTf) (**2*H*-16**) has a strong preference for the isomer **2*H*-16B** represents a marked difference from the behavior of {TpRe(CO)-(RIm)} anisole complexes, which only show high diastereoselectivity when they are protonated directly out of the solid state. For the tungsten system, **2*H*-16B** is heavily favored at equilibrium, relative to its coordination diastereomer **2*H*-16A**. The ORTEP diagram showing the crystal structure of **16** (Figure 2) suggests a steric influence of the PMe₃ ligand, with the W$-$C6 bond length being significantly longer than the W$-$C5 bond. Based on the structural changes observed upon protonation of TpRe(CO)(MeIm)(5,6-η^2-anisole) (**2**) (vide supra), protonation of **16** is expected to result in a shortening of the C1$-$O1 bond length and an overall shortening of the W$-$ring carbon bond lengths. It is speculated that a net effect of these changes is an increase in the steric interaction between the PMe₃ methyl groups and the methoxy group in the **A** diastereoisomer. This interaction apparently disfavors the diastereomer of [TpW(NO)-(PMe₃)(5,6-η^2-(2*H*-anisolium)](OTf) having the methoxy group

directed toward the PMe₃ ligand (**2*H*-16A**) to the extent that the alternate configuration (**2*H*-16B**) dominates by >20:1.

Given the variation in properties that have been reported for complexes of the metal fragments {TpRe(CO)(PMe₃)}, {TpRe-(CO)(Py)}, {TpRe(CO)(RIm)}, and {TpMo(NO)(MeIm)},[12,13] it is interesting that essentially no difference in basicity of naphthalenes bound to these fragments was observed, with complexes TpRe(CO)(BuIm)(3,4-η^2-naphthalene) (**12**), TpRe-(CO)(Py)(3,4-η^2-naphthalene) (**13**), TpRe(CO)(PMe₃)(3,4-η^2-naphthalene) (**14**), and TpMo(NO)(MeIm)(3,4-η^2-naphthalene) (**15**) being completely protonated by diphenylammonium triflate (pK_a 0.8) and the most activated methylimidazole versions **4** and **15** showing no reaction with phosphoric acid (pK_a 2.12). The similar basicity ranges of **12**$-$**15** and the various anisole complexes studied suggest that the latter may show reactivity toward a similar range of electrophiles as that which has been demonstrated for {TpRe(CO)(L)}-bound naphthalenes.[40] The studies of proton exchanges between [TpW(NO)(PMe₃)(5,6-η^2-(2*H*-anisolium)](OTf) (**2*H*-16**) and {TpRe(CO)(BuIm)} anisole complexes (vide supra) suggest that TpW(NO)(PMe₃)(5,6-η^2-anisole) (**16**) is more basic than the analogous rhenium complex TpRe(CO)(BuIm)(5,6-η^2-anisole) (**9**) and approximately as basic as the 3-methyl variant TpRe(CO)(BuIm)(5,6-η^2-(3-methylanisole)) (**10**). These data are consistent with the assertion that the {TpW(NO)(PMe₃)} metal fragment is marginally stronger as a π-base than the {TpRe(CO)(RIm)} metal fragments.[14] A comparison of relative basicities for anisole and naphthalene complexes provides the following general order of π bases: {TpW(NO)PMe₃} > {TpRe(CO)(MeIm)} > {TpMo(NO)(MeIm)} ≫ {Os(NH₃)₅}²⁺.

Conclusion

Arenes coordinated to {TpM(π-acid)(L)} metal fragments experience an even greater degree of π-back-bonding than do those coordinated to the pentaammineosmium(II) fragment, as evidenced by the greater basicities of the former. This enhanced activation is expected to further manifest itself in the activity of TpM(π-acid)(L)(η^2-arene) complexes toward carbon electrophiles. With a greater understanding of the relationship between facial diastereoselectivity of TpM(π-acid)(L)(η^2-arene) complexes and that of the corresponding electrophilic addition products now having been demonstrated, it is hoped that TpM(π-acid)(L)(η^2-arene) complexes will prove to be useful reagents in the synthesis of biologically prominent carbocycles.

