Tungsten(0) and Rhenium(I) η^2-Pyrrole Complexes: Dearomatization of Pyrroles and Their Facile Isomerizations, Protonations, and Reductions

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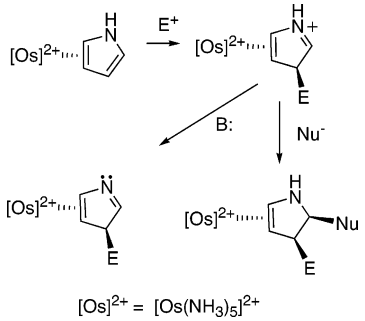
Complexes of the form TpRe(CO)(MeIm)(η^2-L) and TpW(NO)(PMe_3)(η^2-L) have been synthesized, where L = 1-methylpyrrole, 2-methylpyrrole, and 2,5-dimethylpyrrole. Depending on the nature of both the pyrrole and the metal, either a η^2-1*H*- or an η^2-3*H*-pyrrole complex can be isolated. In contrast, for the parent pyrrole, oxidative addition occurs across the N−H bond, generating either a *N*-pyrrolyl or *N*-pyrrolyl hydride. The protonation or methylation of the η^2-pyrrole complexes and the reduction of the resulting pyrrolium species have also been investigated.

Introduction

The pyrrole ring is common in natural products and other compounds of biological significance. It serves as a subunit or precursor to chlorophylls, bile pigments, porphyrins, and corrins, as well as assorted antibiotics.[1] Pyrroles also potentially can serve as synthons for alkaloids and other N-heterocyclic systems, providing up to four activated carbons for elaboration. In recent years, several reports from our laboratory have documented the unusual chemistry that becomes possible for this heterocycle when it is coordinated to the transition metal π base $[Os(NH_3)_5]^{2+}$.[2−4] With the osmium binding across C4 and C5, the uncoordinated portion of the pyrrolic ring is rendered similar to an enamine, showing strongly nucleophilic character at the β carbon, C3 (Scheme 1). Furthermore, this partially *dearomatized* 1*H*-pyrrole ligand was found to readily isomerize to its 2*H*- and 3*H*-pyrrole tautomers.[2−4] Alternatively, coordination of a 1*H*-pyrrole at C3 and C4 was found to transform the heterocycle into an azomethine ylide, and 1,3-dipolar cycloaddition reactions could be achieved that were not possible for the native pyrrole.[5] While this osmium(II)-promoted chemistry provides access to basic organic transformations that are otherwise inaccessible, the high cost and presumed toxicity of osmium (specifically OsO_4)[6] have limited the utility of these reactions. Given the stoichiometric nature of this methodology, an alternative to the osmium(II) pyrrole dearomatization methodology is desirable.

Scheme 1



Recently, we have expanded the family of heavy-metal π dearomatization agents to include the asymmetric systems {TpRe(CO)(MeIm)}[7] and {TpW(NO)(PMe_3)}[8] (Figure 1). Potentially, these systems could activate pyrroles toward organic reactions similar to those already realized for osmium, but with the added advantage of asymmetric induction. The purpose of this study is to (1) assess the ability of these systems to bind pyrroles, (2) determine the coordination diastereomer ratios for these complexes, and (3) compare the chemical properties of these bound heterocycles for the three different metals (W, Re, Os).

Results and Discussion

When pyrrole is allowed to react with the complex TpRe(MeIm)(CO)(benzene) (**1**), the anticipated η^2-pyr-

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(2) Myers, W. H.; Sabat, M.; Harman, W. D. *J. Am. Chem. Soc.* **1991**, *113*, 6682.
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(5) Gonzalez, J.; Koontz, J. I.; Myers, W. H.; Hodges, L. M.; Sabat, M.; Nilsson, K. R.; Neely, L. K.; Harman, W. D. *J. Am. Chem. Soc.* **1995**, *117*, 3405.
(6) Health Council of The Netherlands: Committee on Updating of Occupational Exposure Limits. Osmium Tetraoxide; Health-based Reassessment of Administrative Occupational Exposure Limits. The Hague: Health Council of The Netherlands, 2002; 2000/15OSH/051.
(7) Meiere, S. H.; Brooks, B. C.; Gunnoe, T. B.; Sabat, M.; Harman, W. D. *Organometallics* **2001**, *20*, 1038−1040.
(8) Graham, P.; Meiere, S. H.; Sabat, M.; Harman, W. D. *Organometallics* **2003**, *22*, 4364−4366.

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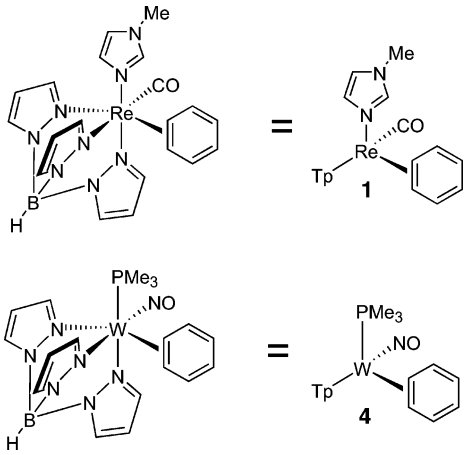
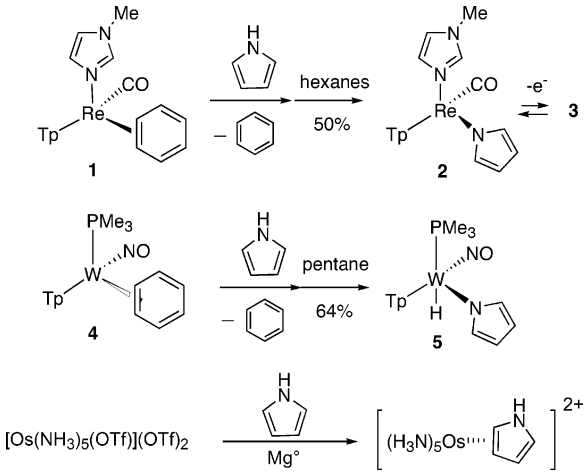


Figure 1.

role complex is not observed. Rather, a paramagnetic material is isolated (**2**) that shows an IR band corresponding to a ν_{CO} at 1816 cm^{-1} and a reversible wave in its cyclic voltammogram at +0.10 V (NHE; 100 mV/s). The ^1H NMR spectrum of **2** shows only broad, featureless waves in the baseline. Mass spectra of this complex were obtained using three different types of instrumentation, and in each case, the spectra showed as their highest mass a cluster of peaks with *m/z* between 574 and 580 with an isotopic distribution consistent with the stoichiometry of [TpRe(CO)(MeIm) + C_4H_4N]. A purported oxidative addition of an NH or CH bond in pyrrole to the metal would produce a Re(III) complex, which should give a recognizable ^1H NMR spectrum. However, these observations could be explained if such a complex formed and then lost the equivalent of a H atom ($H^+ + e^-$). The resulting Re(II)-pyrrolyl complex would be paramagnetic and might be expected to show reversible II/III redox chemistry. Acting on this hypothesis, we prepared a solution of the complex in acetone-d_6 and added 1.5 equiv of the oxidant ferrocenium hexafluorophosphate (0.55 V NHE), in the expectation that this would oxidize the Re(II) to Re(III) conjugate, **3**, which could be observable by proton NMR. Indeed, the originally red solution turned dark green, and a well-resolved ^1H NMR spectrum of **3** was obtained. Cyclic voltammetry confirmed that the original II/III redox couple in **2** was also present in **3**, indicating that the ligand set in these two compounds was identical. While signals in the ^1H NMR spectrum of **3** were consistent with one Tp and one MeIm ligand, only one other resonance was observed (integration: 1H), at ca. 6.3 ppm, just upfield of the Tp triplet region (6.5−6.7 ppm). A COSY spectrum revealed no coupling between the signal at 6.3 ppm and any other. However, when the solution was cooled to −75 °C, this peak was replaced by three new peaks in a 1:2:1 ratio. A COSY spectrum revealed substantial coupling between the center peak and each of the other two, and an HSQC spectrum (^1H-detected proton−carbon correlation) showed that these peaks represented four methine groups with corresponding carbon signals appearing at greater than 100 ppm. Taken together, these data are consistent with both **2** and **3** containing an N-bound pyrrolyl group coordinated to a TpRe(II)(MeIm)(CO) fragment (Scheme 2). The single peak observed in the room-temperature spectrum is presumably from the β protons, which show similar chemical shifts. The fluxionality observed in the

Scheme 2



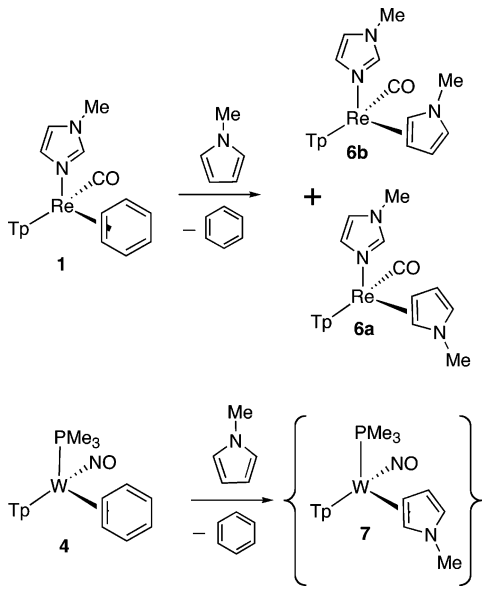
room-temperature spectrum apparently results from a rotation around the M−N bond occurring on the time scale of the NMR measurement. Of note, Gladysz et al. have reported the preparation of $CpRe(NO)(PPh_3)(C_4H_4N)$, a rhenium(I) complex with composition similar to **2** and **3**.[9]

When the tungsten benzene complex $TpW(NO)(PMe_3)(\eta^2$-benzene) (**4**) was combined with pyrrole in DME and allowed to stand, a new compound was formed (**5**) that also incorporated the heterocycle. In this case, the compound was diamagnetic, with a ^1H NMR spectrum indicating the presence of a pyrrolyl ligand and a hydride (Scheme 2). As with other tungsten hydride complexes,[10] the hydride signal was shifted *downfield* from the normal window to 11.36 ppm. Phosphorus coupling (J_{PH} = 125 Hz) and the presence of ^{183}W satellites (J_{WH} = 31.0 Hz) confirmed that this signal was a W−H.[10] Parkin et al. have recently reported the oxidative addition of the pyrrole N−H bond to a molybdenum(0) complex.[11] In contrast to the behavior of the rhenium and tungsten d^6 systems, the reaction of $\{Os(NH_3)_5\}^{2+}$ with pyrrole leads to a stable η^2-pyrrole complex that shows no indication of oxidative addition of the N−H bond (Scheme 2).[12]

The reaction of 1-methylpyrrole with the rhenium benzene complex (**1**) delivered the desired η^2-pyrrole complex with the metal coordinating the C4−C5 bond. Similar to that observed for its osmium analogue,[12] fluxionality is observed in the room-temperature ^1H NMR spectrum. In the case of $[Os(NH_3)_5(1\text{-methylpyrrole})]^{2+}$, this broadening has been shown to involve a linkage isomerization from the C4−C5 bond to the C2−C3 bond, passing through an intermediate in which the metal is bound at C3−C4. We believe a parallel mechanism accounts for the fluxionality seen in the Re(I) system. In the low-temperature spectrum (−90 °C), two diastereomers appear in a 1:6 ratio. In consideration of the chemical shift data for the bound methine groups

(9) Johnson, T. J.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1993**, *12*, 4728−4730.
(10) Caffyn, A. J. M.; Feng, S. G.; Dierdorf, A.; Gamble, A. S.; Eldredge, P. A.; Vossen, M. R.; White, P. S.; Templeton, J. L. *Organometallics* **1991**, *10*, 2842−2848.
(11) Zhu, G.; Tanski, J. M.; Churchill, D. G.; Janak, K. E.; Parkin, G. *Organometallics* **2002**, *124*, 13658−13659.
(12) Cordone, R.; Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1989**, *111*, 5969−5970.

Scheme 3



of the two isomers,[13] the major isomer is **6b** (Scheme 3), in which the pyrrole methyl group is oriented toward the MeIm ligand. When the tungsten-benzene complex **4** was combined with 1-methylpyrrole, electrochemical data from the reaction mixture after 1 h showed an $E_{p,a}$ at −0.48 V, an observation that suggested the formation of an η^2-pyrrole complex, **7** (cf. **4**, $E_{p,a}$ = −0.18 V). Although attempts to isolate this material were unsuccessful due to its gradual decomposition in solution, the purported η^2-pyrrole complex could be trapped as its conjugate acid and isolated as a 3*H*-pyrrolium complex (vide infra).

In contrast to that observed for 1-methylpyrrole, the reactions of the benzene complexes **1** and **4** with 2-methylpyrrole lead to products whose ^{1}H NMR spectra were static on the NMR time scale. Relevant ^{1}H NMR data include absorptions corresponding to a pair of geminal protons, for each of two isomers. An analysis of this and other NMR spectra (1H, COSY, NOESY, HSQC), combined with comparisons to spectra of 1*H*, 2*H*, and 3*H* tautomers of various pyrrole complexes of Os(II),[3] led to our conclusion that the products (**8** and **10**) were complexes of 3*H*-2-methylpyrrole, bound across C4−C5 (Scheme 4). For the rhenium system (**8**), the product appears as two diastereomers, formed in a 2:1 ratio, in which the N is down (major, **8a**) or up (minor, **8b**), relative to the MeIm ligand on the Re(I) (Scheme 4). In the ^{1}H NMR spectrum of each diastereomer, coupling is observed between the proton on C4, the bound β-carbon, and only one of the two geminal protons on C3. This pattern has been previously observed in the corresponding osmium complexes and suggests a H−C3−C4−H dihedral angle approaching 90°. A NOESY spectrum reveals that it is the C3 proton *anti* to the metal that shows coupling with the C4 proton. In the case of the tungsten system, **10a** and **10b** (**10a**:**10b** = 3:1) gradually give way in acetone-d_6 to a new species easily identified in the ^{1}H NMR spectrum as a pyrrolyl hydride (**12**), analogous to what was observed with the parent pyrrole (Scheme 2; compound **5**).

(13) Meiere, S. H.; Harman, W. D. *Organometallics* **2001**, *20*, 3876−3883.

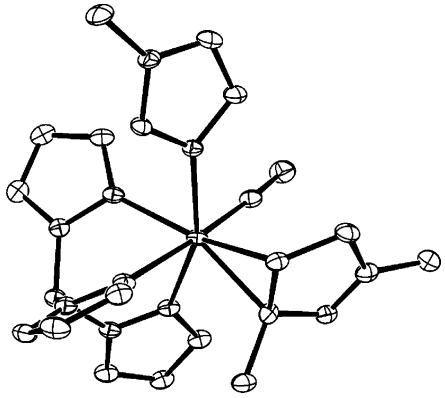
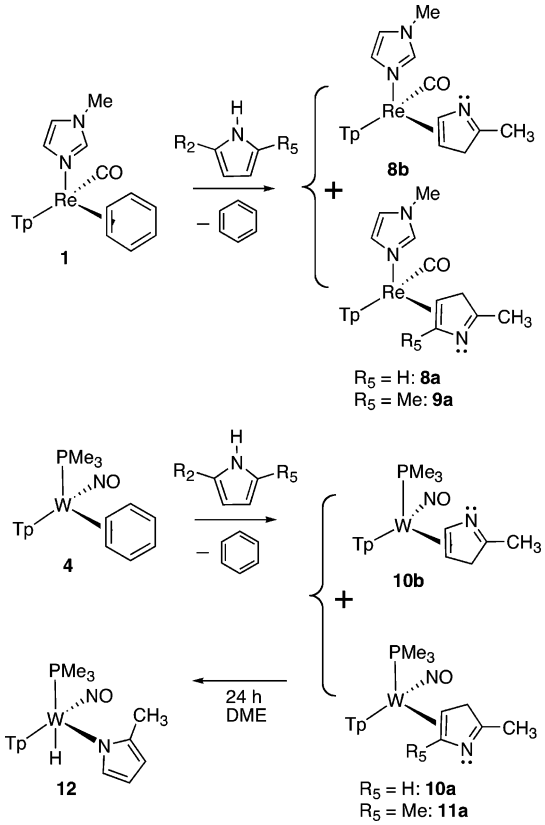


Figure 2. ORTEP diagram for the complex TpRe(CO)(MeIm)(3*H*-2,5-dimethylpyrrole) (**9**).

