Dihapto Coordination of Aromatic Molecules by the Asymmetric π-Bases {TpRe(CO)(L)} (Tp = hydridotris(pyrazolyl)borate; L = ^{t}BuNC, PMe_3, pyridine, 1-methylimidazole, or NH_3)

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A variety of rhenium asymmetric π-basic dearomatization agents of the general formula TpRe(CO)(L)(L_π) (Tp = hydridotris(pyrazolyl)borate; L = ^{t}BuNC, pyridine, PMe_3, 1-methylimidazole, or NH_3; L_π = dihapto-coordinated ligand) have been synthesized via three different routes. By varying the ligand, L, the steric and electronic properties of these complexes can be tuned, and thus the stability and selectivity of the η^2-aromatic systems can be adjusted. Comparisons among the various rhenium complexes are presented as well as comparisons to the established pentaammineosmium(II) system.

Introduction

The pentaammineosmium(II) system has been shown to coordinate a variety of aromatic molecules including benzenes, naphthalenes, pyrroles, furans, and thiophenes in a dihapto fashion.[1] This electron-rich fragment has demonstrated a unique ability to facilitate otherwise inaccessible transformations on the coordinated organic ligand by disrupting the π system of the bound aromatic molecule. Activation of arenes and aromatic heterocycles toward electrophilic additions by the osmium system demonstrates complementary reactivity to the more prevalent η^6-coordinated complexes of aromatic ligands (e.g., $Cr(CO)_3(\eta^6$-aromatic)).[2−7] Despite the utility of the $\{Os(NH_3)_5\}^{2+}$ fragment, the osmium system has several limitations including expense, toxicity, and the achiral nature of the metal center. To address these shortcomings, the development of an asymmetric, isoelectronic rhenium(I) analogue of the $\{Os(NH_3)_5\}^{2+}$ fragment was initiated.

There are a few examples of complexes containing η^2-coordinated aromatic ligands with a variety of metal fragments (e.g., $\{Ni^0(PR_3)_2\}$,[8] $\{Ta^{III}(OSi(^tBu)_3)\}$, $\{Nb^{III}(OSi(^tBu)_3)\}$,[9] $\{Cp^*Rh^I(PMe_3)\}$,[10] and $\{Cp^*Ru^0(NO)\}$[11] (Cp* = pentamethylcyclopentadienyl). Rhenium provides the majority of reported dihapto-coordinated complexes (e.g., $\{CpRe^I(CO)(NO)\}^+$,[12,13] $\{CpRe^I(CO)_2\}$, $\{Cp^*Re^I(CO)_2\}$,[14] and $\{CpRe^I(NO)(PPh_3)\}^+$[15]) (Cp = cyclopentadienyl) apart from the pentaammineosmium(II) fragment. Nevertheless, the preceding examples are not suitable for a dearomatization methodology due to their relative thermal instability, the limited range of aromatic ligands that coordinate to each metal fragment, and the presence of potential alternate sites for electrophilic attack (e.g., the metal itself or Cp rings).[16]

Focusing on the development of a d^6 octahedral rhenium system as the target core, the pursuit of a viable ligand set was undertaken. Rhenium is more electropositive than osmium; thus the addition of a single π-acid (e.g., CO) to the ligand set was found to be essential for creating a similar electronic environment.[17] Lack of a strong π-acid or the presence of more than one[18] has proved detrimental, the metal being too electron-rich or electron-deficient, respectively.

To ensure the designated dihapto-coordination site was positioned *cis* to the π-acidic CO, a facial tridentate ligand was employed. Hydridotris(pyrazolyl)borate (Tp) was chosen to replace the Cp ligand ubiquitous in dihapto-coordinating rhenium fragments. Although both ligands are facially coordinating anionic six-electron donors, Tp was predicted to add more stability to the

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octahedral framework by deterring electrophilic additions to the metal as a result of its larger cone angle.[19]

Initial efforts based on these two parameters led to the coordination of naphthalene (**13**), furan (**14**), and thiophene (**15**) by the {TpRe(CO)(PMe_3)} fragment.[20,21] Significantly, the synthetic approach to the {TpRe(CO)(PMe_3)} system is quite tunable, and a variety of auxiliary ligands (L) can be utilized in lieu of trimethylphosphine. This versatility, an advantage absent for the osmium system,[22] allows for fine adjustments to be made of the steric and electronic properties of the metal complexes. Herein, the synthesis of η^2-coordinated complexes of aromatic ligands by the analogous fragments {TpRe(CO)(L)} (L = ^{t}BuNC, pyridine (py), 1-methylimidazole (MeIm), or NH_3) is reported.

Results and Discussion

The Re(V) oxo complex TpRe(O)$(Cl)_2$ provides a useful synthetic route to the Re(III) precursor TpRe(PMe_3)$(Cl)_2$ via the isolable phosphine oxide complex TpRe(O=PMe_3)$(Cl)_2$.[21] A similar procedure is also applicable for the analogous ^{t}BuNC, py, MeIm, and NH_3 systems. A few minor modifications to this basic methodology allow for higher yields, easier preparation, and the use of less expensive materials. The bromide analogue of the oxo complex, TpRe(O)$(Br)_2$ (**1**), was prepared from aqueous perrhenic acid solution, KTp, and HBr in EtOH, thus affording a complex that was expected to allow for more facile halide removal in subsequent steps. The triethylphospine oxide complex TpRe(O=PEt_3)$(Br)_2$ (**2**) was also employed for the preparations of the ^{t}BuNC and NH_3 systems TpRe(^{t}BuNC)$(Br)_2$ (**3**) and TpRe(NH_3)$(Br)_2$ (**7**) due to the relative cost of triethylphosphine and trimethylphosphine (Scheme 1). Furthermore, the Re(III) pyridine complex TpRe(py)$(Br)_2$ (**5**) was prepared (as previously described for the dichloro analogue)[23] directly from the oxo complex TpRe(O)$(Br)_2$ (**1**) in one pot utilizing PPh_3. TpRe(MeIm)$(Br)_2$ (**6**) was made with slight modifications to the analogous py preparation. Subsequent attempts to produce the ^{t}BuNC complex **3** and NH_3 complex **7** by a similar one-pot procedure failed to give clean products. All the rhenium(III) complexes prepared herein are paramagnetic, but show reasonably sharp ^{1}H NMR spectra with well-defined pyrazole coupling constants (~2 Hz). The synthesis of a variety of Re(III) precursors allows for the tuning of the electronic and steric properties of the metal system. These differences manifest themselves in the stability and selectivity of dihapto-coordinated aromatic complexes of Re(I). The electronic properties of each compound can be probed by cyclic voltammetry (Table 1). The synthesis of Re(I) alkene complexes is important for the establishment of a benchmark for comparison with desired η^2-aromatic complexes. Although olefin complexes are common, the stability and ease of formation of these compounds makes them ideal for modeling the spectroscopic and electrochemical characteristics of aromatic systems. Characteristic features of cyclohexene complexes with a variety of ligands, L, are shown in Table 2.