Experimental Section

[TpRe(CO)(MeIm)(5,6-η^2-(2*H*-anisolium))](OTf) (2*H*-2). This complex was observed under a variety of conditions. In a prototypical experiment, to a mixture of TpRe(CO)(MeIm)(5,6-η^2-anisole) (**2**, 0.0275 g, 4.46×10^{-5} mol) in CD₃CN (~0.3 g) at -35 °C was added a solution of HOTf (0.0735 g, 4.90×10^{-4} mol) and CH₃OH (0.1044 g) in CD₃CN (~0.3 g) at -35 °C. The resulting mixture was then warmed to room temperature, during which time it became a dark red solution. This solution was observed by NMR spectroscopy. X-ray quality crystals were obtained by preparing a mixture of TpRe(CO)(MeIm)(5,6-η^2-anisole) (**2**, 0.0503 g, 3.35×10^{-4} mol) and HOTf (0.1072 g, 7.147×10^{-4} mol) in CD₃OD (~0.7 g) at -35 °C, warming it to room temperature to effect solvation, and chilling the resulting solution to -40 °C. This compound was observed as a single diastereomer having the OCH₃ group directed toward the imidazole ligand. ¹H NMR

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(acetonitrile-d_3, ambient temperature, δ): 8.01 (1H, d, J = 2.4, Tp 3,5), 7.95 (1H, d, J = 1.8, Tp 3,5), 7.85 (1H, d, J = 1.8, Tp 3,5), 7.83 (1H, d, J = 1.8, Tp 3,5), 7.73 (1H, d, J = 2.1, Tp 3,5), 7.39 (1H, bs, Tp 3,5), 7.37 (1H, buried, Im 2), 6.99 (1H, bs, Im 4,5), 6.71 (1H, m, H4), 6.51 (1H, t, J = 2.4, Tp 4), 6.49 (1H, bs, Im 4,5), 6.28 (1H, t, J = 1.8, Tp 4), 6.12 (1H, t, J = 2.1, Tp 4), 5.20 (1H, dt, J = 9.0, 3.9, H3), 4.52 (1H, d, J = 6.6, H6), 4.07 (1H, bs, H5), 3.69 (3H, s, NCH$_3$), 3.54 (3H, s, OCH$_3$), 3.4 (1H, buried, H2), 3.18 (1H, d, J = 19.5, H2) (BH not observed). The structure of this compound was confirmed by single-crystal X-ray diffraction.

[TpRe(CO)(MeIm)(5,6-η^2-(2H-3-methylanisolium))](OTf) (2H-3) and [TpRe(CO)(MeIm)(5,6-η^2-(4H-3-methylanisolium))](OTf) (4H-3). These complexes were observed under a variety of conditions. In a prototypical experiment, to a mixture of TpRe(CO)(MeIm)(5,6-η^2-(3-methylanisole)) (3, 0.0360 g, 5.71 × 10^{-5} mol) in CD$_3$CN ($\sim$0.3 g) at -35 °C was added a solution of HOTf (0.0730 g, 4.87 × 10^{-4} mol) and CH$_3$OH (0.0389 g, 1.2 × 10^{-3} mol) in CD$_3$CN ($\sim$0.3 g) at -35 °C. The resulting mixture was then warmed to room temperature, during which time it became a dark red solution. This solution was observed by NMR spectroscopy. This compound was observed as a 1:1 ratio of 2H and 4H regioisomers, designated as 2H-3 and 4H-3. Both have the OCH$_3$ group directed away from the imidazole ligand. ^{1}H NMR (acetonitrile-d_3, ambient temperature, δ): 6.07 to 8.06 (many signals having combined integration consistent with expected quantities for Tp and Im aromatic protons), (2H-3) 6.32 (1H, d, J = 5.4, H4), 4.83 (1H, dd, J = 6.3, 5.1, H5), 3.80 (1H, d, J = 6.3, H6), 3.71 (3H, s, NCH$_3$, coincident with 4H-3 NCH$_3$), 3.69 or 3.67 (3H, s, OCH$_3$, other is 4H-3), 3.4 to 3.5 (2H, buried, H2), 2.98 or 2.97 (3H, s, 3-pos CH$_3$, other is 4H-3), (4H-3) 6.22 to 6.44 (1H, indiscernible from Tp and Im resonances, H2), 4.65 (1H, dd, J = 7.2, 6.9, H5), 3.71 (3H, s, NCH$_3$, coincident with 2H-3 NCH$_3$), 3.69 or 3.67 (3H, s, OCH$_3$, other is 2H-3), 3.59 (1H, d, J = 5.4, H6), 3.2 (1H, buried, H4), 2.98 or 2.97 (3H, s, 3-pos CH$_3$, other is 2H-3), 2.96 (1H, J = 25.8, H4) (2 × BH not observed).