Scheme 4



Parallel reactions using 2,5-dimethylpyrrole also gave 3*H* tautomers (**9** and **11**), bound at C4−C5, but in only one diastereomeric form with the nitrogen away from the MeIm or PMe_3. For comparison, the analogous complex of osmium was isolated in the 1*H* pyrrole form. However, in water, this species was found to equilibrate to a 9:1 mixture of the 3*H* and 1*H* isomers.[14] A single crystal of complex **9** suitable for X-ray analysis was obtained from slow diffusion of hexanes into a DME solution of the complex containing excess 2,5-dimethylpyrrole. This crystal contained both coordinated and free 2,5-dimethylpyrrole, allowing us to make direct comparisons between the two (Figure 3). Significant features of the structure include bond lengths around the heterocyclic ring consistent with a 3*H*-pyrrole and dihedral angles between C4H and the geminal protons

(14) Hodges, L. M.; Gonzalez, J.; Koontz, J. I.; Myers, W. H.; Harman, W. D. *J. Org. Chem.* **1995**, *60*, 2125.

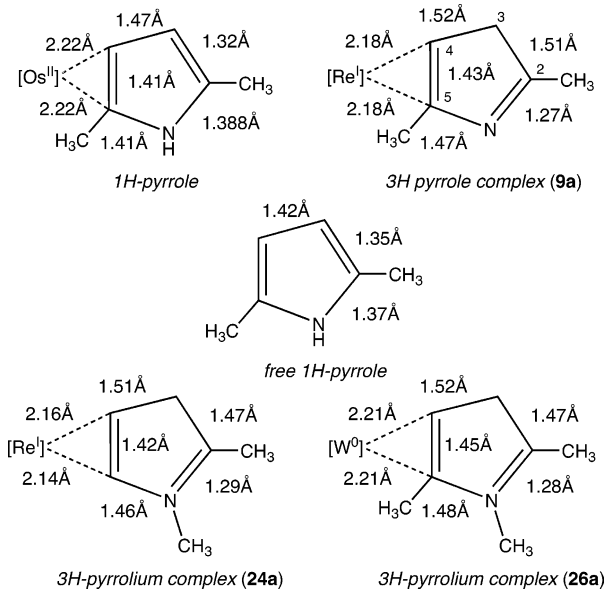
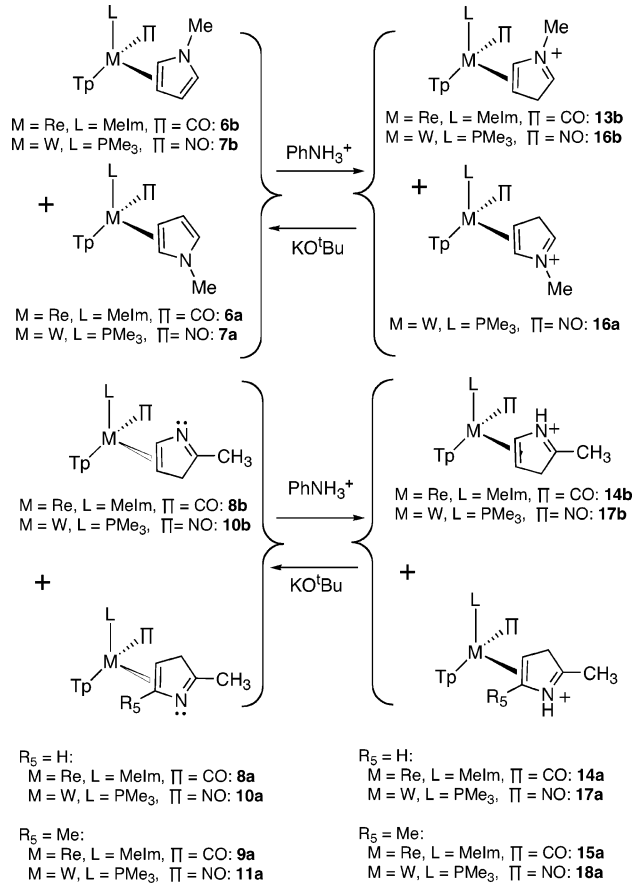


Figure 3. Comparison of bond lengths for 1*H*- and 3*H*-pyrrole complexes, and 3*H*-pyrrolium complexes with the corresponding native pyrrole.

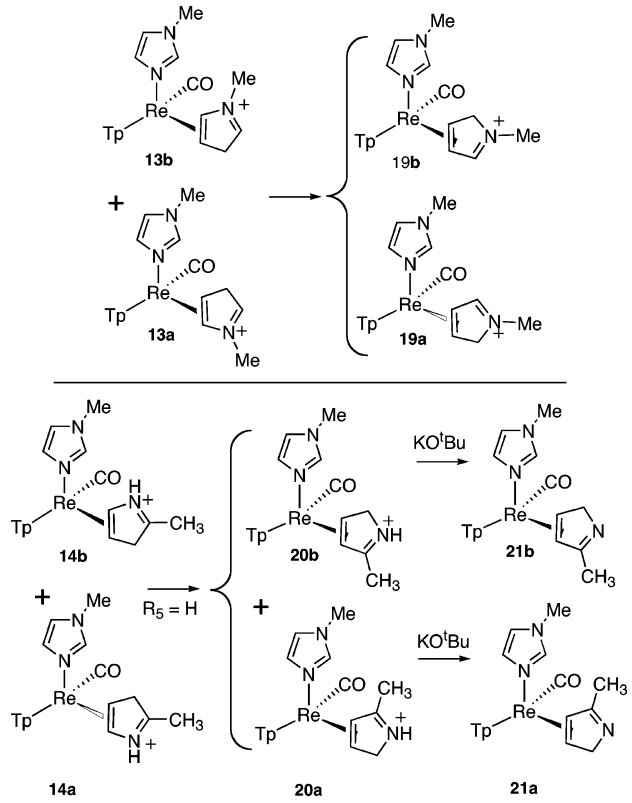
Scheme 5



on C3 consistent with the coupling data in the ^{1}H NMR spectrum (H−C4−C3−H_{syn} = 96.2°; H−C4−C3−H_{anti} =28.5°).

Protonations. The 1*H*- and 3*H*-pyrrole complexes of tungsten and rhenium (**6**−**11**) undergo protonation with Brønsted acids to form the corresponding 3*H*-pyrrolium salts (**13**−**18**) (Scheme 5). Strong acids such as triflic acid in methanol or acids as mild as triethylammonium triflate may be used for this purpose.

Scheme 6



For example, when the rhenium 1-methylpyrrole complex **6** is treated with anilinium triflate, protonation occurs at the β carbon (C3), creating a pair of geminal protons observable in the ^{1}H NMR spectrum of **13**. As was the case with neutral 3*H*-pyrrole complexes, coupling was observed between H4 and the *anti*-proton at C3 ($H3_{anti}$), but not between H4 and $H3_{syn}$. This compound was isolated as a single diastereomer in which the nitrogen of the ring is oriented toward the imidazole of the rhenium (**13b**). The tungsten 1-methylpyrrole complex **7** was not stable enough to be isolated from solution, but when this complex is formed in situ from **4** and then treated with pyridinium triflate, the 3*H*-pyrrolium complex **16** is formed. Compound **16** can be isolated as a combination of two isomers (∼1:1) from the reaction mixture by addition of hexanes. With the 3*H*-pyrrole complexes **8**−**11**, protonation occurs to form 3*H*-pyrrolium complexes **14**, **15**, **17**, and **18.** These 3*H*-pyrrolium complexes are isolated in ratios that are similar to those observed for their precursors: The rhenium and tungsten complexes derived from 2-methylpyrrole (**14** and **17**) are isolated in 4:3 and 4:1 a:b ratios, respectively, while the 2,5-dimethylpyrrole analogues appear as single diastereomers (**15a** and **18a**), in which the ring nitrogen is oriented away from the imidazole or phosphine ligand.

The addition of strong base (potassium *tert*-butoxide) returns the original complexes, **6**−**11**.

When the *N*-methyl-3*H*-pyrrolium complex **13** is allowed to stand in solution, partial conversion to a new complex, the 2*H*-pyrrolium **19** (see Scheme 6), is sometimes observed. This conversion appears to be facilitated by the presence of weak base (aniline, pyridine) in protic solvent (methanol), but even then the reaction is not consistently reproducible. Parallel conversion of **14** to

20 was attempted but with little success. However, the 2*H*-pyrrolium **20** has been observed, albeit in sporadic yields, as a byproduct of **5** in the reaction of the 2-methylpyrrole **8** and H^+/MeOH. Attempts to synthesize the 2*H*-pyrrolium **20** or any other 2*H*-pyrrolium in consistently high yield and purity were unsuccessful, but relatively pure samples could be isolated from solution in low yield by selective reprecipitation with hexanes.

The 2*H*-pyrrolium complexes **19** (5:4 ratio of **a**:**b**) and **20** (5:1 ratio of **a**:**b**) show signals for geminal protons in a region similar to those found for their 3*H* isomers. In both cases, the major diastereomer (**a**) has the iminium carbon (C5) oriented toward the methylimidazole ligand.

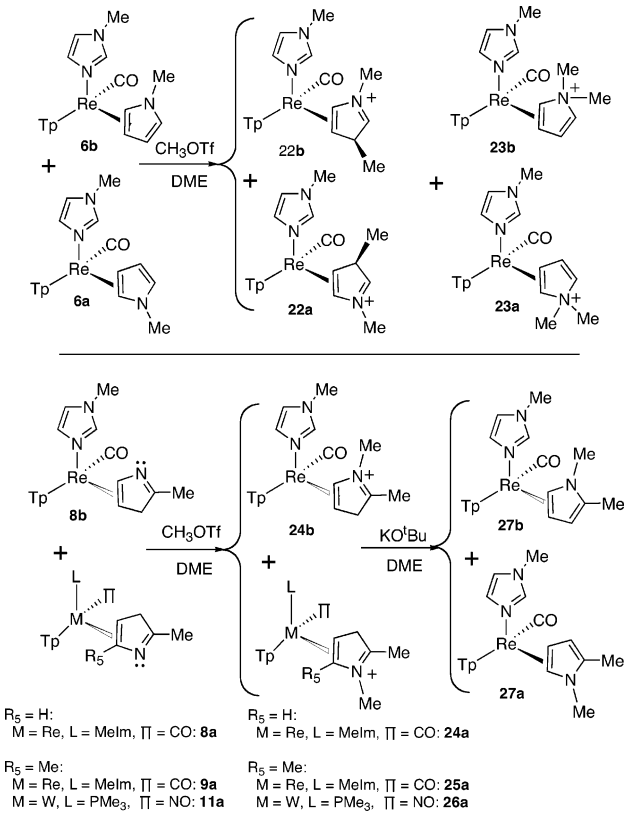
Of note, the signal for the C5 methyl group of 2*H*-pyrrolium **20** slowly degrades in the ^{1}H NMR spectrum relative to other signals for this complex. Apparently, these methyl protons are able to exchange with a deuterium source in the solvent such as adventitious D_2O. Not surprisingly, this phenomenon is more pronounced in acetone-d_6 than in other solvents such as CD_2Cl_2 or CD_3CN. In the case of the 2-methyl-2*H*-pyrrolium **20**, the addition of strong base (potassium *tert*-butoxide) gave a new complex, which appears by its NMR spectra to be a neutral, bound 2*H*-pyrrole (**21**, see Scheme 6). This complex is formed in a 5:1 diastereomer ratio, with the major diastereomer (**21b**) having the iminium carbon (C5) oriented toward the imidazole ligand.

For all 3*H*- and 2*H*-pyrrolium complexes, infrared and electrochemical data indicate a increase of the π acidity of the heterocycle compared to their pyrrole precursors. The NO or CO stretching frequencies increase, as do the anodic peak potentials that correspond to the d^5/d^6 redox couples.

The addition of methyl triflate to the 1-methylpyrrole complex **6** generates a product whose spectral analysis reveals it to be a mixture of 1,3-dimethyl-3*H*-pyrrolium, **22**, and 1,1-dimethylpyrrolium, **23**, complexes (Scheme 7), each present as one dominant diastereomer (the ratio of **a**:**b** is unknown). Attempts to separate these isomers by selective precipitation failed. However, when the methylation is carried out in different solvents and at different temperatures, a modest variation of the isomer ratio is observed, with a **23**:**22** ratio ranging from 1:1 to 5:1. Partial characterization of each species by ^{1}H NMR was possible using difference spectra. Additionally, the comparison of electrochemical data for different product mixtures allowed the assignment of various electrochemical properties. In particular, whereas the anodic wave (0.66 V at 100 mV/s) is chemically irreversible for **22**, similar to other pyrrolium complexes reported herein, the 1,1-dimethylpyrrolium complex shows a reversible couple at 0.88 V (100 mV/s). The IR spectrum was essentially the same for all product mixtures tested.

The addition of methyl triflate to the 3*H*-2-methylpyrrole complex (**8**) generates a new species whose NMR spectra show it to be the 1,2-dimethyl-3*H*-pyrrolium complex, **24**. The addition of the base KO^{t}Bu to a solution of this complex returns the 1*H*-pyrrole complex **27** (see Scheme 7). Crystals of the **a** isomer of the 3*H*-pyrrolium complex (**24a**) suitable for X-ray diffraction

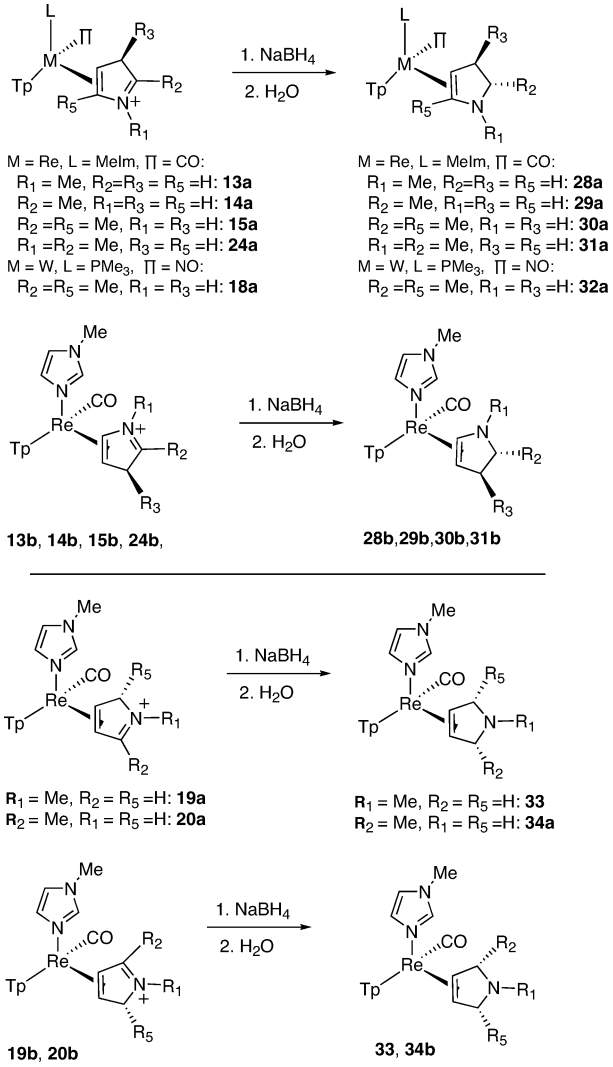
Scheme 7



were prepared by slow diffusion of pentane into a DME solution of **24**. The structure is similar to that of the tungsten 3*H*-pyrrolium complex **26a** (vide supra), and in Figure 3, these structures are presented for comparison along with the neutral 1*H*-pyrrole and 3*H*-pyrrole complexes.