Three different methodologies have been developed in our laboratory for the synthesis of η^2-aromatic

Scheme 1. Synthesis of Re(III) Precursors (3, 5, 6, 7)

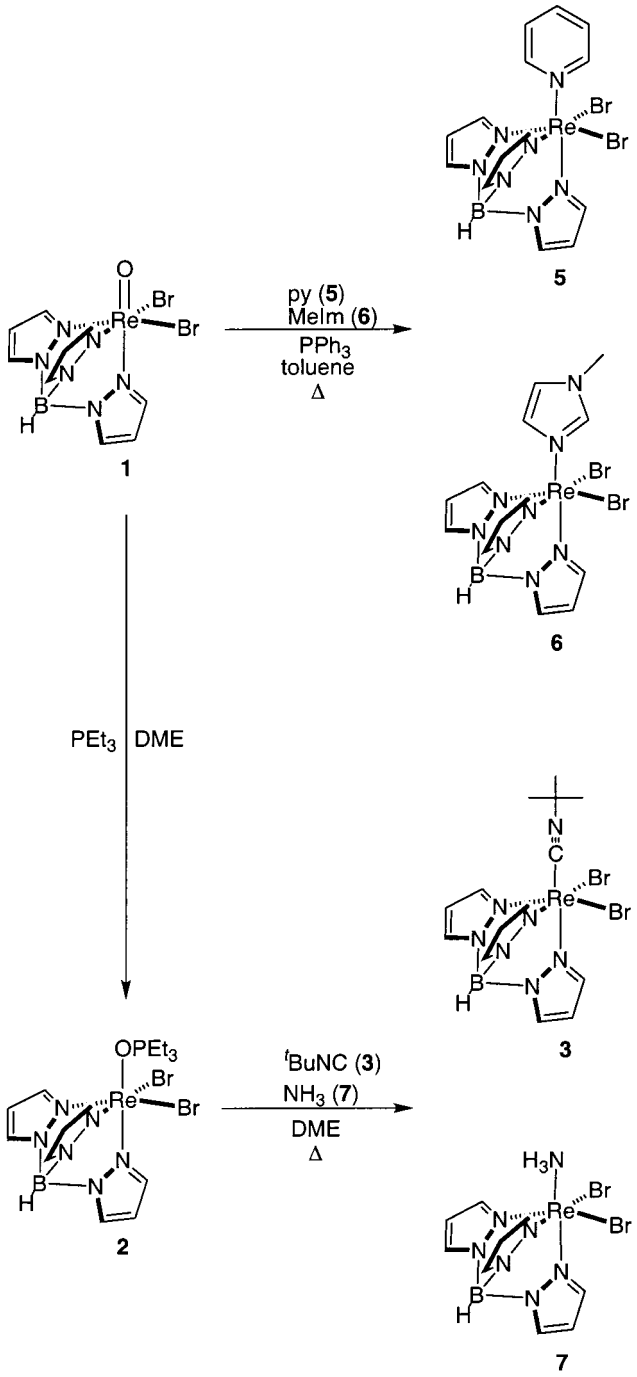

Table 1. Electrochemical Data[a] for TpRe(L)$(Br)_2$ (V)

L	IV/III ($E_{1/2}$)	III/II ($E_{1/2}$)	II/I ($E_{p,a}$)
^{t}BuNC (**3**)	0.92	−0.43	−1.84
PMe_3 (**4**)	0.68	−0.89	−1.83
py (**5**)	0.57	−1.06	<−2.0
MeIm (**6**)	0.42	−1.34	<−2.0
NH_3 (**7**)	0.30	−1.37	<−2.0

[a] 100 mV/s, vs NHE.

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Table 2. ^{13}C NMR, IR, and CV Data[a] for Cyclohexene, Naphthalene, and Furan Complexes

L	L_π	ν_{CO} (cm^{-1})	II/I (V)	^{13}C bound carbons (ppm)
^{t}BuNC (**8**)	cyclohexene	1826	0.45[c]	59.3, 52.8[e]
PMe_3 (**12**)	cyclohexene	1796[b]	0.23[c]	56.0, 48.6[e]
py (**16**)	cyclohexene	1783	0.11[c]	60.7, 56.1[f]
MeIm (**20**)	cyclohexene	1775	−0.05[c]	57.5, 53.8[e]
^{t}BuNC (**9**)	naphthalene	1847	0.47[c]	broad
PMe_3 (**13**)	naphthalene	1825[b]	0.19[c]	57.4, 53.1[f,g]
py (**17**)	naphthalene	1812	0.20[d]	67.2, 62.6[e,g]
MeIm (**21**)	naphthalene	1803	0.02[c]	64.5, 58.6[e,g]
NH_3 (**30**)	naphthalene	1796	0.02[c]	60.7, 57.2[e,g]
^{t}BuNC (**10**)	furan	1846	0.47[d]	broad
PMe_3 (**14**)	furan	1826[b]	0.30[d]	102.5, 48.9[f,h]
py (**18**)	furan	1810	0.16[d]	113.6, 59.5[e,h]
MeIm (**22**)	furan	1798	−0.02[d]	113.9, 56.6[f,h]

[a] 100 mV/s, vs NHE. [b] KBr. [c] $E_{1/2}$. [d] $E_{p,a}$. [e] Acetone-d_6. [f] CD_2Cl_2. [g] Isomer with β ring toward L. [h] Isomer with furan oxygen toward pz.

complexes (classified here according to their respective immediate starting materials). These are tandem oxidation/reduction of TpRe(CO)(L)(L_π) (L_π = dihapto-coordinated ligand), direct reduction of TpRe(L)$(Br)_2$, and direct substitution with TpRe(CO)(L)(L_π) (Scheme 2).