[TpRe(CO)(MeIm)(2,3,4-η^3-(1H-naphthalenium))](OTf) (1H-4). These complexes were observed under a variety of conditions. In an experiment intended to show significant portions of both 1H-4A and 1H-4B, TpRe(CO)(MeIm)(3,4-η^2-naphthalene) (4, 0.002 g, 3 × 10^{-6} mol) was dissolved in acetonitrile-d_3 (0.5 g) to give a yellow solution. This solution was placed in an 83 °C bath for 5 min and then cooled to -40 °C. Triflic acid (0.010 g, 6.7 × 10^{-5} mol) was added, and the resulting solution was observed at ambient temperature by NMR spectroscopy. This compound was observed as a mixture of two diastereomers in a ratio of 3:1. The major diastereomer (1H-4A) has the bulk of the naphthalenium directed toward the imidazole group, and the minor diastereomer (1H-4B) has the bulk of the naphthalenium directed away from the imidazole group. ^{1}H NMR (acetonitrile-d_3, ambient temperature, δ): (major diastereomer (1H-4A)): 8.36 (1H, d, J = 2.5, Tp 3,5), 8.06 (1H, d, J = 2.5, Tp 3,5), 8.04 (1H, dd, J = 2.0, 1.0, Tp 3,5), 7.82 (1H, dd, J = 3.0, 1.0, Tp 3,5), 7.68 (1H, dd, J = 2.5, 0.5, Tp 3,5), 7.50 (1H, d, J = 2.5, Tp 3,5), 7.29 (1H, d, J = 8.0, H8), 7.08 (1H, t, J = 8.0, H7), 7.01 (1H, d, J = 8.0, 1.5, H6), 6.90 (1H, t, J = 1.5, Im), 6.63 (1H, t, J = 2.5, Tp 4), 6.37 (1H, bs, Im), 6.32 (1H, t, J = 2.5, Tp 4), 6.21 (1H, d, J = 7.0, H5), 6.15 (1H, t, J = 2.5, Tp 4), 6.05 (1H, t, J = 1.5, Im), 5.64 (1H, m, H2), 4.87 (1H, t, J = 6.5, H3), 4.84 (1H, dd, J = 6.5, 3.0, H4), 4.5 (1H, very broad, BH), 3.97 (1H, dd, J = 24.0, 2.5, H1), 3.80 (1H, dd, J = 22.0, 3.5, H1), 3.53 (3H, s, NCH$_3$). (minor diastereomer (1H-4B)): 8.21 (1H, d, J = 2.0, Tp 3,5), 8.09 (1H, d, J = 2.5, Tp 3,5), 7.91 (1H, dd, J = 2.5, 0.5, Tp 3,5), 7.78 (1H, d, J = 2.5, Tp 3,5), 7.60 (1H, bs, Im), 7.25 (1H, dd, J = 7.5, 0.5, H8), 7.23 (1H, d, J = 2.5, Tp 3,5), 7.03 (1H, buried, H7), 6.99 (1H, dd, J = 8.0, 1.5, H6), 6.95 (1H, t, J = 1.5, Im), 6.66 (1H, t, J = 2.5, Tp 4), 6.65 (1H, t, J = 2.0, Im), 6.34 (1H, buried, H5), 6.16 (1H, t, J = 2.5, Tp 4), 6.05 (1H, buried, Tp 4), 5.68 (1H, d, J = 2.0, Tp 3,5), 5.43 (1H, m, H2), 4.97 (1H, t, J = 6.5, H3), 4.5 (1H, very

broad, BH), 4.06 (1H, dd, J = 6.0, 2.5, H4), 3.78 (2H, buried, 2 × H1), 3.62 (3H, s, NCH$_3$).

[TpRe(CO)(BuIm)(4,5,6-η^3-(1H-benzenium))](OTf) (1H-5). To TpRe(CO)(BuIm)(η^2-benzene) (5, 0.010 g, 1.6 × 10^{-5} mol) at -80 °C was added a solution of methanesulfonic acid (0.008 g, 8 × 10^{-5} mol) in chloroform (0.672 g) at its melting point. The resulting mixture was observed at -20 °C by NMR spectroscopy. This compound was observed as a 1:1 mixture of isomers. ^{1}H NMR (CDCl$_3$, -20 °C, δ): (1H-5A, select resonances) 6.29 (1H, bs, H3), 5.45 (1H, bs, H6), 5.36 (1H, bs, H2), 4.73 (1H, bs, H5), 3.53 (1H, bs, H4), either 3.51 (1H, buried, H1) and 3.24 (1H, d, J = 25.5, H1) or 3.43 (1H, d, J = 24.5, H1) and 3.19 (1H, d, J = 25.5, H1). (1H-5B, select resonances) 6.32 (1H, bs, H3), 5.39 (2H, buried, H2 and H6), 4.64 (1H, bs, H5), 4.38 (1H, bs, H4), either 3.51 (1H, buried, H1) and 3.24 (1H, d, J = 25.5, H1) or 3.43 (1H, d, J = 24.5, H1) and 3.19 (1H, d, J = 25.5, H1).