Over a period of 24 h, the dimethylpyrrole product **27** cleanly underwent a substitution reaction in which the heterocycle was displaced by the acetone-d_6 solvent.[13] Taking advantage of this lability, we designed a procedure for the methylation of 2-methylpyrrole that would demonstrate the recyclability of the rhenium fragment. In this process, the Re-benzene complex (**1**, 110.0 mg, 0.1872 mmol) was dissolved in a mixture of DME (1.0 g) and 25 equiv of 2-methylpyrrole (383.3 mg, 4.726 mmol). After stirring for 24 h, MeOTf (ca. 31 mg, 0.19 mmol) in DME (ca. 210 mg) was added, followed after 5 min by the addition of KO^{t}Bu (ca. 22.0 mg, 0.19 mmol in 200 mg of DME). This sequence of additions was repeated every 24 h for 16 days, until a total of ca. 3.0 mmol of MeOTf/KO^{t}Bu had been added. An aliquot of the solution was removed at this point and added to hexanes to precipitate any Re complexes. After filtering through a plug of glass wool, this filtrate was subjected to GC/MS analysis. Peaks were identified for ^{t}BuOH, hexane (and its isomers), DME, and two peaks corresponding to the masses of a methylpyrrole and a dimethylpyrrole, in a ratio of 1.44:1.00 (GC). This outcome is consistent with a reaction process in which 2-methylpyrrole complexes to the rhenium and is methylated, deprotonated, then displaced by the starting pyrrole. Had every reagent reacted completely and cleanly, the final ratio of 2-methylpyrrole to 1,2-dimethylpyrrole should have been 0.49:1.00. Assuming that neither of these pyrroles undergo decomposition

Scheme 8



under these reaction conditions, the experimental ratio would correspond to an overall yield of 34% for 16 cycles or a 93% efficiency per cycle.

Similar to that observed for 2-methylpyrrole, when methyl triflate is added to the 2,5-dimethyl-3*H*-pyrrole complex, **9**, methylation occurs at the nitrogen to give the 3*H*-pyrrolium complex of 1,2,5-trimethylpyrrole (**25**). The subsequent addition of base liberated free 1,2,5-trimethylpyrrole along with the complex TpRe(CO)(MeIm)(acetone).[13]

Hydride Additions to 2*H*- and 3*H*-Pyrrolium Complexes. The 2*H*- and 3*H*-pyrrolium complexes of rhenium and tungsten are expected to behave chemically like iminium ions. Accordingly, when $NaBH_4$ is combined with these complexes (**13**, **14**, **15**, **18**, **24**, **19**, **20**), products are formed whose spectral characteristics are consistent with a hydride adding to the iminium carbon (Scheme 8). Such reactions successfully converted the 3*H*-pyrrolium complexes (**13**, **14**, **15**, **18**, **24**) to the 2,3-dihydropyrrole complexes (**28**, **29**, **30**, **31**, **32**) and the 2*H*-pyrrolium complexes **19** and **20** to the 2,5-dihydropyrrole complexes **33** and **34** (see Scheme 8). Infrared and electrochemical data indicate a diminution of the π acidity of the heterocycle upon reduction. The NO or CO stretching frequencies decrease, as do the anodic peak potentials corresponding to the d^5/d^6 redox couples, compared with their iminium precursors.

In addition to the tungsten and rhenium complexes reported herein, and our earlier reports of osmium(II) complexes, Gladysz et al. have reported several σ-bound pyrrole derivatives of the form $CpRe(NO)(PPh_3)(C_4H_5N)^+$.[9] The $\{CpRe(NO)(PPh_3)\}^+$ system is similar in structure to the present rhenium and tungsten systems, but it is far less π basic. For example, consider a comparison of the nitrosyl stretching frequencies of $CpRe(NO)(PPh_3)$(alkene) and $TpW(NO)(PMe_3)$(alkene). Whereas the former is in the range 1710−1720 cm^{-1},[15] the tungsten analogue is typically ∼1560 cm^{-1}.[8] In light of earlier comparisons, this provides four distinct 16-electron transition metal fragments known to form complexes with pyrroles. These can be arranged from least to most π basic in the order $\{CpRe(NO)(PPh_3)\}^+ < \{Os(NH_3)_5\}^{2+} < \{TpRe(CO)(MeIm)\} < \{TpW(NO)(PMe_3)\}$.[16] Table 1 lists the possible structural isomers for pyrrole with a 16 e metal complex fragment (M). These include π and σ complexes of 1*H* (**A**−**F**), 2*H* (**G**−**I**), and 3*H* (**J**−**L**) pyrroles, as well as isomers in which the metal inserts into a C−H or N−H bond (**M**−**W**). Remarkably, seven different isomers have been identified and characterized among these metal systems (**A**, **G**, **I**, **J**, **M Q**, **S**), and an additional three (**D**, **E**, **B**) have been speculated as intermediates on the basis of supporting evidence. For the weakest π base (and strongest Lewis acid) $\{CpRe(NO)(PPh_3)\}$ system, σ complexes **S** and **Q** are observed. With pentaammineosmium(II), the metal is more π basic, and while the π complexes **A**, **J**, and **I** have all been identified, the aromatic from (**A**) dominates. In the cases of the more potent π bases $\{TpRe(CO)(MeIm)\}$ and $\{TpW(NO)(PMe_3)\}$, the increased back-bonding from the metal renders the 3*H*-pyrrole of 2-methylpyrrole (**J**) more stable than the aromatic 1*H*-pyrrole (**A**), and for the tungsten system, the ultimate fate is complete oxidative addition to form the pyrrolyl hydride **M**. Thus, while all four of these 16-electron systems involve a heavy metal in a d^6 electron configuration, when combined with a pyrrole, their ultimate fate strongly depends on both ligand set and transition metal.

In Table 1, we have included the results of a series of semiempirical estimates of the relative energies of the various pyrrole isomers for the TpRe(CO)(MeIm) and $TpW(NO)(PMe_3)$ systems, in the format (value for Re species in kcal/mol/*value for W species in kcal/mol*). While these results must be regarded as approximations of unproven quality, the values are consistent with some experimental observations. The 2,3-η^2 isomer **A** is more stable than any other 1*H*-pyrrole complex, the C=C bound isomers **G** and **J** are more stable than the C=N (**H**, **L**) or N-bound (**I**, **K**) analogues for the 2*H*- and 3*H*-pyrroles, and the most stable isomer for either Re or W system is a seven-coordinate hydride (**N**). Not born out in these calculations is the observed preference for metal insertion into the N−H bond over insertion into the C−H bond, but the inconsistency between computed and observed perference might be ascribed to a kinetic effect in the experiment not reflected in the calculation of thermodynamic stability. We note that the N-bound

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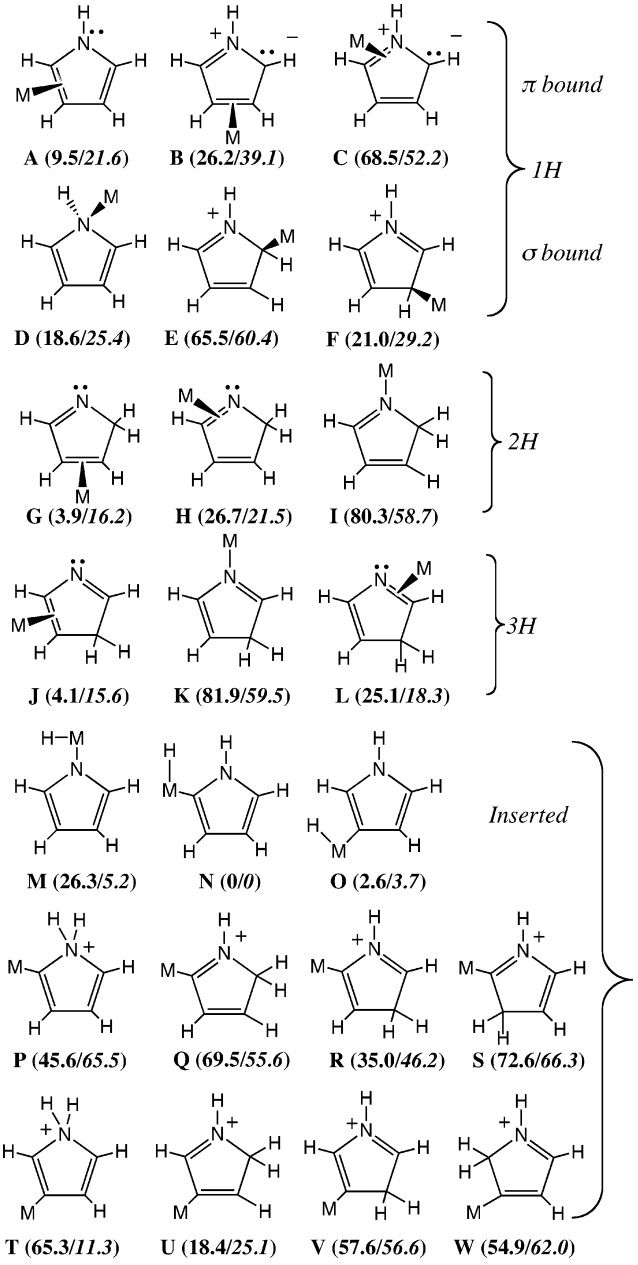
Table 1. Possible Isomers and Associated Energies for a 16e⁻ Metal Complex and Pyrrole[a]



[a] Energies are calculated using the Spartan semiempirical adaptation of the PM3 method (Wavefunction Inc. Irvine CA) and are reported in kcal/mol relative to the lowest energy isomer (TpRe(CO)(MeIm)/TpW(NO)(PMe_3)).

isomer **D**, a possible precursor to N−H activation, is lower in energy than **E** or **F** (potential precursors to C−H activation).

Concluding Remarks. The primary intent of this study was to identify transition metal based dearomatization agents (or π bases) that were capable of forming stable π complexes with pyrroles. In cases where this is possible, numerous opportunities for modification of the heterocycle have been demonstrated. This study shows that electronic requirements for successful complexation are stringent. While a highly π basic metal is required to overcome the aromatic stability of the pyrrole, tautomerization (to either the 2*H*- or 3*H*-pyrrole) and oxidative addition (of the N−H bond) become competitive reactions for these metals (e.g., {TpRe(CO)(MeIm)} or {TpW(NO)(PMe_3)}). Provided that these are reversible reactions, however, access to the η^2-1*H*-pyrrole should still possible, and an exploration of the organic chemistry for both the 1*H*- and 3*H*-pyrrole isomers is currently under way.

Experimental Section

General Procedures. All reactions were performed in a Vacuum Atmospheres glovebox. ^{1}H and ^{13}C NMR spectra, including 2D spectra, were recorded at room temperature (unless otherwise noted) on one of the following spectrometers: a Varian Inova 300 or 500 MHz, a Bruker Avance 300 or 500 MHz, or a GN-300 spectrometer. Chemical shifts are reported in ppm relative to TMS (tetramethylsilane) using residual protonated solvent (acetonitrile-d_2 = δ 1.94 or acetone-d_5 = δ 2.04) as an internal standard. Cyclic voltammograms were recorded in a standard three-electrode cell from +1.7 to −1.7 V utilizing a glassy carbon electrode. All potentials are reported versus NHE and, unless otherwise noted, were determined in CH_3CN or DMA (~0.5 M tetrabutylammonium hexafluorophosphate) at a scan rate of 100 mV/s using colbaltocenium hexafluorophosphate ($E_{1/2}$ = −0.78 V) or ferrocene ($E_{1/2}$ = +0.55 V) in situ as a calibration standard. Infrared spectra were recorded on a MIDAC Prospect (Model PRS) spectrometer as a glaze using a Horizontal Attenuated Total Reflectance Accessory (HATR, Pike Industries). Elemental analyses were performed with a Perkin-Elmer 2400 Series II CHNS/O analyzer or obtained from Atlantic Microlabs (Norcross, GA). Mass spectra were obtained on either a JEOL JMS600 using FAB^+, a Finnagan MAT TSQ7000 using ESI^+, or a Shimadzu GCMS QP5050 by direct inlet.

Solvents and Reagents. All solvents were purified via distillation under nitrogen or by passage through an activated alumina column under inert atmosphere and were purged with nitrogen prior to use. Acetonitrile-d_3 (Cambridge Isotope Labs) was distilled over CaH_2 under an inert atmosphere prior to use. 2-Methylpyrrole was prepared and purified as reported by Garrido et al.[17]

Assignments of peaks in NMR spectra were based on COSY, HSQC, HMBC, and/or NOESY data. An additional factor in peak assignments comes from the observation that, in these metal systems, the η^2-bound ligand has always been found to assume an orientation that is orthogonal to the metal−CO or metal−NO bond, with the bulk of the ligand extending out over the CO or NO ligand. Using a standard orientation in which the metal is under the η^2-bound ligand with the tuning ligand (MeIm for Re; PMe_3 for W) oriented up and the CO oriented to the right, the lower left quadrant represents a pocket between two pyrazoles. Protons (or methyls) that extend into that quadrant are found to have a chemical shift much more upfield than would otherwise be expected, presumably since in that quadrant they find themselves situated between two aromatic rings. Thus, when a product is found as two diastereomers, they almost always can be described as oriented up or down, relative to the tuning ligand, and when the bound carbons of the η^2-bound ligand both have protons attached, the average chemical shifts of those two protons are essentially the same in the two diastereomers, but one of the two protons in each pair will have been shifted upfield from its expected position, and that proton, in each pair, can be assigned to the lower left quadrant. Unless otherwise noted, *J* values for Tp are 2.0 Hz.[7,8]

TpRe(II)(CO)(1-methylimidazole)(η^1-1-pyrrolyl) [2]. [TpRe(CO)(1-methylimidazole)(benzene)] (96.8 mg, 0.164 mmol) was stirred with pyrrole (202.5 mg, 3.018 mmol) in THF (1.455

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(17) Garrido, D. O. A.; Bujldain, G.; Frydman, B. *J. Org. Chem.* **1984**, *49*, 2619.

g). After 29 h, the solution was added to stirring hexanes, giving a precipitate, which was filtered, washed with hexanes, and dried in vacuo. Yield of tan-pink powder: 48.0 mg (0.0834 mmol, 51%). ^{1}H NMR (acetone-d_6): spectrum showed solvent peaks, a cluster of many small peaks in the Tp/Im region (6−8 ppm), another cluster of peaks in the general area where Im-Me is usually seen (3.7−3.9), and two very broad (ca. 0.5 ppm), featureless, low-intensity waves at 9.9 and 11.3 ppm. CV: $E_{1/2}$ = +0.12 V, E_{semirev} = −1.52 V. IR: ν_{CO} = 1816 cm^{-1}. MS: APCI(+) 577 (MH+); ESI(+) 576 (M+); EI(direct inlet) 576 (M+).