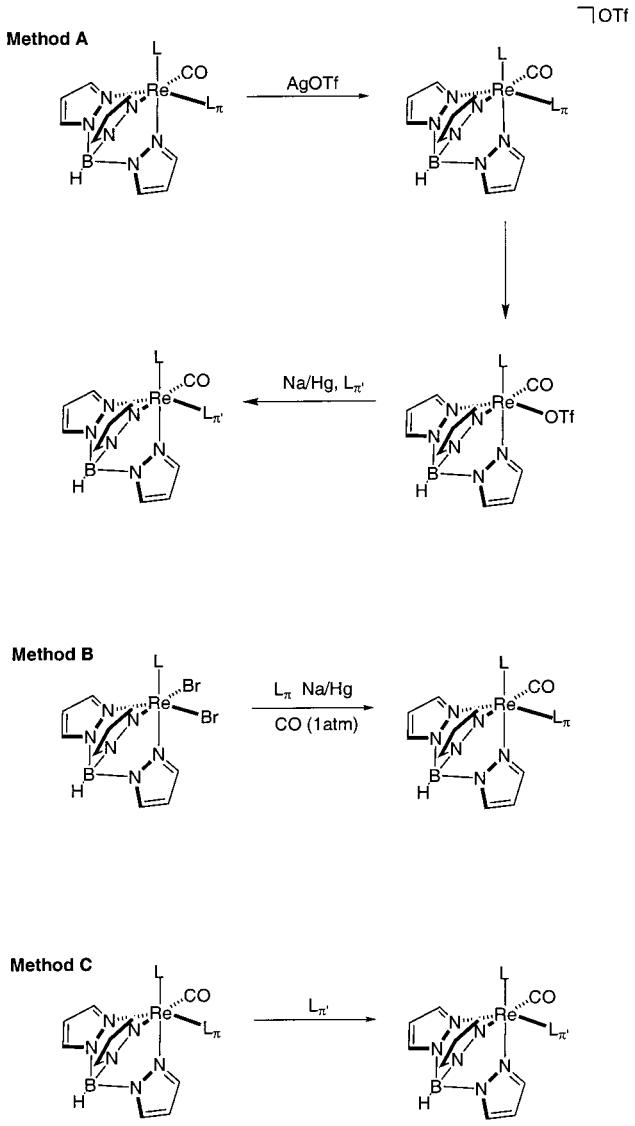
TpRe(CO)(L)(η^2-olefin) complexes were initially utilized in our laboratory for coordinating aromatic molecules in a dihapto fashion to {TpRe(CO)(L)} (L = PMe_3 in earlier work)[20,21] (Scheme 2, method A). For systems of this type, a complexed olefin at Re(I) is not labile, even at elevated (80 °C) temperatures. However, oxidation to Re(II) (e.g., with AgOTf) decreases the electron density at the metal and lessens the back-bonding interaction with the olefin, rendering it significantly more labile. Once the olefin is removed, a triflato complex, TpRe(CO)(L)(OTf), can be formed. Analogous to the $[Os(NH_3)_5(OTf)](OTf)_2$ starting material, this compound can be reduced in the presence of the desired aromatic molecule, resulting in dissociation of the triflato ligand and the generation of the desired η^2-aromatic complex. Yields for these transformations range from 70 to 90%.

Coordination of an aromatic compound directly from the Re(III) stage eliminates the need to isolate a Re(I) precursor (e.g., olefin complexes). This procedure, performed in a manner similar to olefin complexation, allows the Re(III) dihalide to react with Na/Hg and the desired ligand under a CO atmosphere at 20−40 °C (Scheme 2, method B). Isolated yields for these transformations range from 45 to 60%.

Finally, performing a direct substitution at the Re(I) stage is the most straightforward method for binding aromatic ligands. By utilizing a relatively stable complex (i.e., isolable) with a single labile ligand, a substitution can be performed with an aromatic compound present in excess (Scheme 2, method C). Isolated yields for these transformations, which occur quantitatively by NMR, range from 70 to 90%.

Through these three methodologies, a variety of η^2-aromatic compounds were synthesized. Although the ^{t}BuNC and py fragments were found to bind naphthalenes, thiophenes, and furans, these systems failed to form stable complexes with benzenes or pyrroles, as was the case for the PMe_3 system. The more electron-rich MeIm system, however, coordinates a wider variety of aromatic compounds including furans, thiophenes, naphthalenes, benzenes, pyrroles, and 2,6-lutidine. Although the NH_3 system is the most electron-rich of the systems mentioned, to date only the naphthalene complex has been isolated reproducibly.

Scheme 2. Synthesis of Re(I) η^2-Aromatic Complexes



The choice of methodology for the synthesis of aromatic complexes depends on the variable ligand. For the less electron-rich complexes, L = ^{t}BuNC, PMe_3, and py, the tandem oxidation/reduction is employed. Direct reduction of the Re(III) precursor in the presence of CO and excess aromatic ligand yields little or none of the desired complex (<20%). The major compound isolated is TpRe(L)$(CO)_2$, the thermodynamic product. An exception is the complex TpRe(CO)(py)(η^2-naphthalene) (**17**), which can be synthesized in modest yield (45%) from Re(III). Compound **17**, along with the cyclohexene complexes of ^{t}BuNC (**8**) and PMe_3 (**12**), are then employed for the oxidation/reduction sequence.

For MeIm, the other two methodologies are utilized. First, direct reduction of TpRe(MeIm)$(Br)_2$ (**6**) in benzene produces TpRe(CO)(MeIm)(η^2-benzene) (**24**) in moderate yield (50−60%) with trace dicarbonyl formation. The complex **24** is stable at 25 °C under dinitrogen for months with no sign of decomposition. In solution,

the benzene ligand is labile, and therefore **24** is a useful precursor for a variety of other aromatic complexes via a ligand substitution under mild reaction conditions (i.e., no Na/Hg, CO, or heating).[24]

To date, only a few aromatic compounds have been found not to form dihapto complexes with the {TpRe(CO)(MeIm)} fragment. Halogenated benzenes and the parent pyrrole fail to yield isolable η^2-aromatic complexes and are hypothesized to undergo an oxidative addition of C−X or N−H, respectively. Pyridine and 2-picoline can bind η^1 at nitrogen,[25] which leads to formation of an unidentified material whose spectral data are inconsistent with η^1-*N*. Note that dihapto-coordinated 2-methyl- and 2,5-dimethylpyrrole complexes have been synthesized, providing support for a NH bond activation that is sterically hindered in the aforementioned cases. In a similar argument, 2,6-lutidine will bind in a dihapto fashion due to the steric hindrance around the pyridine nitrogen. Finally, *p*-xylene coordination was not observed, presumably due to steric hindrance near the dihapto-coordination site. Efforts to characterize products formed in the unsuccessful dihapto-coordination attempts as well as the control reaction, where no coordinating ligand is present, proved futile. The featureless NMR spectra for these products along with the presence of a relatively low energy ν_{CO} (1830−1810 cm^{-1}) and ν_{BH} suggest the formation of {$TpRe^{II}$(CO)} complexes.