[TpRe(CO)(BuIm)(5,6-η^2-(2H-anisolium))](OTf) (2H-9) and [TpRe-(CO)(BuIm)(5,6-η^2-(4H-anisolium))](OTf) (4H-9). To TpRe(CO)-(BuIm)(5,6-η^2-anisole) (9, 0.096 g, 1.5 × 10^{-4} mol) and diphenyl-ammonium triflate (0.041 g, 1.3 × 10^{-4} mol) at -40 °C was added anisole ($\sim$5 g) at -40 °C. The resulting yellow mixture was stirred at -40 °C for 1.5 h during which time it became a dark red solution. This solution was added to stirring hexanes (100 mL) to give a brownish material in a clear nearly colorless solution. The solution was decanted off, and the brownish material was dissolved in methylene chloride (1 mL) and benzene (5 mL). The resulting dark solution was added to stirring hexanes (100 mL), and the resulting precipitate was collected by filtration, rinsed with hexanes, and dried in vacuo to give a tan solid (102 mg, 98% based on diphenylammonium triflate). Samples of this compound have been observed in a variety of isomeric ratios; however, the isolated material was a mixture of two diastereomers of each of two regioisomers. The regioisomers having a methylene group at the 2 position are designated as 2H, and those having a methylene group at the 4 position are designated as 4H. The diastereomers having the OCH$_3$ group directed toward the imidazole ligand are designated as A, and those having the OCH$_3$ group directed away from the imidazole ligand are designated as B. The isomeric ratio is $\sim$11:8.5: 4.5:1 2H-9B:2H-9A:4H-9B:4H-9A. ^{1}H NMR (acetone-d_6, ambient temperature, δ): (2H-9B): 8.12 (2H, d, J = 2.5, 2 × Tp 3,5), 8.07 (1H, d, J = 2.0, Tp 3,5), 7.82 (1H, dd, J = 2.5,1.0, Tp 3,5), 7.51 (1H, d, J = 2.0, Tp 3,5), 7.34 (1H, t, J = 1.5, Im), 7.29 (1H, d, J = 2.0 Tp 3,5), 6.65 (1H, buried, H4), 6.59 (1H, t, J = 2.0, Tp 4), 6.43 (1H, t, J = 2.0, Tp 4), 6.17 (1H, t, J = 2.0, Tp 4), 5.17 (1H, dt, J = 9.5, 3.0, H3), 5.06 (1H, bs, H5), 4.15 (2H, t, J = 7.0, NCH$_2$), 3.90 (1H, d, J = 6.5, H6), 3.38 (1H, d, J = 26.0, H2), 3.18 (3H, s, OCH$_3$), 3.03 (1H, d, J = 24.5, H2), 1.76 (2H, m, NCH$_2$CH_2), 1.24 (2H, m, CH_2CH$_3$), 0.88 (3H, t, J = 7.5, CH$_2$CH_3), (2 × Im buried or indiscernible from minor resonances; BH not observed). (2H-9A): 8.24 (1H, d, J = 2.0, Tp 3,5), 8.16 (1H, d, J = 2.0, Tp 3,5), 7.96 (1H, dd, J = 2.0, 0.5, Tp 3,5), 7.88 (1H, d, J = 2.0, Tp 3,5), 7.86 (1H, dd, J = 2.5, 0.5, Tp 3,5), 7.41 (1H, d, J = 2.0 Tp 3,5), 7.37 (1H, bs, Im), 6.76 (1H, ddd, J = 9.0, 5.0, 2.5, H4), 6.56 (1H, t, J = 2.0, Tp 4), 6.33 (1H, t, J = 2.0, Tp 4), 6.18 (1H, t, J = 2.0, Tp 4), 5.24 (1H, dt, J = 9.5,3.0, H3), 4.80 (1H, d, J = 6.5, H6), 4.19 (2H, t, J = 7.0, NCH$_2$), 4.12 (1H, bs, H5), 3.74 (3H, s, OCH$_3$), 3.50 (1H, d, J = 21.5, H2), 3.12 (1H, d, J = 27.0, H2), 1.76 (2H, m, NCH$_2$CH_2), 1.24 (2H, m, CH_2CH$_3$), 0.88 (3H, t, J = 7.5, CH$_2$CH_3), (2 × Im buried or indiscernible from minor resonances; BH not observed). (4H-9B, select resonances): 7.02 (1H, m, H3), 6.50 (1H, d, J = 1.8, H2), 4.90 (1H, m, H5), 3.61 (1H, buried, H6), 3.08 (3H, s, OCH$_3$). (4H-9A, select resonances): 7.17 (1H, m, H3), 4.44 (1H, d, J = 7.5, H6), 4.04 (1H, t, J = 7.5, H5), 3.59 (3H, s, OCH$_3$). ^{13}C NMR (acetone-d_6, -20 °C, δ): (2H-9A): 196.0 (C1), 194.8 (CO), 145.3 (Tp 3,5), 143.9 (Tp 3,5), 142.6 (Tp 3,5), 138.0 (Tp 3,5), 137.7 (Tp 3,5), 136.3 (Tp 3,5), 135.5 (C4), 130.2, 122.1 (Im), 115.9 (C3), 108.0 (Tp 4), 107.3 (Tp 4), 107.6 (Tp 4), 64.2 (C5), 61.2 (C6), 59.2 (OCH$_3$), 48.2 (NCH$_2$), 34.0 (C2), 33.2 (NCH$_2$CH$_2$), 19.9 (CH$_2$CH$_3$), 13.6 (CH$_2$CH$_3$), (2 × Im indiscernible from minor resonances). IR:

ν_{CO} = 1855 cm^{-1} (vs), ν_{BH} = 2493 cm^{-1} (w). CV: $E_{p,a}$ = +1.12 V (II/I). Anal. Calcd for C$_{25}$H$_{31}$BF$_3$N$_8$O$_5$ReS: C, 37.09; H, 3.86; N, 13.84. Found: C, 36.99; H, 3.83; N, 13.93.

[TpRe(CO)(BuIm)(2,3,4-η^3-(1*H*-naphthalenium))](OTf) (1*H*-12). To a mixture of TpRe(CO)(BuIm)(3,4-η^2-naphthalene) (12, 0.198 g, 2.92 × 10^{-4} mol) and diphenylammonium triflate (0.089 g, 2.8 × 10^{-4} mol) at −40 °C was added toluene (9.680 g) at −40 °C to give a yellow mixture. This mixture was stirred for 1 h at −40 °C and then for 10 min at ambient temperature, during which time it became a mixture of a dark solution and a dark oil. This mixture was added to stirring hexanes (200 mL) using methylene chloride (1 mL) as rinse solvent to give a thick precipitate in a yellow solution. The solution was decanted off, and the precipitate was dissolved in a 1:5 solution of methylene chloride and toluene (12 mL) and added to stirring hexanes (200 mL). The resulting precipitate was collected by filtration, rinsed with hexanes, and dried in vacuo to give a beige solid (0.179 g, 77.4% based on diphenylammonium triflate). This compound was isolated as a mixture of two diastereomers in ratios ranging from 1.2:1 to 1:2 (1*H*-12A to 1*H*-12B). The diastereomer designated 1*H*-12A has the bulk of the naphthalenium directed toward the imidazole ligand, and the diastereomer designated 1*H*-12B has the bulk of the naphthalenium directed away from the imidazole ligand. ^{1}H NMR (acetone-d_6, ambient temperature, δ): (1*H*-12A): 8.68 (1H, d, J = 2.1, Tp 3,5), 8.30 (1H, d, J = 2.1, Tp 3,5), 8.21 (1H, d, J = 2.1, Tp 3,5), 7.96 (1H, d, J = 2.7, Tp 3,5), 7.86 (1H, dd, J = 2.7, 0.6, Tp 3,5), 7.62 (1H, d, J = 2.4 Tp 3,5), 7.48 (1H, buried, H8), 7.31 (1H, buried, H7), 7.27 (1H, t, J = 1.5, Im), 7.04 (1H, buried, H6), 6.83 (1H, bs, Im), 6.72 (1H, t, J = 2.4, Tp 4), 6.40 (1H, t, J = 2.4, Tp 4), 6.37 (1H, buried, H5), 6.24 (1H, t, J = 2.4, Tp 4), 6.18 (1H, t, J = 1.5, Im), 5.85 (1H, m, H2), 5.16 (1H, dd, J = 6.3, 2.4, H4), 5.04 (1H, t, J = 6.6, H3), 4.13 (2H, t, J = 7.2, NCH$_2$), 3.85 to 4.16 (2H, buried, 2 × H1), 1.73 (2H, m, NCH$_2$CH_2), 1.28 (2H, m, CH_2CH$_3$), 0.91 (3H, t, J = 7.5, CH$_2$CH_3), (BH not observed). (1*H*-12B): 8.58 (1H, d, J = 2.1, Tp 3,5), 8.26 (1H, d, J = 2.1, Tp 3,5), 8.06 (1H, buried, Im), 8.05 (1H, buried, Tp 3,5), 7.95 (1H, dd, J = 2.4, 0.9, Tp 3,5), 7.48 (1H, buried, H8), 7.38 (1H, d, J = 2.4, Tp 3,5), 7.34 (1H, t, J = 1.5, Im), 7.27 (1H, buried, H7), 7.01 (1H, buried, H6), 6.89 (1H, t, J = 1.8, Im), 6.74 (1H, t, J = 2.4, Tp 4), 6.37 (1H, buried, H5), 6.25 (1H, t, J = 2.4, Tp 4), 6.12 (1H, t, J = 2.4, Tp 4), 5.70 (1H, d, J = 2.1, Tp 3,5), 5.67 (1H, m, H3), 5.28 (1H, t, J = 6.3, H2), 4.13 (2H, t, J = 7.2, NCH$_2$), 3.85 to 4.16 (2H, buried, 2 × H1), 3.84 (1H, d, J = 2.4, H4), 1.73 (2H, m, NCH$_2$CH_2), 1.20 (2H, m, CH_2CH$_3$), 0.85 (3H, t, J = 7.5, CH$_2$CH_3), (BH not observed). ^{13}C NMR (acetone-d_6, ambient temperature, δ): (1*H*-12A, select resonances): 199.4 (CO), 99.6 (C2), 79.0 (C3), 73.0 (C4). (1*H*-12B, select resonances): 93.0 (C3), 71.8 (C2 or C4), 71.7 (C2 or C4). IR: ν_{CO} = 1850 cm^{-1}, ν_{BH} = 2502 cm^{-1} (w). CV: $E_{p,a}$ = +1.077 V (II/I). Anal. Calcd for C$_{28}$H$_{31}$BF$_3$N$_8$O$_4$ReS: C, 40.53; H, 3.77; N, 13.51. Found: C, 41.08; H, 3.75; N, 13.03.