[TpRe(III)(CO)(1-methylimidazole)(η^1-1-pyrrolyl)]-PF_6 [3]. A solution was prepared of **2** (16 mg, 0.028 mmol) in acetone-d_6 (ca. 1 mL) and added to ferrocenium hexafluorophosphate (12 mg, 0.036 mmol). An immediate color change from red to deep green was observed. ^{1}H NMR (22 °C, acetone-d_6, δ): 8.10 (br, 2H, Tp+Im), 8.05 (d, 1H, Tp), 7.78 (d, 1H, Tp), 7.62 (d, 1H, Tp), 7.55 (d, 1H, Tp), 7.47 (d, 1H, Tp), 7.17 (d, 1H, Tp), 6.89 (br t, 1H, Im), 6.65 (br t, 1H, Tp), 6.58 (br t, 1H, Tp), 6.48 (br t, 1H, Tp), 6.30 (br, 1H, pyrrole ring proton(s)). CV: $E_{1/2}$ = ca. +0.10 V (complex), $E_{1/2}$ = +0.55 V (ferrocene). IR: 1910 (sh), 1853 cm^{-1}.

TpW(NO)(PMe_3)(η^1-1-pyrrolyl)H [5]. Pyrrole (1.5 mL) was added to a solution of TpW(NO)(PMe_3)(η^2-benzene) (286.9 mg, 0.494 mmol) in DME (2 mL). After 4 h, the solution was reduced to dryness under reduced pressure. The resulting residue was dissolved in THF and added to pentane, precipitating a light brown solid. The precipitate was collected via filtration and dried in vacuo. Yield of light brown solid: 179.8 mg (0.315 mmol, 64%). ^{1}H NMR (acetone-d_6, δ, Hz): 11.36 (1H, d (J = 125), hydride), 8.17 (1H, s, Tp), 8.11 (1H, s, Tp), 8.08 (1H, d (J = 2.0), Tp), 8.00 (1H, d (J = 2.0), Tp), 7.62 (1H, d (J = 2.0), Tp), 6.78 (1H, d (J = 2.0), Tp), 6.50 (1H, t (J = 2.0), Tp), 6.46 (1H, t (J = 2.0 Hz), Tp), 6.42 (2H, t (J = 2.0), C^{2}H and C^{5}H), 5.91 (1H, t (J = 2.0), Tp), 5.84 (2H, t (J = 2.0), C^{3}H and C^{4}H), 1.39 (9H, d (J = 10.5), PMe_3). ^{13}C NMR (acetone-d_6, δ, Hz): 146.8 (s, Tp), 146.0 (s, Tp), 142.9 (s, Tp), 139.3 (s, Tp), 138.0 (s, Tp), 135.3 (s, Tp), 129.5 (s, C^2 and C^5), 108.2 (s, Tp), 107.6 (s, C^3 and C^4), 107.3 (s, Tp), 106.1 (s, Tp), 16.7 (d (J = 33.8), PMe_3). IR: ν_{NO} = 1590 cm^{-1}.

[TpRe(CO)(1-methylimidazole)(4,5-η^2-1-methyl-1*H*-pyrrole) [6]. [TpRe(CO)(1-methylimidazole)(benzene)] (693.5 mg, 1.18 mmol) was stirred with 1-methylpyrrole (5.5630 g, 68.6 mmol) overnight (16 h). Volatiles were removed with vacuum, and the remaining liquid was added to stirring hexanes (100 mL) to give a brown precipitate. The precipitate was collected via filtration and dried in vacuo. Yield of light brown powder: 556.9 mg (0.943 mmol, 80%). ^{1}H NMR (acetone-d_6, δ): 7.99 (s, 1H), 7.83 (s, 2H), 7.52 (s, 1H), 7.49 (s, 1H), 7.25 (s, 1H), 6.36 (s, 1H), 6.25 (s, 1H), 6.21 (s, 1H), 6.15 (s, 1H), 6.12 (s, 1H), 5.66 (br s, 1H), 3.83 (s, 3H), 3.55 (br s, 1H), 3.11 (s, 3H), C^3 and C^2 protons unassigned. ^{13}C NMR (acetone-d_6, δ): 198.6 (CO), 142.5, 142.3, 139.9, 135.9, 135.2, 135.0, 130.4, 121.9, 117.9, 106.5, 106.1 (2C), 108.3, 107.9, 87.4, 64.9, 34.0 (Im-CH_3), N-CH_3 unassigned. IR: ν_{CO} = 1784 cm^{-1}. CV: $E_{p,a}$ = 0.66 V, $E_{1/2}$ = −0.21 V.

TpRe(CO)(1-methylimidazole)(4,5-η^2-2-methyl-3*H*-pyrrole) [8]. [TpRe(CO)(1-methylimidazole)(benzene)] (312.8 mg, 0.532 mmol) was stirred with 2-methylpyrrole (657.0 mg, 8.11 mmol) in THF (2.0 g) overnight (18 h). Volatiles were removed with a nitrogen stream, and the residue was taken up in DME. Addition to stirring hexanes resulted in a precipitate, which was filtered and dried in vacuo. Yield of light brown powder: 169.2 mg (0.2865 mmol, 54%). ^{1}H NMR (acetone-d_6, δ, Hz): two diastereomers observed in a ratio of 2:1. **8a** (major, pyrrole N away from Im): 8.63 (br s, 1H, Tp/Im), 7.85 (br s, 1H, Tp/Im), 7.72 (br s, 1H, Tp/Im), 7.70 (d, 1H, Tp/Im), 7.48 (d, 1H, Tp/Im), 7.22 (d, 1H, Tp/Im), 7.05 (br s, 1H, Tp/Im), 6.62 (br s, 1H, Tp/Im), 6.28 (t, 1H, Tp/Im), 6.19 (t, 1H, Tp/Im), 6.12 (d, 1H, Tp/Im), 6.08 (t, 1H, Tp/Im), 4.67 (d (J = 4.6), 1H, C^{5}H), 3.92 (dd (J = 20,5.6), 1H, C^{3}H$_2$(*anti*)), 3.82 (s, 3H, Im-Me), 3.54 (d (J = 20), 1H, C^{3}H$_2$(*syn*)), 3.22 (dd (J = 5.6,4.6), 1H, C^{4}H), 2.19 (s, 3H, C^{2}CH$_3$). **8b** (minor, pyrrole N toward Im): 8.13 (d, 1H, Tp/Im), 7.92 (br s, 1H, Tp/Im), 7.77 (d, 1H, Tp/Im), 7.76 (m, 1H, Tp/Im), 7.75 (d, 1H, Tp/Im), 7.31 (d, 1H, Tp/Im), 7.24 (d, 1H, Tp/Im), 6.91 (t, 1H, Tp/Im), 6.57 (d, 1H, Tp/Im), 6.25 (t, 1H, Tp/Im), 6.23 (t, 1H, Tp/Im), 6.12 (t, 1H, Tp/Im), 5.29 (d (J = 4.8), 1H, C^{5}H), 4.04 (dd (J = 5.5,15), 1H, C^{3}H$_2$(*anti*)), 3.80 (d (J = 15), 1H, C^{3}H$_2$(*syn*)), 3.78 (s, 3H, Im-Me), 2.70 (dd (J = 5.5,4.8), 1H, C^{4}H), 2.25 (s, 3H, C^2-Me). ^{13}C NMR (acetone-d_6, δ): two diastereomers observed. **8a** (major): 198.5 (CO), 168.2 (C^2), 147.6 (Tp/Im), 143.2 (Tp/Im), 140.9 (Tp/Im), 139.9 (Tp/Im), 135.0 (2 Tp/Im), 131.1 (Tp/Im), 122.3 (Tp/Im), 106.4 (Tp/Im), 106.3 (Tp/Im), 106.1 (Tp/Im), 55.0, 50.9 (C^3, C^4), 95.0 (C^5), 34.4 (Im-Me), 18.8 (C^2-Me). **8b** (minor): 198.5 (CO), 168.2 (C^2), 144.8 (Tp/Im), 143.3 (Tp/Im), 142.6 (Tp/Im), 140.5 (Tp/Im), 136.1 (Tp/Im), 135.0 (2 Tp/Im), 132.0 (Tp/Im), 121.3 (Tp/Im), 106.6 (Tp/Im), 106.3 (2 Tp/Im), 93.6 (C^5), 52.1, 51.3 (C^3,C^4), 34.4 (Im-Me), 18.7 (C^2-Me). IR: ν_{CO} = 1794 cm^{-1}. CV: $E_{p,a}$ = 0.52 V, $E_{1/2}$ = 0.11 V. MS: ESI(+) 591, 592 (M+, MH+), FAB(+) 590 (M − H+). Anal. Calcd for $C_{19}H_{23}N_9BORe$: C, 38.65; H, 3.93; N, 21.35. Found: C, 38.61; H, 4.02; N, 21.31.

TpRe(CO)(1-methylimidazole)(4,5-η^2-2,5-dimethyl-3*H*-pyrrole) [9]. [TpRe(CO)(1-methylimidazole)(benzene)] (304.0 mg, 0.517 mmol) was stirred with 2,5-dimethylpyrrole (777.3 mg, 8.16 mmol) in THF (2.0 g) overnight (18 h). Volatiles were removed with a stream of nitrogen, and the residue was then dissolved in DME and added to stirring hexanes. The resulting precipitate was filtered and dried in vacuo. Yield of yellow powder: 271.3 mg (0.449 mmol, 87%). ^{1}H NMR (acetone-d_6, δ, Hz): one diastereomer. **9a** (pyrrole N away from Im): 8.53 (d, 1H, Tp), 7.85 (d, 1H, Tp), 7.77 (br s, 1H, Im), 7.73 (d, 1H, Tp), 7.71 (d, 1H, Tp), 7.65 (d, 1H, Tp), 7.13 (d, 1H, Tp), 7.07 (d, 1H, Im), 6.74 (d, 1H, Im), 6.30 (t, 1H, Tp), 6.22 (d, 1H, Tp), 6.03 (t, 1H, Tp), 3.96 (ddd (J = 19.8, 5.7, 0.7), 1H, C^{3}H$_2$(*anti*)), 3.84 (s, 3H, Im-Me), 3.37 (d (J = 19.5), 1H, C^{3}H$_2$(*syn*)), 2.81 (d, J = 5.7, 1H, C^{4}H), 2.16 (s, 3H, C^2-Me), 0.97 (s, 3H, C^5-Me). ^{13}C NMR (acetone-d_6, δ): 198.6 (CO), 165.8 (C2), 147.4 (Tp/Im), 142.8 (Tp/Im), 141.1 (Tp/Im), 140.8 (Tp/Im), 135.9 (Tp/Im), 135.1 (Tp/Im), 134.7 (Tp/Im), 131.1 (Tp/Im), 122.1 (Tp/Im), 106.3 (Tp (center)), 106.2 (Tp (center)), 106.0 (Tp (center)), 54.7 (C^5), 54.8, 52.5, 34.3, 21.3, 18.5 (C^{2}CH$_3$/C^{5}CH$_3$/Im-CH$_3$/C^4/C^3). IR: ν_{CO} = 1792 cm^{-1}. CV: $E_{1/2}$ = 0.10 V. MS ESI(+) 606 (MH+); FAB(+) 604 (M − H+).

TpW(NO)(PMe_3)(4,5-η^2-2-methyl-3*H*-pyrrole) [10]. TpW(NO)(PMe_3)(η^2-benzene) (522.2 mg, 0.899 mmol) was dissolved in a solution of 2-methylpyrrole (1.5 g) and DME (5.8 g). After 5.5 h, the reaction solution was evaporated to dryness. The resulting residue was dissolved in minimal benzene and subsequently chromatographed on alumina using 1:1 benzene/ethyl ether as the eluent. A dark yellow fraction was collected and evaporated to dryness under reduced pressure. Minimal THF was used to dissolve the resulting residue. The solution was then added to stirring pentane, precipitating a yellow solid. The precipitate was collected via filtration and dried in vacuo. Yield of light yellow solid: 156.9 mg (0.2686 mmol, 30%). ^{1}H NMR (acetone-d_6, δ, Hz): two diastereomers observed in a ratio of 3:1. **10a** (minor, pyrrole N directed away from PMe_3): 8.85 (1H, d (J = 2.1), Tp), 8.01 (1H, d (J = 2.1), Tp), 7.96 (1H, d (J = 2.1), Tp), 7.86 (1H, d (J = 2.2), Tp), 7.75 (1H, d (J = 2.1), Tp), 7.42 (1H, d (J = 2.2), Tp), 6.39 (1H, t (J = 2.1), Tp), 6.28 (1H, t (J = 2.1), Tp), 6.22 (1H, t (J = 2.2), Tp), 4.32 (1H, dd (J = 19.6, 6.3), C^{3}H$_2$ (*anti*)), 3.88 (1H, br, C^{5}H), 3.50 (1H, d (J = 19.6), C^{3}H$_2$ (*syn*)), 3.26 (1H, dt (J = 12.6, 6.3), C^{4}H), 2.17 (3H, s, C^2-Me), 1.29 (9H, d (J = 8.5), PMe_3). **10b** (major, pyrrole N directed toward PMe_3): 8.34 (1H, d (J = 2.2), Tp), 8.03 (1H, d (J = 2.2), Tp), 7.92 (1H, d (J = 2.2), Tp), 7.86 (1H, d (J = 2.2), Tp), 7.78 (1H, d (J = 2.2), Tp), 7.53 (1H, d (J = 2.2), Tp), 6.47 (1H, t (J = 2.2), Tp), 6.29 (1H, t (J = 2.2), Tp), 6.25 (1H, t (J = 2.2), Tp), 5.37 (1H, dd (J = 13.0, 5.9), C^{5}H), 4.32 (1H, dd (J = 19.2, 6.4), C^{3}H$_2$ (*anti*)), 3.94 (1H, d (J = 19.2), C^{3}H$_2$ (*syn*)), 2.15 (3H, s, C^2-Me), 1.88 (1H, ddd (J = 6.4, 5.9, 2.8), C^{4}H), 1.43 (9H, d (J = 8.7), PMe_3). ^{13}C NMR

(acetone-d_6, δ, Hz): two diastereomers observed. **10a** (minor): 166.0 (s, C^2), 146.3 (s, Tp), 144.7 (s, Tp), 142.0 (s, Tp), 137.4 (s, Tp), 137.0 (s, Tp), 135.6 (s, Tp), 107.2 (s, Tp), 106.6 (buried, Tp), 106.3 (s, Tp), 94.4 (s, C^5), 51.2 (buried, C^4), 50.4 (s, C^3), 17.3 (s, C^2-Me), 14.0 (d (J = 28.1), PMe_3). **10b** (major): 166.2 (s, C^2), 145.4 (s, Tp), 142.7 (s, Tp), 142.2 (s, Tp), 137.5 (s, Tp), 136.7 (s, Tp), 136.1 (s, Tp), 107.1 (s, Tp), 106.6 (s, Tp), 106.5 (s, Tp), 96.1 (d(J = 14.0), C^5), 51.3 (s, C^4), 50.3 (s, C^3), 17.3 (s, C^2-Me), 14.4(d (J = 28.1), PMe_3). IR: ν_{NO} = 1559 cm^{-1}. CV: $E_{p,a}$ = 0.40 V.