The most diagnostic feature of the TpRe(CO)(L)(L_π) systems is the upfield shifts of the bound carbons and, subsequently, the adjacent protons. Additionally, IR and CV data are useful by providing characteristic ν_{co} and II/I potentials, respectively (Table 2). These compounds range in color from orange to yellow to white. Due to their neutrality, they are soluble in a wide range of solvents from methanol to diethyl ether. They are insoluble in water and, in most cases, hexanes. Almost all of the complexes herein (the 1-methylpyrrole complex being an exception), unlike their osmium counterparts, are stable to silica or alumina chromatographic separation and/or purification.

Perhaps the most intriguing aspect of the rhenium complexes mentioned here is the chiral nature of the systems, a feature that is absent for the pentaammineosmium fragment. Earlier studies have shown the coordinated double bond orients orthogonal to the rhenium−carbonyl bond to optimize back-bonding.[21] With this restriction in place, four orientations are possible. Of these four, however, only two diastereomers are observed by NMR. Studies have indicated the pyrazole (pz) ring *trans* to CO sterically hinders formation of the two species where the bound aromatic ring is oriented away from CO.[26] The selectivity between the remaining two isomers (where the bound aromatic ring is oriented above CO) is dependent on the auxiliary ligand, as it compares sterically to the pz ring *trans* to it. Thus, the choice of L affects not only electronics but selectivity as well.

Almost all of the η^2-aromatic complexes mentioned in this report are present in solution as two diastereomers.[27] In many cases, one of these diastereomers shows broadening in the ^{1}H NMR spectrum. This observation can be explained by one diastereomer having access to a rotamer via 180° rotation about the η^2-metal bond. The rotamer, where the bulk of the aromatic ring is placed adjacent to the pz ring *trans* to the CO, is not energetically favorable due to a steric interaction with this pz ring. However, if the equilibrium between rotamers does not heavily favor one form, broadening due to the weighted averaging of these resonances can occur.[28−30] Interconversion between the diastereomers themselves can also cause broadening for both species depending on the rate and difference in their chemical shifts.

Assignment of the diastereomers stems from NOE data and phosphorus coupling information that have been utilized for the {TpRe(CO)(PMe_3)} system.[21] This study revealed an anisotropic upfield shift for bound carbons (and adjacent protons) oriented toward the pz ring *trans* to the auxiliary ligand. This observation facilitates assignments of diastereomers. For example, the ^{1}H NMR of TpRe(CO)(MeIm)(η^2-furan) (**22**) shows β-bound proton resonances at 4.1 and 3.4 ppm. The most upfield resonance, a result of the anisotropic shift, is assigned to the diastereomer with the oxygen oriented toward the imidazole. Similarly, the α-bound resonances at 7.0 and 6.4 ppm can be assigned accordingly (oxygen oriented toward MeIm, oxygen oriented toward pz, respectively). Note that the $\Delta\delta$'s for the two β-bound and the two α-bound resonances are similar. ^{13}C NMR data follow the same trend.

In a related study, the dynamic processes for interconversion of diastereomers were explored.[27] After NOE and spin-saturation experiments were performed on many complexes, it was determined that the compounds undergo interfacial (face-flip) and/or intrafacial (ring-walk) isomerizations. The rates for these processes were calculated, and on the basis of the results, it was concluded that the more electron-rich systems have slower rates of interconversion with a strong correlation observed between $\Delta G^{\ddagger}$ and ν_{CO} or E(II/I).

The kinetic stability of these systems is also related to the electronic properties of the metal. Under a nitrogen atmosphere, the rate of dissociation of dihapto-coordinated aromatic ligands decreases as the fragment becomes more electron-rich. For example, the MeIm−naphthalene complex (**21**) is more stable than the isonitrile analogue (**9**) (Table 3). Dissociation of L_π in acetone-d_6 was established as the standard for measuring half-life ($t_{1/2}$) under pseudo-first-order kinetics. This process is likely to be predominantly dissociative in character on the basis of the observation of only small changes observed for $t_{1/2}$ in a variety of solvents (Table 4) as well as similar ligand exchange rates for **24**.

The stability of these compounds to air demonstrates a somewhat inverse trend. Whereas η^2-aromatic complexes for the ^{t}BuNC and PMe_3 systems do show some acceleration of decomposition rates, the py and MeIm

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Table 3. Half-Lives of TpRe(CO)(L)(L_π) Complexes in Acetone-d_6

compound	$t_{1/2}$ (h)	T (K)	$\Delta G^\ddagger$ (kcal/mol)
TpRe(CO)(^{t}BuNC)(η^2-naphthalene) (**9**)	12.1	296	23.8
TpRe(CO)(^{t}BuNC)(η^2-furan) (**10**)	42.5	296	24.6
TpRe(CO)(^{t}BuNC)(η^2-thiophene) (**11**)	24.4	296	24.2
TpRe(CO)(PMe_3)(η^2-naphthalene) (**13**)	5.9	296	23.4
TpRe(CO)(PMe_3)(η^2-furan) (**14**)	168	296	25.4
TpRe(CO)(PMe_3)(η^2-thiophene) (**15**)	134	296	25.2
TpRe(CO)(py)(η^2-naphthalene) (**17**)	0.7	373	28.1
TpRe(CO)(py)(η^2-furan) (**18**)	1.9	373	28.8
TpRe(CO)(py)(η^2-thiophene) (**19**)	0.6	373	28.0
TpRe(CO)(MeIm)(η^2-naphthalene) (**21**)	1.3	373	28.5
TpRe(CO)(MeIm)(η^2-furan) (**22**)	2.8	373	29.1
TpRe(CO)(MeIm)(η^2-thiophene) (**23**)	3.2	373	29.2
TpRe(CO)(MeIm)(η^2-benzene) (**24**)	1.6	296	22.6
TpRe(CO)(MeIm)(η^2-anisole) (**25**)	9.0	296	23.6
TpRe(CO)(MeIm)(η^2-*N*-methylpyrrole) (**26**)	4.4	296	23.2
TpRe(CO)(MeIm)(η^2-2,6-lutidine) (**27**)	41.7	296	24.6
TpRe(CO)(MeIm)(η^2-*N*-ethylaniline) (**28**)	1.1	296	22.4
TpRe(CO)(NH_3)(η^2-naphthalene) (**30**)	2.8	373	29.1

Table 4. Half-Life of TpRe(CO)(MeIm)(η^2-benzene) (24) in a Variety of Solvents (296 K)

solvent	$t_{1/2}$ (h)
acetone-d_6	1.6
THF-d_8	1.7
CD_2Cl_2	0.9
CD_3CN	2.6
CD_3OD	0.9

Table 5. Air Stability in Solution of TpRe(CO)(L)(η^2-furan)

L	$t_{1/2}$ nitrogen (h)[a]	T (K)	$t_{1/2}$ air (h)[b]	T (K)
^{t}BuNC (**10**)	42.5	296	1.2	296
PMe_3 (**14**)	168	296	12	296
py (**18**)	1.9	373	0.6	296
MeIm (**22**)	2.8	373	0.2	296

[a] Acetone-d_6. [b] $CDCl_3$ with K_2CO_3 (to eliminate trace acid).