[TpMo(NO)(MeIm)(2,3,4-η^3-(1*H*-naphthalenium))](OTf) (1*H*-15). In a prototypical experiment, to TpMo(NO)(MeIm)(3,4-η^2-naphthalene) (15, 0.028 g, 5.1 × 10^{-5} mol) was added acetone-d_6 (0.5 g) to give an orange mixture. This mixture was cooled to −60 °C and then added to diphenylammonium triflate (0.021 g, 6.6 × 10^{-5} mol) at −60 °C. The resulting mixture was agitated at ambient temperature to give an orange solution which was observed at −20 °C by NMR spectroscopy. This compound was observed as a mixture of two diastereomers in a A:B ratio of 8:1. The major diastereomer (1*H*-15A) has the bulk of the naphthalenium directed toward the imidazole group, and the minor diastereomer (1*H*-15B) has the bulk of the naphthalenium directed away from the imidazole group. ^{1}H NMR (acetone-d_6, −20 °C, δ): (major diastereomer (1*H*-15A)): 8.50 (1H, bs, Tp 3,5), 8.35 (1H, bs, Tp 3,5), 8.24 (1H, d, J = 1.5, Tp 3,5), 8.11 (1H, d, J = 2.0, Tp 3,5), 7.93 (1H, d, J = 1.5, Tp 3,5), 7.91 (1H, m, H8), 7.50 (1H, dd, J = 6.5, 3.5, H7), 7.44 (1H, bs, Tp 3,5), 7.40 (1H, bs, Im), 7.16 (1H, buried, H6), 7.15 (1H, buried, Im), 7.05 (1H, m, H2), 6.67 (1H, bs, Tp 4), 6.49 (1H, bs, Tp 4), 6.41 (1H, bs, Im), 6.26 (1H, d, J = 6.0, H5), 6.23 (1H, bs, Tp

4), 5.80 (1H, dd, J = 6.0, 6.0, H3), 5.27 (1H, d, J = 6.0, H4), 4.83 (2H, bs, 2 × H1), 3.83 (3H, s, NCH$_3$), (BH not observed). (minor diastereomer (1*H*-15B), select resonances): 7.30 (1H, d, J = 7.5, H2), 5.50 (1H, dd, J = 7.5, 7.5, H3), 5.37 (1H, d, J = 7.0, H4), 4.62 (1H, d, J = 26.0, H1), 4.55 (1H, d, J = 27.5, H1). ^{13}C NMR (acetone-d_6, −20 °C, δ): (1*H*-15A, select resonances): 143.4 (C2), 101.7 (C3), 88.1 (C4), 33.4 (C1).