TpW(NO)(PMe_3)(4,5-η^2-2,5-dimethyl-3*H*-pyrrole) [11]. A solution of 2,5-dimethylpyrrole (1.8 g) and pentane (19.8 g) was added to TpW(NO)(PMe_3)(η^2-benzene) (1.06 g, 1.82 mmol) to give a suspension, which was stirred overnight (15 h). The suspension was added to stirring pentane. Excess solid in the reaction vessel was dissolved in minimal DME and added to the stirring pentane solution. The solid was collected via filtration and dried in vacuo. Yield of tan solid: 0.926 g (1.55 mmol, 85%). ^{1}H NMR (acetone-d_6, δ, Hz): 8.68 (1H, d (J = 2.3), Tp), 7.96 (1H, d (J = 2.1), Tp), 7.92 (1H, d (J = 2.1), Tp), 7.88 (1H, d (J = 2.3), Tp), 7.79 (1H, d (J = 2.3), Tp), 7.58 (1H, d (J = 2.3), Tp), 6.35 (1H, t (J = 2.3), Tp), 6.32 (1H, t (J = 2.1), Tp), 6.26 (1H, t (J = 2.3), Tp), 4.47 (1H, dd (J = 18.8, 6.9), C^3H_2(*anti*)), 3.42 (1H, dd (J = 18.8, 2.3), C^3H_2(*syn*)), 2.73 (1H, dd (J = 12.2, 6.9), C^4H), 2.16 (3H, s, C^2-Me), 1.31 (9H, d (J = 8.1), PMe_3), 1.08 (3H, d (J = 1.1), C^5-Me). ^{13}C NMR (acetone-d_6, δ, Hz): 164.3 (s, C^2), 146.0 (s, Tp), 144.3 (s, Tp), 142.6 (s, Tp), 137.2 (s, Tp), 136.8 (s, Tp), 135.7 (s, Tp), 107.4 (s, Tp), 106.7 (s, Tp), 106.5 (s, Tp), 98.9 (d (J = 50.0), C^5), 53.6 (s, C^4), 52.6 (s, C^3), 22.0 (s, C^5-Me), 17.2 (s, C^2-Me), 13.9 (d (J = 27.5), PMe_3). IR: ν_{NO} = 1559 cm^{-1}. CV: $E_{p,a}$ = 0.25 V. Anal. Calcd for $C_{18}H_{28}BN_8OPW$: C, 36.15; H, 4.72; N, 18.74. Found: C, 36.19; H, 4.70; N, 18.74.

TpW(NO)(PMe_3)(η^1-1-(2-methylpyrrolyl))H [12]. 2-Methylpyrrole (392.8 mg, 4.842 mmol) was added to a solution of TpW(NO)(PMe_3)(η^2-benzene) (118.8 mg, 0.204 mmol) in DME (1.4 g) and allowed to stand overnight (18 h). The solution was then reduced to dryness under reduced pressure. The resulting oil was dissolved in minimal DME, and the solution was chromatographed on alumina using 1:1 THF/ethyl ether as the eluent. A yellow fraction was collected and reduced to dryness under reduced pressure. The resulting residue was dissolved in DME and added to pentane, precipitating a light brown solid. The precipitate was collected via filtration and dried in vacuo. Yield of light brown solid: 36.6 mg (0.063 mmol, 31%). ^{1}H NMR (acetone-d_6, δ, Hz): 11.36 (1H, d (J = 128.4), hydride), 8.17 (1H, s, Tp), 8.10 (1H, s, Tp), 8.07 (1H, d (J = 2.4), Tp), 7.72 (1H, d (J = 1.8), Tp), 7.69 (1H, d (J = 2.1), Tp), 6.95 (1H, d (J = 2.1), Tp), 6.49 (1H, t (J = 2.4), Tp), 6.39 (1H, t (J = 2.4), Tp), 6.00 (1H, t (J = 2.1), Tp), 5.64 (1H, m, C^3H), 5.44 (1H, t (J = 2.4), C^4H), 4.85 (1H, s, C^5H), 2.47 (3H, s, C^2-Me), 1.45 (9H, d (J = 9.9), PMe_3). ^{13}C NMR (acetone-d_6, δ, Hz): 146.7 (s, Tp), 145.3 (d (J = 4.1), Tp), 144.3 (s, Tp), 140.0 (s, C^2), 139.2 (s, Tp), 137.8 (s, Tp), 135.4 (s, Tp), 128.7 (s, C^5), 108.0 (s, Tp), 107.1 (s, Tp), 106.7 (d (J = 8.3), C^4), 106.2 (s, Tp), 105.8 (s, C^3), 19.5 (s, C^2-Me), 17.0 (d (J = 33.8), PMe_3). IR: ν_{NO} = 1594 cm^{-1}.

[TpRe(CO)(1-methylimidazole)(4,5-η^2-1-methyl-3*H*-pyrrolium)](OTf) [13]. Product **6** (80 mg, 0.135 mmol) was dissolved in DME (600 mg), to which anilinium triflate (32.9 mg, 0.135 mmol) was added. After 5 min, the reaction mixture was added to stirring hexanes to form a light brown precipitate, which was filtered and dried in vacuo. Yield of light brown powder: 29.0 mg (0.039 mmol, 29%). ^{1}H NMR (acetone-d_6, δ, Hz): 8.55 (br s, 1H, C^2H), 8.07 (m, 2H, Tp^2/Im), 7.99 (d, 1H, Tp^3), 7.87 (d, 1H, Tp^2), 7.81 (d, 1H, Tp^3), 7.77 (d, 1H, Tp^1), 7.72 (d, 1H, Tp^1), 7.30 (t, 1H, Im), 7.18 (t, 1H, Im), 6.43 (t, 1H, Tp^3), 6.31 (t, 1H, Tp^2), 6.17 (t, 1H, Tp^1), 5.85 (d (J = 6.0), 1H, C^5H), 4.15 (br s, 1H, C^3H_2(*anti*), 3.86 (s, 3H, Im-CH_3), ca. 3.6 (m, 1H, C^3H_2(*syn*, under N-Me)), 3.57 (s, 3H, N−CH_3), 2.94 (m, 1H, C^4H). ^{13}C NMR (acetone-d_6, δ): 196.8 (CO), 166.6 (C^2), 143.2 (Tp/Im), 141.1 (Tp/Im), 140.1 (Tp/Im), 135.8 (Tp/Im), 135.6 (Tp/Im), 134.7 (Tp/Im),132.0 (Tp/Im), 122.4 (Tp/Im), 106.2 (Tp), 105.9 (Tp),105.8 (Tp), 87.8, 48.2, 44.6 (C^3/C^4/C^5), 39.8 (N-Me), 33.7 (Im-Me). IR: ν_{CO} = 1824 cm^{-1}. CV: $E_{p,a}$ = 0.69 V, $E_{p,c}$ = −1.35 V. MS: ESI(+) 592 (TpRe(CO)(MeIm)-$(C_4H_5NMe)^+$.

[TpRe(CO)(1-methylimidazole)(4,5-η^2-2-methyl-3*H*-pyrrolium)](OTf) [14]. Product **8** (60.7 mg, 0.103 mmol) was dissolved in methanol to which triflic acid (18.3 mg, 0.122 mmol) had been added. After 5 min the reaction mixture was added to stirring hexanes to give an oil. The oil was taken up in THF and added again to stirring hexanes to give a precipitate. After filtration the product was dried in vacuo. Yield of yellow powder: 52.8 mg (0.0713 mmol, 69%). ^{1}H NMR (acetone-d_6, δ, Hz): two diastereomers observed in a ratio of 4:3 (**14a**:**14b**): 8.15 (d (J = 1.5) 2H, Tp/Im), 7.98 (dd (J = 1.2, 0.4), 1H, Tp/Im), 7.96 (dd (J = 1.4, 0.4), 1H, Tp/Im), 7.90 (br s, 1H, Tp/Im), 7.89 (br s, 1H, Tp/Im), 7.87 (dd (J = 2.4, 0.6), 1H, Tp/Im), 7.86 (dd (J = 2.4, 0.7), 1H, Tp/Im), 7.83 (dd (J = 2.4, 0.7), 1H, Tp/Im), 7.82 (dd (J = 2.5, 0.6), 1H, Tp/Im), 7.68 (d (J = 1.9) 1H, Tp/Im), 7.52 (d (J = 1.9), 1H, Tp/Im), 7.41 (d (J = 2.2), 1H, Tp/Im), 7.35 (dd (J = 2.1, 0.6), 1H, Tp/Im), 7.19 (t (J = 1.5), 1H, Tp/Im), 7.13 (t (J = 1.6), 1H, Tp/Im), 6.63 (t (J = 1.3), 1H, Tp/Im), 6.39 (t (J = 2.2), 1H, Tp/Im), 6.37 (d (J = 1.6), 1H, Tp/Im), 6.36 (t (J = 2.2), 1H, Tp/Im), 6.32 (t (J = 1.8), 1H, Tp/Im), 6.32 (t (J = 2.6), 1H, Tp/Im), 6.16 (t (J = 2.0), 1H, Tp/Im), 6.15 (t (J = 2.0), 1H, Tp/Im), 5.59 (d (J = 5.1), 1H, C^5H minor), 4.90 (d (J = 5.3), 1H, C^5H major), 4.27 (m, 1H, C^3H_2(*anti*) minor), 4.22 (dd (J = 6.6) 23.9), 1H, C^3H_2-(*anti*) major), 3.95 (d (J = 23.9) 1H, C^3H_2(*syn*) major), 3.86 (s, 3H, Im-Me major), 3.84 (s, 3H, Im-Me minor), 3.66 (dd (J = 5.3, 6.6), 1H, C^4H major), 3.66 (m, 1H, C^3H_2(*syn*) minor), 2.89 (m, 1H, C^4H minor), 2.72 (s, 3H, C^2-Me minor), 2.69 (s, 3H, C^2-Me major), 13.2 (br s, 1H, NH major), 13.1 (br s, 1H, NH minor). ^{13}C NMR (acetone-d_6, δ): two diastereomers observed: 198.7 (CO major), 197.1 (CO minor), 184.3 (C^2 major), 184.6 (C^2 minor), 147.3 (Tp/Im major),144.5 (Tp/Im minor), 143.8 (Tp/Im major), 143.5 (Tp/Im minor), 143.0 (Tp/Im minor), 141.5 (Tp/Im major), 140.9 (Tp/Im minor), 140.3 (Tp/Im major), 137.0 (Tp/Im major), 136.7 (Tp/Im both), 136.3 (Tp/Im minor), 135.7 (Tp/Im major), 135.5 (Tp/Im minor), 130.7 (Tp/Im both), 130.6 (Tp/Im major), 123.1 (Tp/Im major), 122.9 (Tp/Im minor), 107.5 (Tp/Im major), 107.0 (Tp/Im major), 106.9 (Tp/Im minor (3C's)), 80.8 (C^5 major), 82.4 (C^5 minor), 50.6 (C^4 or C^3 major), 50.1 (C^4 or C^3 minor), 50.0 (C^4 or C^3 major), 47.8 (C^4 or C^3 minor), 34.6 (Im-Me both), 17.1 (C^2-Me major), 16.9 (C^2-Me minor). IR: ν_{CO} = 1816 cm^{-1}. CV: $E_{p,a}$ = 0.59 V.

[TpRe(CO)(1-methylimidazole)(4,5-η^2-2,5-dimethyl-3*H*-pyrrolium)](OTf) [15]. Product **9** (38.1 mg, 0.0630 mmol) was dissolved in DME (400 mg) to which anilinium triflate (18.3 mg, 0.0753 mmol) had been added. After 10 min the reaction mixture was added to stirring hexanes and the resulting precipitate was filtered and dried in vacuo. Yield of yellow powder: 31.5 mg (0.0425 mmol, 68%). ^{1}H NMR (acetone-d_6, δ, Hz): 8.20 (d, 1H, Tp^2), 7.98 (d, 1H, Tp^3(back)), 7.92 (br s, 1H, Im), 7.89 (d, 1H, Tp^2(back)), 7.87 (d, 1H, Tp), 7.79 (d, 1H, Tp^1(back)), 7.28 (d, 1H, Tp^1), 7.21 (t, 1H, Im), 6.74 (t, 1H, Im), 6.42 (t, 1H, Tp^3), 6.36 (t, 1H, Tp^2), 6.11 (t, 1H, Tp^1), 4.26 (dd (J = 24.2, 6.6), 1H, C^3H_2(*anti*)), 3.86 (s, 3H, Im-CH_3), 3.81 (d (J = ∼24.2), 1H, C^3H_2(*syn*)), 3.28 (d (J = ∼6.6), 1H, C^4H), 2.65 (s, 3H, C^2CH_3), 1.08 (s, 3H, C^5CH_3). ^{13}C NMR (acetone-d_6, δ): 197.9 (CO), 147.7 (Tp/Im), 143.9 (Tp/Im), 141.7 (Tp/Im), 141.6 (Tp/Im), 137.0 (Tp/Im), 136.7 (Tp/Im), 135.7 (Tp/Im), 130.9 (Tp/Im), 123.2 (Tp/Im), 107.8 (Tp/Im), 107.0 (Tp/Im), 106.9 (Tp/Im), 87.4 (C^5), 51.3 (C^3), 51.2 (C^4), 34.7 (Im-CH_3), 18.1 (C^5CH_3), 16.9 (C^2CH_3). IR: ν_{CO} = 1812 cm^{-1}. CV: $E_{1/2}$ = 1.04 V.

TpW(NO)(PMe_3)(4,5-η^2-1-methyl-3*H*-pyrrolium)(OTf) [16]. TpW(NO)(PMe_3)(η^2-benzene) (53.4 mg, 0.0919 mmol) was dissolved in *N*-methylpyrrole (1.52 g). After 4 h, a solution of pyridinium triflate (22.0 mg, 0.102 mmol) in DME (1.3 g) was added to the reaction solution. After 1 h the reaction solution

was added to stirring ethyl ether, precipitating a light brown solid. The precipitate was collected via filtration and dried in vacuo. Yield of light brown solid: 35.7 mg (0.0486 mmol, 53%). ^{1}H NMR (acetone-d_6, δ, Hz): two diastereomers observed in a ratio of 10:9 (**16a**:**16b**): 8.31 (1H, d (J = 1.8), Tp), 8.29 (1H, m, minor C^{2}H), 8.21 (1H, d (J = 2.1), Tp), 8.20 (2H, t (J = 1.8), 2 Tp's), 8.15 (1H, m, major C^{2}H), 8.11 (1H, d (J = 2.1), Tp), 8.07 (1H, d (J = 2.4), Tp), 8.04 (1H, d (J = 2.4), Tp), 8.03 (1H, d (J = 2.4), Tp), 7.92 (1H, d (J = 3.6), Tp), 7.91 (1H, d (J = 2.4), Tp), 7.77 (1H, d (J = 2.4), Tp), 7.52 (1H, d (J = 2.1), Tp), 6.53 (1H, t (J = 2.4), Tp), 6.50 (1H, t (J = 2.1), Tp), 6.41 (1H, t (J = 2.4), Tp), 6.39 (1H, t (J = 2.4), Tp), 6.38 (1H, t (J = 2.4), Tp), 6.36 (1H, t (J = 2.4), Tp), 6.00 (1H, m, minor C^{5}H$_2$), 4.70 (1H, dd (J = 24.6, 9.0), major C^{3}H$_2$), 4.62 (1H, dd (J = 24.6, 9.0), minor C^{3}H$_2$), 4.54 (1H, m, major C^{5}H), 4.18 (1H, m, minor C^{3}H$_2$), 4.05 (3H, s, major N-Me), 3.94 (3H, s, minor N-Me), 3.73 (1H, m, major C^{3}H), 3.49 (1H, m, major C^{4}H), 1.91 (1H, m, minor C^{4}H), 1.28 (9H, d (J = 8.7), minor PMe$_3$), 1.26 (9H, d (J = 8.7), major PMe$_3$). ^{13}C NMR (acetone-d_6, δ, Hz): 168.3 (s, minor C^2), 165.8 (s, major C^2), 146.5 (s, Tp), 145.4 (s, Tp), 145.3 (s, Tp), 142.8 (s, Tp), 142.5 (s, Tp), 141.0 (s, Tp), 138.3 (s, 2 Tp's), 138.1 (s, Tp), 138.0 (s, Tp), 137.7 (s, Tp), 137.5 (s, Tp), 108.4 (s, Tp), 108.1 (s, Tp), 107.9 (s, Tp), 107.7 (s, Tp), 107.3 (s, Tp), 107.0 (s, Tp), 86.7 (s, minor C^5), 85.9 (s, major C^5), 50.1 (s, major C^4), 49.2 (s, minor C^4), 44.9 (s, major C^3), 42.5 (s, minor N-Me), 42.4 (s, minor C^3), 42.3 (s, major N-Me), 13.6 (d (J = 29.3), minor PMe$_3$), 12.9 (d (J = 30.0), major PMe$_3$). IR: ν_{NO} = 1569 cm^{-1}. CV: $E_{p,a}$ = 1.11 V. Anal. Calcd for $C_{18}H_{27}BF_3N_8O_4PSW$: C, 29.45; H, 3.71; N, 15.26. Found: C, 29.85; H, 3.84; N, 15.28.