Table 6. Half-Life Comparisons with Pentaammineosmium(II) (CD_3CN Solution)

compound	$t_{1/2}$ (h)	T (K)
TpRe(CO)(^{t}BuNC)(η^2-furan) (**10**)	57.4	295
TpRe(CO)(py)(η^2-furan) (**18**)	1.4	373
TpRe(CO)(MeIm)(η^2-benzene) (**24**)	2.6	295
$\{Os(NH_3)_5(\eta^2\text{-furan})\}^{2+}$ [a]	4.0	373
$\{Os(NH_3)_5(\eta^2\text{-benzene})\}^{2+}$ [a]	5.5	298

[a] Ref 1.

systems decompose rapidly in solution when stirred in air (Table 5). The lower reduction potential of these complexes renders them more susceptible to oxidation. Therefore, the ^{t}BuNC and PMe_3 systems may be handled in air for small amounts of time (e.g., for workup procedures), while the py and MeIm systems are best kept under nitrogen. Importantly, olefin complexes, even of the electron-rich MeIm system, show a much higher degree of stability (days to months) in air.

Although the rhenium systems as a whole are more electron-rich than their osmium counterparts (based on d^6/d^5 couples), they have a somewhat faster rate of dissociation. This property is likely due to the increased steric profile of the ligand set. However, the more electron-rich fragments (e.g., L = MeIm) possess only slightly shorter half-lives (Table 6).

X-ray quality crystals were obtained for a variety of complexes. Select bond distances are listed in Table 7. Crystal data for TpRe(CO)(py)(η^2-naphthalene) (**17**) (Figure 1) and TpRe(CO)(MeIm)(η^2-thiophene) (**23**) (Figure 2) are presented in Table 8. When moving from the ^{t}BuNC to PMe_3 to NH_3 complexes of cyclohexene or cyclopentene (**8**, **12**, **29**, respectively), trends of increasing M−CO and C1−C2 distances and decreasing CO, M−C1, and M−C2 distances are observed, consistent with moving to a more electron-rich metal.

The crystal structure of TpRe(CO)(py)(η^2-naphthalene) (**17**) shows a metal-bound C1−C2 bond length of 1.44 Å, a significant increase from that of free naphthalene (1.37 Å)[31] and the pentaammineosmium(II) analogue (1.40 Å),[32] demonstrating the high degree of donation from the metal to the π^* orbital. Furthermore, the naphthalene C3−C4 bond length shortens to 1.35 Å (Table 9).

Although there are examples of X-ray diffraction studies for η^1, η^4, and η^5 thiophene complexes,[33] to our knowledge there are no reports for a crystal structure of an η^2-thiophene complex.[34−37] The crystal structures of TpRe(CO)(^{t}BuNC)(η^2-thiophene) (**11**) and TpRe(CO)(MeIm)(η^2-thiophene) (**23**) were obtained, and comparisons between the bond lengths of the bound thiophene ring of **23** and free thiophene[33,38] have been made (Table 10). The bound double bond lengthens from 1.370 to 1.433 Å, while the uncoordinated double bond shortens to 1.325 Å. The C−S bond length also increases from 1.714 to 1.797 (bound C) and 1.742 Å (unbound C). These differences demonstrate the significant effect of the electron-rich rhenium fragment on the aromatic system.

Another important facet of these rhenium systems is the absence of binuclear formation. For the osmium system, the coordination of two metals to a bridging aromatic ligand is the "thermodynamic sink" for this type of complex.[1] For the previously reported {TpRe(CO)$_2$} fragment, binuclear products for *N*-methylpyrrole, naphthalene, and furan were reported.[18] However,

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Table 7. Select Bond Lengths for Various Re(I) Compounds (Å)

compound	Re−CO	CO	Re−C1[a]	Re−C2	C1−C2
TpRe(CO)(^{t}BuNC)(η^2-cyclohexene) (**8**)	1.863(7)	1.181(8)	2.234(6)	2.283(6)	1.402(9)
TpRe(CO)(^{t}BuNC)(η^2-thiophene) (**11**)	1.89(1)	1.15(1)	2.23(1)	2.26(1)	(1.48)[b]
TpRe(CO)(PMe_3)(η^2-cyclohexene) (**12**)	1.846(9)	1.177(10)	2.193(8)	2.235(8)	1.42(1)
TpRe(CO)(py)(η^2-naphthalene) (**17**)	1.849(7)	1.179(8)	2.218(7)	2.246(7)	1.438(1)
TpRe(CO)(py)(η^2-furan) (**18**)	1.86(1)	1.16(2)	2.15(1)	2.24(1)	1.45(2)
TpRe(CO)(MeIm)(η^2-thiophene) (**23**)	1.844(2)	1.179(3)	2.174(2)	2.196(2)	1.433(4)
TpRe(CO)(MeIm)(η^2-benzene) (**24**)	1.839(6)	1.181(6)	2.216(5)	2.217(5)	1.442(7)
TpRe(CO)(NH_3)(η^2-cyclopentene) (**29**)	1.82(1)	1.22(1)	2.175(9)	2.148(9)	1.43(1)

[a] C1 toward pz. [b] Thiophene ring disordered

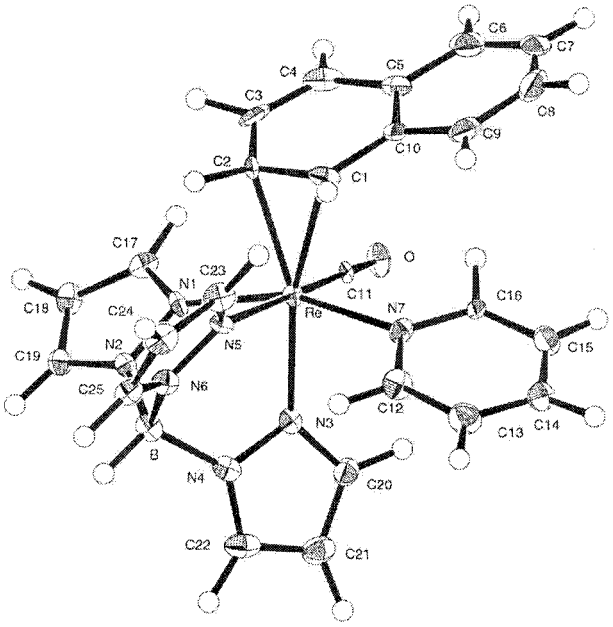

Figure 1. ORTEP diagram of TpRe(CO)(py)(η^2-naphthalene) (**17**; 30% ellipsoids).