TpW(NO)(PMe$_3$)(5,6-η^2-anisole) (16). To a 1 L flame-dried round-bottom flask with a stir bar were added TpW(NO)(PMe$_3$)Br (19.924 g, 0.0338 mol),[14] dimethoxyethane (4 mL), dry anisole (900 mL), and sodium (7.7829 g, 0.340 mol). The resulting mixture was stirred at ambient temperature, and over the course of ~24 h it became a very dark mixture. Reaction progress was monitored by CV, and, after 70 h, the ratio of the height of the $E_{p,a}$ at −0.175 V to that of the oxidation wave in the reversible couple at −1.411 V was >20:1. At this time, the reaction mixture was filtered through a plug of 1 in. of Celite on top of 1 in. of sand packed with anisole in a 150 mL coarse fritted Büchner funnel. The reaction flask and plug were rinsed with anisole (2 × 50 mL). The filtrate was then loaded onto a 450 mL plug of silica packed with anisole in a 600 mL medium fritted Büchner funnel. The transfer flask and plug were rinsed with anisole (2 × 50 mL). The plug was eluted with ether, and a series of bright yellow fractions (4.4 L total) was collected, all of which had a strong absorbance in the range of 1557−1569 cm^{-1} in the IR spectrum. The fractions were combined, and the total volume was reduced to by evaporation. At a volume of 3.5 L, precipitate was evident. At a volume of 2 L, hexanes (2 L) was added, and the precipitate was collected by filtration, rinsed with hexanes, and dried in vacuo to yield a dark yellow solid (8.420 g, 40.3%). X-ray quality crystals were obtained by loading an anisole solution onto a silica plug, eluting the plug with ether to arrive at a concentrated solution, and then layering that solution with hexanes. This compound was observed as a 3.5:1 ratio of diastereomers, the major (16A) having the methoxy group directed toward the imidazole ligand and the minor (16B) having the methoxy group directed away from the imidazole ligand. ^{1}H NMR (acetone-d_6, ambient temperature, δ): (major diastereomer (16A)): 8.19 (1H, d, J = 1.5, Tp 3,5), 7.96 (1H, d, J = 2.1, Tp 3,5), 7.95 (1H, d, J = 2.4, Tp 3,5), 7.89 (1H, d, J = 2.1, Tp 3,5), 7.82 (1H, d, J = 2.1, Tp 3,5), 7.32 (1H, d, J = 2.1, Tp 3,5), 6.52 (1H, dd, J = 8.7, 5.7, H4), 6.33 (1H, t, J = 2.1, Tp 4), 6.29 (1H, t, J = 2.4, Tp 4), 6.27 (1H, J = 2.4, Tp 4), 5.66 (1H, dd, J = 9.0, 6.9, H3), 5.14 (1H, d, J = 6.6, H2), 4.6 (1H, very broad, BH), 4.08 (1H, ddd, J = 16.8, 10.5, 0.9, H6), 3.70 (3H, s, OCH$_3$), 2.22 (1H, ddd, J = 10.5, 5.7, 1.8, H5), 1.27 (9H, d, J = 8.4, P(CH$_3$)$_3$). (minor diastereomer (16B), select resonances): 8.11 (1H, bs, Tp 3,5), 7.94 (1H, d, J = 2.4, Tp 3,5), 7.75 (1H, d, J = 2.1, Tp 3,5), 7.42 (1H, d, J = 2.1, Tp 3,5), 6.26 (1H, buried, H4), 6.18 (1H, t, J = 2.1, Tp 4), 5.63 (1H, buried, H3), 4.87 (1H, d, J = 6.6, H2), 4.15 (1H, buried, H5), 3.61 (3H, s, OCH$_3$), 2.32 (1H, d, J = 11.4, H6), 1.26 (9H, d, J = 8.4, P(CH$_3$)$_3$). ^{13}C NMR (acetone-d_6, ambient temperature, δ): (major diastereomer (16A)) 144.7 (Tp 3,5), 141.8 (Tp 3,5), 141.5 (Tp 3,5), 137.4 (Tp 3,5), 136.7 (Tp 3,5), 136.4 (Tp 3,5), 126.2 (C4), 106.9 (Tp 4), 106.8 (Tp 4), 106.0 (Tp 4), 117.1 (C3), 91.5 (C2), 64.0 (C5), 58.7 (C6), 53.9 (OCH$_3$), 13.9 (P(CH$_3$)$_3$), (C1 not observed, correlation spectroscopy suggests ~164.5). (minor diastereomer (16B), select resonances): 123.9 (C4), 117.8 (C3), 88.8 (C2), 64.8 (C5), 59.8 (C6), 54.1 (OCH$_3$), 13.2 (P(CH$_3$)$_3$), (C1 not observed, correlation spectroscopy suggests ~168.5). IR: ν_{NO} = 1568 cm^{-1} (vs), ν_{BH} = 2489 cm^{-1} (w). CV: $E_{p,a}$ = −0.175 V. Anal. Calcd for C$_{19}$H$_{27}$BN$_7$O$_2$PW: C, 37.34; H, 4.45; N, 16.04. Found: C, 37.48; H, 4.53; N, 16.09. The structure of this complex was confirmed by single-crystal X-ray diffraction.

[TpW(NO)(PMe$_3$)(5,6-η^2-(2*H*-anisolium))](OTf) (2*H*-16). Two diastereomers of this complex were observed. When TpW(NO)(PMe$_3$)-(5,6-η^2-anisole) (16, 0.010 g, 1.3 × 10^{-5} mol) and diphenylammonium triflate (0.014 g, 4.4 × 10^{-5} mol) were cooled to −80 °C, and dissolved in acetone-d_6 at −80 °C, a single diastereomer (2*H*-16A) was observed by ^{1}H NMR spectroscopy at −80 °C. When a solution of 2*H*-16A was