TpW(NO)(PMe$_3$)(4,5-η^2-2-methyl-3*H*-pyrrolium)(OTf) [17]. Product **10** (75.9 mg, 0.130 mmol) was dissolved in a solution of pyridinium triflate (32.4 mg, 0.141 mmol) in methylene chloride (1.8 mg). After 30 min the reaction solution was added to stirring ethyl ether, precipitating a yellow solid. The precipitate was collected via filtration and dried in vacuo. Yield of yellow solid: 51.7 mg (0.070 mmol, 50% yield). ^{1}H NMR (acetone-d_6, δ, Hz): two diastereomers observed in a ratio of 4:1. **17a** (minor, pyrrole N directed away from PMe$_3$): 8.36 (1H, d (J = 2.3), Tp), 8.17 (1H, d (J = 2.3), Tp), 8.08 (1H, d (J = 2.3), Tp), 8.00 (1H, d (J = 2.3), Tp), 7.87 (1H, d (J = 2.3), Tp), 7.66 (1H, d (J = 2.3), Tp), 6.50 (1H, t (J = 2.3), Tp), 6.37 (1H, t (J = 2.3), Tp), 6.36 (1H, t (J = 2.3), Tp), 4.80 (1H, dd (J = 23.4, 8.5), C^{3}H$_2$), 4.25 (1H, m, C^{5}H), 3.82 (1H, d (J = 23.4), C^{3}H$_2$), 3.47 (1H, ddd (J = 16.1, 8.5, 1.2), C^{4}H), 2.69 (3H, s, C^2-Me), 1.33 (9H, d (J = 8.8), PMe$_3$). **17b** (major, pyrrole N directed toward PMe$_3$): 8.32 (1H, d (J = 2.3), Tp), 8.19 (1H, d (J = 2.3), Tp), 8.08 (1H, d (J = 2.3), Tp), 8.00 (1H, d (J = 2.3), Tp), 7.91 (1H, d (J = 2.3), Tp), 7.60 (1H, d (J = 2.3), Tp), 6.51 (1H, t (J = 2.3), Tp), 6.38 (1H, t (J = 2.3), Tp), 6.36 (1H, t (J = 2.3), Tp), 5.74 (1H, dd (J = 10.0, 6.5), C^{5}H), 4.74 (1H, ddd (J = 23.8, 7.6, 2.3), C^{3}H$_2$), 4.40 (1H, d (J = 23.8), C^{3}H$_2$), 2.67 (3H, s, C^2-Me), 1.95 (1H, ddd (J = 7.6, 6.5, 1.9), C^{4}H), 1.36 (9H, d (J = 8.8), PMe$_3$). ^{13}C NMR (acetone-d_6, δ, Hz, major diastereomer, **17b**, only): 183.3 (s, C^2), 145.7 (s, Tp), 142.7 (s, Tp), 141.9 (s, Tp), 138.3 (s, Tp), 138.0 (s, Tp), 137.2 (s, Tp), 108.1 (s, Tp), 107.5 (s, Tp), 107.0 (s, Tp), 82.1 (d (J = 15.4), C^5), 48.7 (s, C^3 or C^4), 47.0 (s, C^3 or C^4), 15.6 (s, C^2-Me), 13.7 (d (J = 29.5), PMe$_3$). IR: ν_{NO} = 1569 cm^{-1}. CV: $E_{p,a}$ = 1.01 V. Anal. Calcd for $C_{18}H_{27}BF_3N_8O_4PSW$: C, 29.45; H, 3.71; N, 15.26. Found: C, 29.59; H, 3.71; N, 14.60.

TpW(NO)(PMe$_3$)(4,5-η^2-2,5-dimethyl-3*H*-pyrrolium)-(OTf) [18]. Product **11** (234.3 mg, 0.392 mmol) was dissolved in a solution of pyridinium triflate (91.2 mg, 0.398 mmol) in methylene chloride (3.8 g). After 30 min the reaction solution was added to stirring ethyl ether, precipitating a yellow solid. The precipitate was collected via filtration and dried in vacuo. Yield of yellow solid: 260.5 mg (0.348 mmol, 89% yield). ^{1}H NMR (acetone-d_6, δ, Hz): 8.28 (1H, d (J = 2.3), Tp), 8.13 (1H, d (J = 2.3), Tp), 8.04 (1H, d (J = 2.3), Tp), 8.02 (1H, d (J = 2.3), Tp), 7.93 (1H, d (J = 2.3), Tp), 7.82 (1H, d (J = 2.3), Tp), 6.47 (1H, t (J = 2.3), Tp), 6.43 (1H, t (J = 2.3), Tp), 6.40 (1H, t (J = 2.3), Tp), 4.90 (1H, dd (J = 23.1, 8.1), C^{3}H$_2$(*anti*)), 3.83 (1H, d (J = 23.1), C^{3}H$_2$(*syn*)), 2.99 (1H, t d (J = 8.1), C^{4}H), 2.69 (3H, s, C^2-Me), 1.33 (9H, d (J = 8.8), PMe$_3$), 1.28 (3H, d (J = 0.9), C^5-Me). ^{13}C NMR (acetone-d_6, δ, Hz): 178.3 (s, C^2), 146.9 (s, Tp), 145.3 (s, Tp), 143.0 (s, Tp), 138.2 (s, Tp), 137.8 (s, Tp), 136.9 (s, Tp), 107.9 (s, Tp), 107.5 (s, 2 Tp's), 88.5 (s, C^5), 51.3 (d (J = 14.4), C^4), 49.4 (s, C^3), 18.8 (s, C^5-Me), 15.0 (s, C^2-Me), 13.1 (d (J = 28.8), PMe$_3$). IR: ν_{NO} = 1569 cm^{-1}. CV: $E_{p,a}$ = 0.95 V. Anal. Calcd for $C_{19}H_{29}BF_3N_8O_4PSW$: C, 30.50; H, 3.91; N, 14.98. Found: C, 30.81; H, 3.84; N, 14.80.

[TpRe(CO)(1-methylimidazole)(3,4-η^2-1-methyl-2*H*-pyrrolium)](OTf) [19]. Product **6** (43.8 mg, 0.0742 mmol) was dissolved in methanol (550 mg), and to it was added anilinium triflate (18.5 mg, 0.0761 mmol). After 10 min, aniline (32.5 mg, 0.406 mmol) was added. The reaction was allowed to proceed for 4 days (95 h), at which time volatiles were removed with a nitrogen stream. The residue was taken in DME and added to stirring hexanes to form a light brown precipitate. After filtration, the product was dried in vacuo. Yield of light brown powder: 41.6 mg (0.0562 mmol, 76%). ^{1}H NMR (acetone-d_6, δ, Hz): two diastereomers observed in ratio of 5:4: 9.58 (s, 1H, C^{2}H major), 9.36 (s, 1H, C^{2}H minor), 8.17 (d (J = 1.8), 1H, Tp/Im), 8.15 (d (J = 1.7), 1H, Tp/Im), 8.01 (t (J = 2.5), 1H, Tp/Im), 7.96 (s, 1H, Tp/Im), 7.93 (d (J = 2.0), 1H, Tp/Im), 7.91 (d, 1H, Tp/Im), 7.90 (s, 1H, Im), 7.85 (d (J = 2.6), 1H, Tp/Im), 7.84 (d (J = 2.6), 1H, Tp/Im), 7.70 (d (J = 2.0), 1H, Tp/Im), 7.45 (d (J = 2.0), 1H, Tp/Im), 7.36 (d (J = 2.0), 1H, Tp/Im), 7.20 (s, 1H, Im), 7.15 (s, 1H, Im), 6.60 (t (J = 1.3), 1H, Tp/Im), 6.44 (d+d, 2H, Tp/Im), 6.41 (t (J = 2.2), 1H, Tp/Im), 6.33 (t (J = 2.2), 1H, Tp/Im), 6.16 (dt (J = 2.2, 0.9), 1H, Tp/Im), 5.30 (dd (J = 5.2, 18.5), 1H, C^{5}H$_2$(*anti*) minor), 5.24 (dd (J = 5.5, 19.5), 1H, C^{5}H$_2$(*anti*) major), 5.12 (d (J = 18.0), 1H, C^{5}H$_2$(*syn*) minor), 4.79 (d (J = 18.2), 1H, C^{5}H$_2$(*syn*) major), 4.29 (d, 1H, C^{3}H minor), 4.26 (d (J = 5.7), 1H, C^{4}H major), 3.90 (s, 3H, N-Me major), 3.85 (s, 3H, Im-Me major), 3.84 (s, 3H, N-Me minor), 3.81 (s, 3H, Im-Me minor), 3.42 (d (J = 5.5), 1H, C^{3}H major). ^{13}C NMR (acetone-d_6, δ): two diastereomers are observed in the ^{13}C spectrum; however, only Tp/Im peaks are observed for the minor diastereomer: 188.8 (Tp/Im), 188.5 (Tp/Im), 149.8 (Tp/Im), 144.6 (Tp/Im), 142.4 (Tp/Im), 140.5 (Tp/Im), 137.1 (3 Tp/Im), 135.8 (Tp/Im), 130.2 (3 Tp/Im), 123.4 (2 Tp/Im), 123.1 (Tp/Im), 120.1 (Tp/Im), 107.9 (Tp/Im), 107.2 (3 Tp/Im), 107.0 (Tp/Im), 106.8 (Tp/Im), 68.9, 63.5, 61.7, 60.3 (C^2/C^3/C^4/C^5), 37.7 (N-CH$_3$), 34.8 (Im-CH$_3$). IR: ν_{CO} = 1821 cm^{-1}. CV: $E_{p,a}$ = 0.78 V. MS: ACPI(+) 592 (TpRe(CO)(MeIm)(C$_4$H$_5$-NMe)$^+$, the cation from the product); ACPI(−) 149 (−OTf).

[TpRe(CO)(1-methylimidazole)(3,4-η^2-5-methyl-2*H*-pyrrolium)](OTf) [20]. Compound **8** (70.8 mg, 0.1199 mmol) was dissolved in MeOH (195 mg), and a separately prepared solution of HOTf (31.0 mg, 0.02067 mmol) in MeOH (200 mg) was added and the resulting mixture stirred. After 5 min, the mixture was added to stirring hexanes, giving a dark oil. Numerous attempts to produce a precipitate from this oil followed, using one of a variety of solvents (including CH_2Cl_2, acetone, MeOH, or DME) to dissolve the oil and addition to stirring hexanes to bring the material back out of solution, but none succeeded. Finally a small amount of microcrystals was observed in the oil at the end of one such dissolving/ppting cycle, and at that point the material was put under vacuum (dynamic and then static) overnight. The resulting yield of microcrystals and powder together was ca. 15 mg, 17%. The product appeared by NMR to consist of two diastereomers in ca. 5:1 ratio (6.5:1 for the microcrystalline material and 4:1 for the powder). ^{1}H NMR (acetone-d_6, δ, Hz): **20b** (minor diastereomer, only observed peaks are listed): 8.08 (br, 1H), 8.03 (d, 1H, Tp), 7.99 (m, 1H, Tp), 7.93 (br, 1H, Im), 7.90 (d, 1H, Tp), 7.80 (m, 1H, Tp), 7.36, (d, 1H, Tp), 7.18 (t, 1H, Im), 6.60 (t, 1H, Im), 6.47 (t, 1H, Tp), 6.33 (t, 1H, Tp), 6.124 (t, 1H, Tp), 5.08 (m, 1H, C^{2}H$_2$(*anti*)), 4.73 (br d (J = 19.3), 1H, C^{2}H$_2$-(*syn*)), 4.33 (m, 1H, C^{3}H), 3.40 (m, 1H, C^{4}H). **20b** (major

diastereomer): 10.4 (1H, br s, NH), 8.05 (1H, d, Tp^2), 8.01 (1H, d, Tp^3), 8.00 (1H, t, Im), 7.95 (1H, d, Tp^3), 7.87 (1H, d, Tp^2), 7.81 (1H, d, Tp^1), 7.71 (1H, d, Tp^1), 7.26 (1H, t, Im), 7.07 (1H, t, Im), 6.45 (1H, t, Tp^3), 6.30 (1H, t, Tp^2), 6.17 (1H, t, Tp^1), 5.09 (1H, dd (J = 17.9, 4.8), C^2H_2(*anti*)), 4.96 (1H, d (J = 17.7, 2.3), C^2H_2(*syn*)), 4.27 (1H, dd (J = 2.3, 5.2), C^4H), 3.85 (3H, s, Im-CH_3), 3.37 (1H, dd (J = 5.2, 4.8), C^3H), 2.13 (3H, s, C^5-CH_3). ^{13}C (acetone-d_6, δ, major diastereomer, **20a**, only): 198.6 (CO), 144.5 (Tp/Im), 143.3 (Tp/Im), 142.6 (Tp/Im), 141.0 (Tp/Im), 137.2 (Tp/Im), 136.9 (Tp/Im), 135.9 (Tp/Im), 132.6 (Tp/Im), 123.4 (Tp/Im), 107.3 (Tp), 107.1 (Tpx2), 63.6, 61.2, 60.8 (C^2/C^3/C^4), 34.8 (Im-CH_3), 17.6 (C^5CH_3) (C^5 not observed). IR: ν_{CO} = 1825 cm^{-1}. CV: $E_{p,a}$ = +0.80 V, $E_{p,c}$ = −1.50 V. MS: APCI(+) 592 (TpRe(CO)(MeIm)$(C_4H_5NCH_3)^+$, the cation from the product).