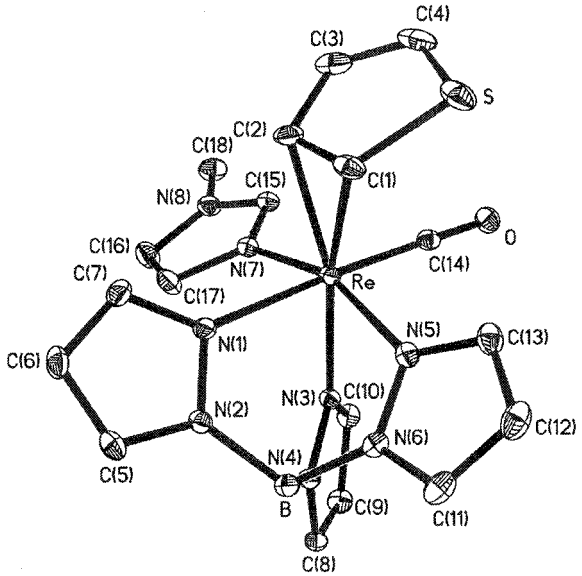

Figure 2. ORTEP diagram of TpRe(CO)(MeIm)(η^2-thiophene) (**23**; 30% ellipsoids).

for the systems mentioned herein, binuclear products have not been observed. The TpRe(CO)(MeIm)(η^2-benzene) complex (**24**), for example, shows no evidence of binuclear formation after stirring in neat benzene for 24 h. This characteristic allows for more flexibility during organic transformations. The basis for this observation is still unknown, as crystal data and modeling

Table 8. Crystal Data for Compounds 17 and 23

	17	**23**
empirical formula	$C_{25}H_{23}BN_7ORe$	$C_{18}H_{20}BN_8OReS$
fw	634.52	593.49
cryst dimens, mm	0.24 × 0.15 × 0.41	0.44 × 0.48 × 0.54
crys syst	monoclinic	monoclinic
space group	*C*2/*c*	$P2_1/n$
a, Å	34.78(1)	12.0167(6)
b, Å	7.875(2)	12.6884(6)
c, Å	20.679(5)	14.4357(7)
β, deg	123.09(1)	109.275(1)
V, Å^3	4745(2)	2077.67(17)
Z	8	4
D_{calcd}, Mg m^{-3}	1.776	1.897
T, K	173(2)	153(2)
goodness-of-fit on F^2	1.12	0.955
no. of reflns	3689	28 081
no. of unique reflns	3617	7518
μ, mm^{-1}	5.158	5.977
final *R* factors	R1 = 0.028, wR2 = 0.036 [$I > 3\sigma(I)$]	R1 = 0.0206, wR2 = 0.0461 [$I > 2\sigma(I)$]

Table 9. Naphthalene Bond Lengths (Å)

bond	naphthalene	Os−naphthalene[a]	Re−naphthalene[b,c]
C1−C2	1.37	1.40(2)	1.44(1)
C2−C3	1.41	1.45(2)	1.43(1)
C3−C4	1.37	1.35(2)	1.35(1)
C5−C6	1.37	1.38(2)	1.38(1)
C6−C7	1.41	1.38(2)	1.37(1)
C7−C8	1.37	1.39(2)	1.38(1)
C8−C9	1.42	1.38(2)	1.40(1)
C9−C10	1.42	1.39(2)	1.42(1)

[a] $[Os(NH_3)_5(\eta^2$-naphthalene)$](OTf)_2$. [b] TpRe(CO)(py)(η^2-naphthalene) (**17**). [c] Numbering adjusted from ORTEP to match conventional naphthalene numbering scheme.

Table 10. Thiophene Bond Lengths (Å)

bond[a]	thiophene	Re−thiophene[b]
S−C1	1.714	1.797(2)
C1−C2	1.370	1.433(4)
C2−C3	1.424	1.482(4)
C3−C4	1.370	1.325(4)
C4−S	1.714	1.742(3)

[a] Atoms numbered as in ORTEP. [b] TpRe(CO)(MeIm)(η^2-thiophene) (**23**).

studies fail to show any steric congestion to hinder binuclear formation. A proposed argument is that the electron-donating power of the rhenium fragment (greater than that of $\{Os(NH_3)_5\}^{2+}$ or $\{TpRe(CO)_2\}$) renders the unbound portion of the aromatic ligand less π-acidic and therefore less likely to bind to another electron-rich metal center. Thus, it is energetically more favorable for a second electron-rich metal fragment to bind a free aromatic (a stronger π-acid) than an aromatic already bound to another metal center (a weaker π-acid).

In conclusion, a new class of η^2-aromatic systems have been synthesized that allows, for the first time, a

systematic adjustment of electronic and steric properties. This versatility of the rhenium systems, made possible by the various ligands, allows the modulation of diastereomeric selectivity, rate of dissociation, and air stability of the η^2-aromatic complexes. Accordingly, these systems have distinct advantages over the pentaammineosmium(II) fragment. They are less expensive, soluble in a wider range of solvents, more conducive to common chromatographic purification techniques, and are chiral. Studies concerning organic transformations on these systems are currently underway.