warmed to 20 °C, a diastereomer having the methoxy group directed away from the PMe$_3$ ligand (**2H-16B**) was observed in a ratio of >20:1 by ^{1}H NMR spectroscopy. This second isomer (**2H-16B)** was isolated as follows. The complex TpW(NO)(PMe$_3$)(5,6-η^2-anisole) (**16**, 0.103 g, 1.67 × 10^{-4} mol) and diphenylammonium triflate (0.047 g, 1.5 × 10^{-4} mol) were cooled to −40 °C. To this mixture was added liquid anisole (5 g) at its freezing point. The resulting initially yellow mixture was stirred at −40 °C for 1.5 h, during which time it became a dark red solution. This solution was added to stirring hexanes (100 mL) at ambient temperature to give a dark orange precipitate in a yellow solution. The solution was decanted off, and the precipitate was dissolved in methylene chloride (3 mL) and benzene (3 mL). The resulting dark solution was added to stirring hexanes (100 mL), and the resulting precipitate was collected by filtration, rinsed with hexanes, and dried in vacuo to give a tan solid (112 mg, 99% based on diphenylammonium triflate). ^{1}H NMR (acetone-d_6, −80 °C, δ): (**2H-16A**): 8.35 (1H, d, J = 2.0, Tp 3,5), 8.32 (1H, d, J = 2.0, Tp 3,5), 8.29 (1H, d, J = 2.0, Tp 3,5), 8.27 (1H, d, J = 2.0, Tp 3,5), 8.09 (1H, d, J = 2.0, Tp 3,5), 7.90 (1H, d, J = 2.0 Tp 3,5), 6.68 (1H, m, H4), 6.62 (1H, t, J = 2.5, Tp 4), 6.58 (1H, t, J = 2.5, Tp 4), 6.38 (1H, t, J = 2.5, Tp 4), 4.93 (1H, dt, J = 9.0, 4.5, H3), 4.80 (1H, m, H6), 4.65 (3H, s, OCH$_3$), 4.29 (1H, d, J = 27.0, H2), 3.46 (1H, d, J = 27.5, H2), 2.78 (1H, t, J = 11.5, H5), 1.15 (9H, d, J = 9.0, PMe$_3$), (BH not observed). (**2H-16B**, ambient temperature): 8.31 (1H, d, J = 2.1, Tp 3,5), 8.24 (1H, d, J = 2.1, Tp 3,5), 8.22 (1H, d, J = 2.1, Tp 3,5), 8.12 (1H, d, J = 2.4, Tp 3,5), 8.09 (1H, d, J = 2.4, Tp 3,5), 7.58 (1H, d, J = 2.1 Tp 3,5), 6.62 (1H, t, J = 2.4, Tp 4), 6.55 (1H, buried, H4), 6.53 (1H, t, J = 2.4, Tp 4), 6.44 (1H, t, J = 2.4, Tp 4), 4.97 (1H, m, H3), 4.7 (1H, very broad, BH), 4.61 (1H, m, H5), 3.74 (1H, d, J = 23.7, H2), 3.46 (2H, buried, H2 and H6), 3.42 (3H, s, OCH$_3$), 3.38 (1H, d, J = 26.0, H2), 3.18 (3H, s, OCH$_3$), 1.39 (9H, d, J = 9.9, PMe$_3$). ^{13}C NMR (acetone-d_6, −20 °C, δ): (**2H-16A**): 205.5 (C1), 144.7 (Tp 3,5), 143.3 (Tp 3,5), 143.1 (Tp 3,5), 139.0 (Tp 3,5), 138.5 (Tp 3,5), 137.6 (Tp 3,5), 132.9 (C4), 111.1 (C3), 108.6 (Tp 4), 108.1 (Tp 4), 106.9 (Tp 4), 68.4 (C5), 63.7 (C6), 60.2 (OCH$_3$), 32.8 (C2), 11.7 (d, J = 30.2, PMe$_3$). (**2H-16B**): 195.5 (C1), 146.3 (Tp 3,5), 142.8 (Tp 3,5), 142.7 (Tp 3,5), 139.6 (Tp 3,5), 139.2 (Tp 3,5), 139.0 (Tp 3,5), 128.1 (C4), 113.4 (C3), 108.6 (Tp 4), 108.5 (Tp 4), 108.0 (Tp 4), 70.2 (d, J = 13.7, C5), 63.7 (C6), 58.5 (OCH$_3$), 33.0 (C2), 12.9 (d, J = 32.1, PMe$_3$). IR: ν_{NO} = 1622 cm^{-1} (vs), ν_{BH} = 2510 cm^{-1} (w). CV (CH$_3$CN): $E_{p,a}$ = +1.39 V (II/I). Anal. Calcd for C$_{20}$H$_{28}$BF$_3$N$_7$O$_5$-PSW: C, 31.56; H, 3.71; N, 12.88. Found: C, 30.92; H, 3.64; N, 12.81.

Supporting Information Available: General experimental details for compounds not previously reported (PDF) and crystallographic information (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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