[TpRe(CO)(1-methylimidazole)](3,4-η²-5-methyl-2*H*-pyrrole) [21]. NMR Tube Reaction. A sample of **8** was taken in acetone-d_6, an excess of was added, and the solution was mixed. A ^1H NMR of this solution showed a spectrum similar to that of **20**, but shifted upfield. Product appeared to be two diastereomers in a 5:1 ratio. Major diastereomer, **21a**, appeared to have the iminium carbon up, toward the imidazole. ^1H NMR (acetone-d_6, δ, Hz): **21b** (minor diastereomer, only observed peaks reported): 8.08 (br, 1H, Tp/Im), 7.09 (br, 1H, Tp/Im), 7.85 (br, 1H, Tp/Im), 7.67 (br, 1H, Tp/Im), 7.25 (br, 1H, Tp/Im), 7.06 (br, 1H, Tp/Im), 6.61 (br, 1H, Tp/Im), 6.23 (br, 1H, Tp/Im), 6.05 (br, 1H, Tp/Im), 5.02 (m, 1H, C^2H_2(*anti*)), 4.64 (d (J = 18.3), 1H, C^2H_2(*syn*)). **21a** (major diastereomer): 8.07 (br, 1H, Tp^2), 7.87 (d (J = 2.5), 1H, Tp^3), 7.84 (br, 1H, Im), 7.75 (d (J = 3.1), 1H, Tp^2), 7.71 (br, 2H, Tp^1, Tp^3), 7.52 (br, 1H, Tp^1), 7.13 (br, 1H, Im), 6.98 (br, 1H, Im), 6.34 (br, 1H, Tp^3), 6.21 (br, 1H, Tp^2), 6.08 (br, 1H, Tp^1), 5.12 (br d (J = 19.6), 1H, C^2H_2(*anti*)), 4.91 (d (J = 19.6), 1H, C^2H_2(*syn*)), 3.8 (s, 3H, Im-CH_3), 3.76 (d (J = 6.0), 1H, C^3H), 3.15 (br m, 1H, C^4H), 1.71 (s, 3H, C^5CH_3). IR: ν_{CO} = 1796 cm^{-1}. CV: $E_{p,a}$ = +0.18 V.

[TpRe(CO)(1-methylimidazole)(4,5-η²-1,3-dimethyl-3*H*-pyrrolium)](OTf) [22] and [TpRe(CO)(1-methylimidazole)(4,5-η²-1,1-dimethyl-1*H*-pyrrolium)](OTf) [23]. a. Solutions of **6** (83.3 mg, 0.1411 mmol) in DME (1.62 g) and of CH_3OTF (26.7 mg, 0.1628 mmol) in DME (0.85 g) were prepared and cooled to −40 °C. After 20 min, the CH_3OTf solution was quickly transferred to the solution of **6**, and the mixture left at −40 °C for 6 h. Some solid was observed in the mixed solutions, so the slurry was filtered and the filtrate allowed to drop into stirring hexanes (50 mL), giving a tan precipitate, which was filtered, washed with hexanes, and dried in vacuo. Yield of tan solid: 72.9 mg (0.0966 mmol, 68.5%). A ^1H NMR of the product showed **23** and **22** in a 5:1 ratio. When this reaction was conducted at room temperature, the product ratio was 1:1, with a yield of 78%.

b. Room-temperature solutions of **6** (50.6 mg, 0.0857 mmol) in CH_2Cl_2 (1.02 g) and of CH_3OTf (18.5 mg, 0.1128 mmol) in CH_2Cl_2 (0.91 g) were prepared, mixed, and allowed to stir for 6 h. The initially green solution of **6** turned red when the CH_3-OTf solution was added. Some solid was observed in the mixed solutions, so the slurry was filtered and the filtrate allowed to drop into stirring hexanes (35 mL). A little more CH_2Cl_2 was used to rinse out the vial and to wash the solid in the frit. The tan precipitate that had formed in the hexanes was filtered, washed with hexanes, and dried in vacuo. Yield of tan solid: 60.1 mg (0.797 mmol, 92.3%). A ^1H NMR of the product showed **23** and **22** in a 1:2 ratio. (nb: When this reaction was conducted with both solutions cooled to −40 °C before and during reaction, the product ratio was 1:1, with a yield of 67.0%.)

23: ^1H NMR (acetone-d_6, δ, Hz): 8.17 (1H, d, Tp), 8.03 (1H, d, Tp), 8.02 (1H, d, Tp), 7.98 (1H, d, Tp), 7.86 (1H, d, Tp), 7.83 (1H, d, Tp), 7.81 (1H, d, Tp), 7.23 (1H, br s, Im), 7.22 (1H, br s, Im), 7.18 (1H, br d, (J = 2), C^2H), 6.45 (1H, t, Tp), 6.30 (1H, t, Tp), 6.18 (1H, t, Tp), 6.12 (1H, br s, C^3H), 5.83 (1H, d (J = 5.2), C^5H), 3.83 (3H, s, Im-CH_3), 3.62 (3H, s, N-CH_3), 3.15 (3H, s, N-CH_3), 3.02 (1H, dd (J = 5.2, 2.2), C^4H). IR: ν_{CO} = 1820 cm^{-1}. CV: $E_{1/2}$ = +0.88 V, $E_{p,c}$ = −1.58 V. **22**: ^1H NMR (acetone-d_6, δ, Hz): 8.48 (1H, s, C^2H), 8.07 (1H, d, Tp), 8.06 (1H, d, Tp), 7.98 (1H, d, Tp), 7.87 (1H, d, Tp), 7.81 (1H, t, Im), 7.78 (1H, d, Tp), 7.73 (1H, d, Tp), 7.29 (1H, t, Im), 7.18 (1H, t, Im), 6.43 (1H, t, Tp), 6.31 (1H, t, Tp), 6.17 (1H, t, Tp), 5.81 (1H, dd (J = 4.8, 1.5), C^5H), 4.23 (1H, m, C^3H), 3.85 (3H, s, Im-CH_3), 3.55 (3H, s, N-CH_3), 2.77 (1H, d (J = 4.8), C^4H), 1.43 (3H, d (J = 7.5, C^3CH_3). IR: ν_{CO} = 1820 cm^{-1}. CV: $E_{p,a}$ = +0.66 V, $E_{p,c}$ = −1.12 V. Anal. Calcd for $C_{21}H_{26}N_9BF_3O_4ReS$ (compounds **23** + **22**): C, 33.43; H, 3.47; N, 16.71. Found: C, 33.02; H, 3.42; N, 16.83.

[TpRe(CO)(1-methylimidazole)(4,5-η²-1,2-dimethyl-3*H*-pyrrolium)](OTf) [24]. Methyl triflate (18.1 mg, 0.110 mmol) was added to a solution of **8** (48.6 mg, 0.0823 mmol) in DME (600 mg). After 2 h the reaction mixture was added to stirring hexanes, giving a precipitate, which was filtered and dried in vacuo. Yield of cream colored powder: 43 mg (0.0570 mmol, 69%). ^1H NMR (acetone-d_6, δ, Hz): two diastereomers observed in a ratio of 12:1 (minor not characterized): 8.12 (d, 1H, Tp), 8.04 (br s, 1H, Im), 7.96 (d, 1H, Tp), 7.85 (d, 1H, Tp), 7.79 (d, 1H, Tp), 7.76 (d, 1H, Tp), 7.70 (d, 1H, Tp), 7.28 (br, 1H, Im), 7.18 (br, 1H, Im), 6.41 (t, 1H, Tp), 6.30 (t, 1H, Tp), 6.15 (t, 1H, Tp), 5.84 (d (J = 5.1), 1H, C^5H), 4.28 (m, 1H, C^3H_2(*anti*)), 3.85 (s, 3H, Im-CH_3), 3.37 (m, 4H, N-CH_3/C^3H_2(*syn*)), 2.75 (m, 1H, C^4H), 2.59 (s, 3H, C^2CH_3). IR: νCO = 1810 cm^{-1}. CV: $E_{p,a}$ = +0.61 V. Anal. Calcd for $C_{21}H_{26}BF_3N_9O_4ReS$: C; 33.43; H, 3.47; N, 16.48. Found: C, 33.98; H, 3.64; N, 16.48.

[TpRe(CO)(1-methylimidazole)(4,5-η²-1,2,5-trimethyl-3*H*-pyrrolium)](OTf) [25]. Product **9** (47.5 mg, 0.0786 mmol) was dissolved in DME (1.0 g), to which was added methyl triflate (14.6 mg, 0.0890 mmol). After 90 min, the reaction mixture was added to stirring hexanes and the resulting precipitate was filtered and dried in vacuo. Yield of light yellow powder: 43.9 mg (0.0571 mmol, 72.6%). ^1H NMR (acetone-d_6, δ, Hz): two diastereomers observed in a ratio of 10:1 (**25a**:**25b**). **25a** (major): 8.19 (d, 1H, Tp), 8.06 (d, 1H, Tp), 8.01 (d, 1H, Tp), 7.93 (d, 1H, Tp), 7.90 (br s, 1H, Im), 7.76 (d, 1H, Tp), 7.32 (d, 1H, Tp), 7.20 (t, 1H, Im), 6.74 (t, 1H, Im), 6.47 (dd, 1H, Tp), 6.39 (dd, 1H, Tp), 6.08 (dd, 1H, Tp), 4.28 (ddd (J = 24, 7, 2), 1H, C^3H_2(*anti*)), 3.85 (s, 3H, Im-CH_3), 3.78 (s, 3H, N-CH_3), 3.67 (d (J = 24.5), 1H, C^3H_2(*syn*)), 3.32 (d (J = 7.0), 1H, C^4H), 2.58 (s, 3H, C^2CH_3), 1.26 (s, 3H, C^5CH_3). **25b** (minor, only observed peaks shown): 7.97 (d, 1H, Tp/Im), 7.88 (d, 1H, Tp/Im), 7.87 (d, 1H, Tp/Im), 7.78 (d, 1H, Tp/Im), 7.27 (d, 1H, Tp/Im), 6.41 (d, 1H, Tp/Im), 6.36 (t, 1H, Tp/Im), 6.11 (d, 1H, Tp/Im), 3.86 (s, 3H, N-CH_3), 3.85 (d, 1H, C^3H_2(*syn*)), 2.65 (s, 3H, C^2CH_3), 1.15 (s, 3H, C^5CH_3), ∼4.3 (dd, 1H, C_3H_2(*anti*)), ∼2.6 (d, 1H, C_4H). ^{13}C NMR (acetone-d_6, δ): two diastereomers observed in a ratio of 10:1 (minor not characterized): 197.6 (CO), 179.9 (C2), 148.7 (Tp/Im), 143.9 (Tp/Im), 141.8 (Tp/Im), 141.7 (Tp/Im), 137.4 (Tp/Im), 137.1 (Tp/Im), 135.6 (Tp/Im), 130.9 (Tp/Im), 123.1 (Tp/Im), 107.7 (Tp/Im), 107.0 (Tp/Im), 106.7 (Tp/Im), 90.9 (C^5), 51.1, 49.8 (C^3/C^4), 35.7 (N-CH_3), 34.7 (Im-CH_3), 18.3, 16.4 (C^2CH_3/C^5CH_3). IR: ν_{CO} = 1809 cm^{-1}. CV: $E_{1/2}$ = +0.65 V, $E_{p,c}$ = −1.59 V. Anal. Calcd for $C_{22}H_{28}BF_3N_9O_4ReS$: C; 34.38; H, 3.67; N, 16.40. Found: C, 34.19; H, 3.64; N, 16.42.

TpW(NO)(PMe_3)(4,5-η²-1,2,5-trimethyl-3*H*-pyrrolium)(OTf) [26]. Product **11** (199.5 mg, 0.334 mmol) was dissolved in a solution of methyl triflate (55.0 mg, 0.335 mmol) in methylene chloride (5.4 g). The reaction solution was added to stirring ethyl ether, precipitating a yellow solid. The precipitate was collected via filtration and dried in vacuo. Yield of yellow solid: 192.4 mg (0.253 mmol, 76% yield). ^1H NMR (acetone-d_6, δ, Hz): 8.29 (1H, d (J = 2.3), Tp), 8.12 (1H, d (J = 2.3), Tp), 8.04 (1H, d (J = 2.3), Tp), 8.03 (1H, d (J = 2.3), Tp), 7.97 (1H, d (J = 2.3), Tp), 7.94 (1H, d (J = 2.3), Tp), 6.46 (1H, t (J = 2.3), Tp), 6.45 (1H, t (J = 2.3), Tp), 6.43 (1H, t (J = 2.3), Tp), 4.94 (1H, ddd (J = 23.6, 8.4, 2.2), C^3H_2(*anti*)), 3.79

(3H, s, N-Me), 3.75 (1H, d (J = 23.6), C^3H_2(*syn*)), 2.96 (1H, dd (J = 9.6, 8.4), C^4H), 2.63 (3H, s, C^2-Me), 1.46 (3H, d (J = 1.2), C^5-Me), 1.25 (9H, d (J = 8.8), PMe_3). ^{13}C NMR (acetone-d_6, δ, Hz): 178.2 (s, C^2), 146.5 (s, Tp), 145.5 (d (J = 1.9), Tp), 143.5 (s, Tp), 138.6 (s, Tp), 138.1 (s, Tp), 138.0 (s, Tp), 108.1 (s, Tp), 107.9 (s, Tp), 107.6 (s, Tp), 99.6 (d (J = 2.3), C^5), 50.9 (d (J = 15.5), C^4), 49.7 (d (J = 4.8), C^3), 35.9 (s, N-Me), 18.6 (d (J = 2.3), C^5-Me), 15.0 (s, C^2-Me), 12.8 (d (J = 29.4), PMe_3). IR: ν_{NO} = 1561 cm^{-1}. CV: $E_{p,a}$ = 0.96 V, $E_{p,c}$ = −1.90 V. Anal. Calcd for $C_{20}H_{31}BF_3N_8O_4PSW$: C, 31.52; H, 4.10; N, 14.70. Found: C, 31.33; H, 4.09; N, 14.71.

TpRe(CO)(1-methylimidazole)(4,5-η^2-1,2-dimethyl-1*H*-pyrrole) [27]. Compound **24** (32.5 mg, 0.0431 mmol) was dissolved in acetone (385 mg), and a solution of KO^{t}Bu (8.7 mg, 0.0776 mmol) in acetone (216 mg) was added. A color change from reddish yellow to green was observed. After ca. 3 min, the solution was added to stirring hexanes (25 mL), giving a tan-brown precipitate, which was filtered and dried in vacuo. Yield of tan solid: 15.3 mg (0.0253 mmol, 58.7%). ^1H NMR (acetone-d_6, δ, Hz): 8.15 (br, 1H, Tp/Im), 7.78 (br, 1H, Tp/Im), 7.75 (br d, 1H, Tp/Im), 7.67 (br, 2H, Tp/Im), 7.24 (br with upfield shoulder, 2H, Tp/Im), 7.06 (br, 1H, Tp/Im), 6.95 (br d, 1H, Tp/Im/ringCH), 6.50 (v br, 1H, Tp/Im/ringCH), 6.22 (br, 1H, Tp), 6.19 (br, 1H, Tp), 6.02 (br, 1H, Tp), 5.30 (br, 1H, ring CH), 4.30 (br, 1H, ring CH), 3.79 (br, 3H, Im-CH_3), 2.75 (br, 3H, NCH_3), 1.94 (br, 3H, C^2CH_3). IR: ν_{CO} = 1775 cm^{-1}. CV: $E_{1/2}$ = −0.32 V.