Experimental Section

General Methods. NMR spectra were obtained on a 300 or 500 MHz Varian INOVA spectrometer. All chemical shifts are reported in ppm and are referenced to tetramethylsilane (TMS) utilizing residual ^{1}H or ^{13}C signals of the deuterated solvents as an internal standard. Coupling constants (*J*) are reported in hertz (Hz). Resonances in the ^{1}H NMR due to pyrazole ligands are listed by chemical shift and multiplicity only (all pyrazole coupling constants are 2 Hz). Infrared spectra (IR) were recorded on a MIDAC Prospect Series (model PRS) spectrometer as a glaze on a Horizontal Attenuated Total Reflectance (HATR) accessory (Pike Industries). Electrochemical experiments were performed under a dinitrogen atmosphere using a PAR model 362 potentiostat driven by a PAR model 175 universal programmer. Cyclic voltammograms (CV) were recorded (Kipp and Zonen BD90 XY recorder) at 100 mV/s (25 °C) in a standard three-electrode cell from +1.8 to −2.0 V with a glassy carbon working electrode, *N*,*N*-dimethylacetamide (DMAc) solvent, and tetrabutylammonium hexafluorophosphate (TBAH) electrolyte (∼0.5 M). All potentials are reported versus NHE (normal hydrogen electrode) using cobaltocenium hexafluorophosphate ($E_{1/2}$ = −0.78 V) or ferrocene ($E_{1/2}$ = 0.55 V) as an internal standard. The peak-to-peak separation was less than 100 mV for all reversible couples. Elemental analysis (EA) was performed with a Perkin-Elmer 2400 Series II CHNS/O analyzer. Satisfactory analysis was not obtained for compounds **26** and **28** (thermal decomposition), **27** (trace Re(II) impurity), and **30** (trace amounts of compound **29**). Unless otherwise noted, all synthetic reactions and electrochemical experiments were performed under a dry nitrogen atmosphere. CH_2Cl_2, benzene, THF (tetrahydrofuran), and hexanes were purged with nitrogen and purified by passage through a column packed with activated alumina.[39] Other solvents were thoroughly degassed with nitrogen prior to use. Deuterated solvents were used as received from Cambridge Isotopes.

Sodium amalgam (1 wt %), a liquid, was prepared by slowly adding small pieces of sodium to mercury under an inert atmosphere. Furan and *N*-methylpyrrole were dried (KOH and CaH_2, respectively) and distilled prior to use. Other reagents were used as received. Compounds **12**−**15** were previously reported.[20]

TpRe(O)(Br)$_2$ (1). A modified preparation of the one reported by Mayer was used.[23] EtOH (100%, 1.5L) was added to a dry 3 L round-bottom flask containing a stir bar. After purging with nitrogen (20 min), KTp (75.0 g, 297 mmol), HBr (48%, 500 mL), and $HReO_4$ (70.1%, 35.3 g, 98.8 mmol) were added sequentially. The mixture was refluxed under nitrogen (1.5 h), yielding a bright blue suspension. After cooling in an ice bath (1 h), the product was filtered (350 mL medium frit). The blue solid was washed with water (6 × 250 mL) and EtOH (3 × 100 mL) and was dried in vacuo to afford 46.8 g (82%) of product. ^{1}H NMR (acetone-d_6, 20 °C, δ): 8.41, 8.29, 7.69, 7.43 (6H, 2:1:2:1, each a d, Tp 3,5), 7.73, 6.05 (3H, 2:1, each a t, Tp 4). CV: $E_{1/2}$ = −0.55 V (quasi-reversible).

TpRe(O=PEt$_3$)(Br)$_2$ (2). To a solution of TpRe(O)(Br)$_2$ (**1**) (5.269 g, 9.15 mmol) in 1,2-dimethoxyethane (DME) (500 mL) was added PEt_3 (3.205 g, 27.1 mmol). The mixture was stirred at room temperature for approximately 2.5 h to give an orange suspension. The volume of the mixture was reduced by two-thirds, and the product was filtered. The orange solid was washed with hexanes (100 mL) and dried in vacuo to give 5.82 g (92%) of the product. ^{1}H NMR (acetone-d_6, δ): 24.63, 20.99, −2.40, −13.32 (6H, 1:1:2:2, each a d, Tp 3,5), 7.90, 4.91 (3H, 2:1, each a t, Tp 4), 0.40 (3H, dt, J = 8, 17, PEt_3 CH_3), −1.27 (2H, dq, J = 8, 13, PEt_3 CH_2). CV: $E_{1/2}$ = 0.23 V, $E_{p,c}$ = −1.80 V.

TpRe(^{t}BuNC)(Br)$_2$ (3). To a solution of TpRe(O=PEt$_3$)(Br)$_2$ (**2**) (2.49 g, 3.59 mmol) in DME (500 mL) was added ^{t}BuNC (0.95 g, 11.5 mmol). The mixture was refluxed (18 h). The dark brown-red solution was reduced in volume by two-thirds, and hexanes (∼200 mL) were added to precipitate the product. The resulting red-brown solid was filtered, rinsed with hexanes (100 mL) and ether (25 mL), and dried in vacuo to afford 2.14 g (93%) of the product. ^{1}H NMR (acetone-d_6, 20 °C, δ): 13.93 (1H, d, Tp 3,5), 12.77 (1H, t, Tp 4), 3.69 (2H, t, Tp 4), −2.12 (1H, d, Tp 3,5), −10.16 (2H, d, Tp 3,5), −15.19 (2H, d, Tp 3,5), 8.21 (9H, s, ^{t}BuNC). CV: $E_{1/2}$ = 0.92 V (IV/III), −0.43 V (III/II), $E_{p,c}$ = −1.84 V (II/I).

TpRe(PMe$_3$)(Br)$_2$ (4). Formation of **4** was performed as earlier reported[20] by substituting **1** for TpRe(O)(Cl)$_2$. Yield: 85%. ^{1}H NMR (acetone-d_6, 20 °C, δ): 11.20, −4.22 (2H, 1:1, each a d, Tp 3,5), −11.01, −15.72 (4H, 1:1, each a d, Tp 3,5), 11.71 (1H, t, Tp 4), 4.70 (2H, t, Tp 4), 2.80 (9H, d, J = 9, PMe_3). CV: $E_{1/2}$ = 0.68 V (IV/III), $E_{1/2}$ = −0.89 V (III/II), $E_{p,a}$ = −1.83 V (II/I). Anal. Calcd for $C_{12}H_{19}N_6BPBr_2Re$: C, 22.69; H, 3.02; N, 13.23. Found: C, 22.81; H, 3.02; N, 12.98.