(TpRe(CO)(1-methylimidazole)(4,5-η^2-1-methyl-2,3-dihydro-1*H*-pyrrole) [28]. Product **6** (49.6 mg, 0.0840 mmol) and anilinium triflate (19.9 mg, 0.0819 mmol) were dissolved in 1:1 CH_3CN/C_2H_5CN and mixed to form product **13** in situ. $NaBH_4$ was then dissolved in a minimum of methanol and added to the reaction at −70 °C. After 2 h, volatiles were removed via nitrogen stream, and the remaining residue was taken in DME and added to stirring hexanes. The resulting precipitate was filtered and dried in vacuo. Yield of green-brown powder: 48.1 mg (0.0812 mmol, 97% (contaminated with triflate salts)). ^1H NMR (acetone-d_6, δ, Hz): two diastereomers observed in a 5:1 ratio, only major diastereomer reported: 8.00 (s, 1H, Im), 7.98 (dd, 1.4,0.6, 1H, Tp^2), 7.83 (d, 2.2, 1H, Tp^3), 7.71 (d, 2.2, 1H, Tp^2), 7.69 (d, 2.0, 1H, Tp^1), 7.67 (d, 1.0, 1H, Tp^3), 7.64 (d, 1.6, 1H, Tp^1), 7.08 (s, 1H, Im), 7.03 (s, 1H, Im), 6.33 (t, 2.0, 1H, Tp^3), 6.16 (t, 2.2, 1H, Tp^2), 6.08 (t, 2.0, 1H, Tp^1), 5.17 (d, 4.3, 1H, C^5H), 3.85 (s, 3H, N-Me), 3.78 (s, 3H, Im-Me), 2.96 (m, 2H, C^3H_2(*anti*)+C^2H_2(*syn*)), 2.64 (m, 1H, C^3H_2(*syn*)), 2.38 (m, 1H, C^2H_2(*anti*)), 2.24 (m, 1H, C^4H). IR: ν_{CO} = 1797 cm^{-1}. CV: $E_{p,a}$ = +0.78 V. MS: APCI(+) 594 (MH^+).

(TpRe(CO)(1-methylimidazole)(4,5-η^2-2-methyl-2,3-dihydro-1*H*-pyrrole) [29]. Pyridinium triflate (18.8 mg, 0.0821 mmol) was added to **8** (47.7 mg, 0.0808 mmol) dissolved in DME (300 mg), to produce product **14** in situ. After 5 min, a solution of $NaBH_4$ (3.5 mg, 0.0926 mmol) in methanol (150 mg) was added to the reaction and stirred for 5 min. The reaction was then added to stirring hexanes, and the resulting precipitate was filtered and dried in vacuo. Yield of gray powder: 41.3 mg (0.0697 mmol, 86% (contaminated with triflate salts)). ^1H NMR (acetone-d_6, δ, Hz): two diastereomers observed in a ratio of 5.4:8.13 (dd, 1H, Tp major), 8.11 (d, 1H, Tp minor), 7.83 (2 d (overlapping), 2H, 2 Tp), 7.76 (s, 1H, Im minor), 7.73 (m, 6H, Tp, 3 major + 3 minor), 7.68 (s, 1H, Im major), 7.42 (d, 1H, Tp major), 7.37 (d, 1H, Tp minor), 7.32 (d, 1H, Tp minor), 7.03 (t, 1H, Im minor), 7.01 (t, 1H, Im major), 6.63 (t, 1H, Im minor), 6.59 (t, 1H, Im major), 6.27 (t, 1H, Tp 3 minor), 6.26 (t, 1H, Tp 3 major), 6.19 (t, 1H, Tp 2 major), 6.19 (t, 1H, Tp 2 minor), 6.10 (t, 1H, Tp 1 minor), 6.10 (t, 1H, Tp 1 major), 4.96 (d (J = 3.8, 1H, C^5H major), 4.51 (d, 1H, C^5H minor), 3.87 (m, 2H, C^2H + C^3H *syn* major), 3.37 (m, 1H, C^4H minor), 3.13 (m, 1H, C^3H *anti* major), 2.91 (m, 1H, C^4H major), 2.85 (m, 1H, C^3H *anti* minor), 1.30 (d (J = 6.4), 3H, C^2-Me major), 1.29 (d (J = 6.3), 3H, C^2-Me minor). ^{13}C NMR (acetone-d_6, δ): two diastereomers observed (not distinguished): Tp/Im(24 peaks): 145.2, 144.6, 143.6, 143.5 (2 overlapped), 141.1 (2 overlapped), 140.2, 136.1 (2 overlapped), 135.6 (2 overlapped), 134.8 (2 overlapped), 131.6 (2 overlapped), 124.0, 122.3, 122.0 (2 overlapped), 106.4 (2 overlapped), 106.3 (2 overlapped); C^2,C^3,C^4,C^5(8 peaks): 69.04, 63.53, 63.17, 62.50, 60.30, 48.16(2 overlapped), 43.48; Im-Me: 34.28 (2 overlapped); C^2-Me: 18.77 (2 overlapped). IR: ν_{CO} = 1790 cm^{-1}. CV: $E_{p,a}$ = 0.74 V.

TpRe(CO)(1-methylimidazole)(4,5-η^2-2,5-dimethyl-2,3-dihydro-1*H*-pyrrole) [30]. Pyridinium triflate (20.2 mg, 0.0882 mmol) was added to **9** (51.2 mg, 0.0847 mmol) dissolved in DME (400 mg) to generate product **15** in situ. After 10 min a solution of $NaBH_4$ (3.4 mg, 0.0899 mmol) in methanol (150 mg) was added to the reaction and stirred for 5 min. The reaction was then added to stirring hexanes, and the resulting precipitate was filtered and dried in vacuo. Yield of light brown powder: 40.0 mg (0.0656 mmol, 78%). ^1H NMR (acetone-d_6, δ, Hz): 8.33 (d, 1H, Tp^2), 7.93 (d, 1H, Tp^3), 7.85 (d, 1H, Tp^2), 7.85 (br s, 1H, Im), 7.78 (d, 1H, Tp^3), 7.77 (d, 1H, Tp^1), 7.36 (d, 1H, Tp^1), 7.13 (br t, 1H, Im), 6.71 (br t, 1H, Im), 6.37 (t, 1H, Tp^3), 6.32 (t, 1H, Tp^2), 6.13 (t, 1H, Tp^1), 4.7 (br q, 1H, BH), 4.41 (ddq (J = 6.4, 10.7, 8.3), 1H, C^2H), 3.84 (s, 3H, Im-CH_3), 3.38 (ddd (J = 12.8, 6.9, 8.3), 1H, C^3H_2(*anti*)), 3.15 (dd (J = 6.9, 2.4), 1H, C^4H), 3.03 (ddd (J = 10.7, 2.4, 12.8), 1H, C^3H_2-(*syn*)) 1.46 (d, 6.4, 3H, C^2-CH_3), 1.12 (s, 3H, C^5-CH_3). IR: ν_{CO} = 1783 cm−1. CV: $E_{1/2}$ = +0.72 V, +1.02 V. MS: APCI(+) 608 (weak, MH^+).

TpRe(CO)(1-methylimidazole)(4,5-η^2-1,2-dimethyl-2,3-dihydro-1*H*-pyrrole) [31]. Some **8** (38.7 mg, 0.0655 mmol) was treated with a solution of methyl triflate (11.5 mg, 0.070 mmol) in DME (350 mg) to generate product **24** in situ. After 30 min a solution of $NaBH_4$ (2.5 mg, 0.0662 mmol) in methanol (150 mg) was added and the mixture stirred for 5 min. The solution was then added to stirring hexanes, and the resulting precipitate was filtered and dried in vacuo. Yield of light brown powder: 27 mg (0.045 mmol, 69% yield). ^1H NMR (acetone-d_6, δ, Hz): two diastereomers observed in a ratio of 10:1 (minor not characterized): 8.06 (d, 1H, Tp), 7.80 (d, 2H, Tp+Im), 7.73 (d, 1H, Tp^1), 7.69 (d, 1H, Tp^2), 7.35 (d, 1H, Tp^3), 7.25 (d, 1H, Tp), 6.99 (t, 1H, Im), 6.48 (br, 1H, Im), 6.23 (t, 1H, Tp^3), 6.18 (t, 1H, Tp^2), 6.10 (t, 1H, Tp^1), 4.40 (d (J = 6.6), 1H, C^5H), 3.81 (s, 3H, Im-Me), 3.32 (m, 2H, C^3H_2), 3.15 (m, 1H, C^2H), 2.57 (m, 1H, C^4H), 2.15 (s, 3H, N-Me). ^{13}C NMR (acetone-d_6, δ): Tp/Im (12 peaks): 144.7, 143.9, 141.3, 140.2, 136.0, 135.5, 134.8, 131.5, 121.4, 106.5, 106.3, 106.1; 98.09 (C^5), 72.36 (C^2), 48.10, 45.03, 44.53(C^3, C^4, N-Me), 34.21 (Im-Me), 18.18 (C^2-Me). IR: ν_{CO} = 1813 cm^{-1}. CV: $E_{p,a}$ = +0.70 V.

TpW(NO)(PMe_3)(4,5-η^2-2,5-dimethyl-2,3-dihydro-1*H*-pyrrole) [32]. To a solution of product **18** (57.8 mg, 0.0773 mmol) dissolved in DME (0.8 g) was added a solution of $NaBH_4$ (4.2 mg, 0.11 mmol) dissolved in MeOH (110 mg). After 50 min, the reaction solution was added to stirring pentane, precipitating a white solid. The precipitate was collected via filtration and dried in vacuo. Yield of pale yellow solid: 40.2 mg (0.0670 mmol, 87% yield). ^1H NMR (acetone-d_6, δ, Hz): 8.24 (1H, d (J = 1.2), Tp), 8.07 (1H, d (J = 1.5), Tp), 7.93 (1H, d (J = 1.8), Tp), 7.87 (1H, d (J = 1.8), Tp), 7.81 (1H, d (J = 2.1), Tp), 7.60 (1H, d (J = 1.5), Tp), 6.39 (1H, t (J = 2.1), Tp), 6.33 (1H, t (J = 2.1), Tp), 6.27 (1H, t (J = 2.1), Tp), 3.70 (1H, m, C^2H), 3.20 (1H, m, C^3H_2), 2.73 (1H, m, C^4H), 2.56 (1H, t (J = 7.0), C^3H_2), 1.30 (9H, d (J = 5.4), PMe_3), 1.17 (3H, d (J = 6.0), C^2-Me), 1.10 (3H, s, C^5-Me). ^{13}C NMR (acetone-d_6, δ, Hz): 145.3 (s, Tp), 144.6 (d (J = 9.8), Tp), 142.9 (s, Tp), 137.5 (s, Tp), 136.9 (s, Tp), 136.3 (s, Tp), 107.3 (s, Tp), 106.8 (s, 2 Tp's), 66.2 (s, C^5), 63.4 (d (J = 13.5), C^4), 62.4 (s, C^2), 46.2 (d (J = 3.8), C^3), 26.0 (d (J = 3.0), C^5-Me), 16.9 (s, C^2-Me), 14.5 (d (J = 27.8), PMe_3).

TpRe(CO)(1-methylimidazole)(3,4-η^2-1-methyl-2,5-dihydro-1*H*-pyrrole) [33]. Product **19** (40.0 mg, 0.0502 mmol) was dissolved in DME (300 mg), and $NaBH_4$ (2.2 mg, 0.0582

mmol) was dissolved in methanol (100 mg). After the above solutions were mixed the reaction was stirred for 5 min and then added to stirring hexanes. The resulting precipitate was filtered and dried in vacuo. Yield of orange-brown powder: 35.8 mg (0.0604 mmol, 112% (contaminated with triflate salt)). ^{1}H NMR (acetone-d_6, δ, Hz): 8.04 (d (J = 2.0), 1H, Tp^2), 7.88 (d (J = 2.2), 1H, Tp^3), 7.75 (d (J = 2.1), 1H, Tp^1), 7.74 (d (J = 2.3), 1H, Tp^2), 7.72 (s, 1H, Im), 7.59 (d (J = 1.9), 1H, Tp^3), 7.32 (d (J = 2.2), 1H, Tp^1), 7.04 (s, 1H, Im), 6.60 (s, 1H, Im), 6.32 (dd (J = 1.9, 2.2), 1H, Tp^3), 6.20 (dd (J = 2.0, 2.3), 1H, Tp^2), 6.10 (dd (J = 2.2, 2.1), 1H, Tp^1), 3.95, 4.18 (m, 4H, C^2-CH$_2$+C^{5}CH$_2$), 3.80 (s, 3H, Im-Me), 3.16 (d (J = 6.0), 1H, C^{3}H), 2.69 (br s, 3H, N-Me), 2.59 (d (J = 6.0), 1H, C^{4}H). ^{13}C NMR (acetone-d_6, δ): 144.6 (Tp/Im), 143.2 (Tp/Im), 141.4 (Tp/Im), 139.5 (Tp/Im), 136.0 (Tp/Im), 135.6 (Tp/Im), 134.8 (Tp/Im), 131.6 (Tp/Im), 128.9 (Tp/Im), 122.1 (Tp/Im), 106.3 (Tp), 106.2 (Tp), 106.1 (Tp), 65.6, 64.9, 63.2, 60.2, 41.8 (C^2,C^3,C^4,C^5,N-Me), 34.3 (Im-Me). IR: ν_{CO} = 1788 cm^{-1}. CV: $E_{p,a}$ = +1.22 V. MS: APCI(+) 594 (MH$^+$).

TpRe(CO)(1-methylimidazole)(3,4-η^2-2-methyl-2,5-dihydro-1*H*-pyrrole) [34]. A slurry of **20** (32.0 mg, 0.432 mmol) was prepared in DME (260 mg) and added to a solution of $NaBH_4$ (1.8 mg, 0.0476 mmol) in MeOH (ca. 75 mg). Additional DME (180 mg) was used to rinse the slurry into the other solution. A color change from reddish brown to greenish brown was observed. Additional MeOH (ca. 75 mg) was used to get everything into solution. After ca. 20 min of stirring, the solution was added to stirring hexanes (70 mL), giving a pale green-gray precipitate, which was filtered, washed with hexanes, and dried in vacuo. Yield of green-gray powder: 27.2 mg (0.0459 mmol, 106.2%) (sodium salt impurity probably present). Two diastereomers in 3:1 ratio; major diastereomer has a C^{2}CH$_3$ group up toward imidazole. ^{1}H NMR (acetone-d_6, δ, Hz): major: 4.2 (dq (J = 6.6, 3.9), 1H, C^{2}H), 3.85 (dd (J = 12.5, 2.7), 1H, C^{5}H$_2$(anti)), 3.53 (d (J = 12.5), 1H, C^{5}H$_2$(syn)), 3.22 (dd (J = 6.3, 3.9), 1H, C^{3}H), 2.48 (dd (J = 6.3, 2.7), 1H, C^{4}H), 0.90 (d (J = 6.6), 3H, C^{2}CH$_3$), 3.79 (s, 1H, Im-CH$_3$), 8.05 (br, 1H, Tp/Im), 7.91 (br, 1H, Tp/Im), 7.88 (br, 1H, Tp/Im), 7.86 (br, 1H, Tp/Im), 7.77 (br, 1H, Tp/Im), 7.72 (br, 1H, Tp/Im), 7.71 (br, 2H, Tp/Im), 7.03 (br, 1H, Tp/Im), 6.35 (m, 1H, Tp), 6.16 (m, 1H, Tp), 6.10 (m, 1H, Tp); minor: 4.2 (m, 1H, C^{2}H), 3.8 (m, 1H, C^{5}H$_2$), 3.0 (m, 1H, C^{5}H$_2$), 2.3 (m, 1H, C^{3}H), 3.3 (m, 1H, C^{4}H), 1.56 (d (J = 6.9), 3H, C^{2}CH$_3$), 3.82 (s, 3H, Im-CH$_3$), 8.12 (br, 1H, Tp/Im), 7.84 (br, 1H, Tp/Im), 7.74 (br, 1H, Tp/Im), 7.67 (br, 1H, Tp/Im), 7.12 (br, 1H, Tp/Im), 6.99 (br, 1H, Tp/Im), 6.54 (br, 1H, Tp/Im), 6.39 (br, 1H, Tp), 6.22 (br, 1H, Tp), 6.13 (br, 1H, Tp) (2 Tp/Im not seen).

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Supporting Information Available: Crystallographic details for compound **9a**, **24a**, and **26a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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