TpRe(py)(Br)$_2$ (5). Formation of **5** was performed as earlier reported[23] by substituting **1** for TpRe(O)(Cl)$_2$. Yield: 90%. ^{1}H NMR (acetone-d_6, 20 °C, δ): 2.66, −9.84 (2H, 1:1, each a d, Tp 3,5), −10.36, −14.74 (4H, 1:1, each a d, Tp 3,5), 5.12 (1H, t, Tp 4), 10.54 (2H, t, Tp 4), 16.50 (2H, t, J = 7, py 3,5), −4.72 (1H, t, J = 7, py 4), −8.12 (2H, d, J = 7, py 2,6). CV: $E_{1/2}$ = 0.57 V (IV/III), $E_{1/2}$ = −1.06 V (III/II).

TpRe(MeIm)(Br)$_2$ (6). 6 was prepared in a fashion similar to **5**. Toluene (1.0 L) was placed into a dry 2 L round-bottom flask charged with a stir bar and purged with nitrogen (20 min). TpRe(O)(Br)$_2$ (**1**) (10.0 g, 17.4 mmol), 1-methylimidazole (6.9 g, 84 mmol), and triphenylphosphine (6.0 g, 23 mmol) were added, and the mixture was refluxed under nitrogen (4 h). After allowing the reaction to cool (20 °C), the suspension was filtered on a 150 mL frit (coarse porosity). The precipitate was washed with MeOH (2 × 40 mL), toluene (2 × 40 mL), hexanes (2 × 40 mL), and ether (2 × 40 mL). The product was dried overnight in vacuo and isolated as a burgundy red solid, 9.11 g (82%). ^{1}H NMR (acetone-d_6, 20 °C, δ): −5.35, −15.12 (2H, 1:1, each a d, Tp 3,5), −6.89, −16.68 (4H, 1:1, each a d, Tp 3,5), 8.32 (1H, t, Tp 4), 5.95 (2H, t, Tp 4), 7.89, 1.10 (2H, 1:1, each a t, J = 1.5, Im), −19.96 (1H, br t, Im), 10.88 (1H, s, NMe). CV: $E_{1/2}$ = 0.42 V (IV/III), $E_{1/2}$ = −1.34 V (III/II). Anal. Calcd for $ReC_{13}H_{16}N_8BBr_2$: C, 24.35; H, 2.52; N, 17.48. Found: C, 24.35; H, 2.45; N, 17.53.

TpRe(NH$_3$)(Br)$_2$ (7). A solution of TpRe(O=PEt$_3$)(Br)$_2$ (**2**) (2.20 g, 3.17 mmol) in DME (500 mL) was refluxed under a purge of NH_3 (18 h) in a two-neck round-bottom flask. The dark brown solution was reduced in volume by two-thirds, and hexanes (200 mL) were added to precipitate the product. The resulting red-brown solid was filtered, washed with hexanes (100 mL) and ether (50 mL), and dried in vacuo to afford 1.79 g (98%) of the product. ^{1}H NMR (acetone-d_6, 20 °C, δ): 8.19 (1H, t, Tp 4), 6.15 (2H, t, Tp 4), −4.53 (1H, d, Tp 3,5), −6.82 (2H, d, Tp 3,5), −14.83 (1H, d, Tp 3,5), −15.57 (2H, d, Tp 3,5), 130.8 (3H, s, NH_3). CV: $E_{1/2}$ = 0.30 V (IV/III), −1.37 V (III/II).

TpRe(CO)(^{t}BuNC)(η^2-cyclohexene) (8). TpRe(^{t}BuNC)(Br)$_2$ (**3**) (2.13 g. 3.32 mmol) was placed in a two-neck round-bottom flask along with benzene (500 mL), cyclohexene (7.00

(39) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518−1520.

g, 85.2 mmol), and Na/Hg (17.52 g, 7.64 mmol). The mixture was refluxed (~18 h) under a purge of CO and was then filtered through a frit containing Celite. The benzene was removed from the filtrate under reduced pressure. The crude material was chromatographed on silica gel utilizing hexanes followed by 1:1 hexanes/CH_2Cl_2 to elute the pale yellow product. The solvent was removed from the eluate under reduced pressure to give a white foam. This material was dissolved in MeOH (~100 mL). Aqueous NH_4PF_6 solution (0.1 M) was added dropwise with an addition funnel to precipitate the purified product as a white solid. The solid was filtered, washed with water (25 mL), and dried in vacuo to give 1.35 g (63% yield). ^{1}H NMR (acetone-d_6, 20 °C, δ): 8.28, 7.97, 7.83, 7.75, 7.73, 7.56 (6H, 1:1:1:1:1:1, each a d, Tp 3, 5), 6.31, 6.24, 6.19 (3H, 1:1:1, each a t, Tp 4), 3.48 (1H, m, cyclohexene), 3.18 (1H, m, cyclohexene), 2.88 (3H, m, cyclohexene), 2.25 (1H, m, cyclohexene), 1.65 (2H, m, cyclohexene), 1.48 (9H, s, ^{t}BuNC), 1.39 (2H, m, cyclohexene). ^{13}C NMR (acetone-d_6, 20 °C, δ): 201.8 (CO), 165.5 (^{t}BuN*C*), 145.8, 143.4, 140.4, 136.1, 136.0, 135.25 (Tp 3,5), 106.7, 106.4, 106.2 (Tp 4), 59.3 (bound cyclohexene), 57.3 (C, ^{t}BuNC), 52.8 (bound cyclohexene), 32.0 (CH_3, ^{t}BuNC), 31.6 (cyclohexene), 31.2 (cyclohexene), 24.7 (cyclohexene), 23.2 (cyclohexene). IR: ν_{CN} 2095 cm^{-1}, 2055 cm^{-1} (s); ν_{CO} 1826 cm^{-1} (vs). CV: $E_{1/2}$ = 0.45 V (II/I). Anal. Calcd for $C_{21}H_{29}N_7OBRe$: C, 42.57; H, 4.93; N, 16.55. Found: C, 42.71; H, 5.47; N, 16.61.

TpRe(CO)(^{t}BuNC)(η^2-naphthalene) (9). The naphthalene complex was prepared in a manner similar to the furan complex **10** using TpRe(CO)(^{t}BuNC)(η^2-cyclohexene) (**8**) (0.333 g, 0.561 mmol), AgOTf (0.318 g, 1.24 mmol), naphthalene (1.816 g, 14.2 mmol), and Na/Hg (6.998 g, 3.00 mmol). Following chromatography (silica gel, 1:1 hexanes/CH_2Cl_2), the purified product was precipitated from MeOH solution using aqueous NH_4PF_6 solution (0.1 M). The product was filtered, washed with water (25 mL), and dried in vacuo to give 0.188 g (51%) of the yellow product. Assignments were made with naphthalene bound in the 1, 2 positions. Major isomer orients the β ring toward ^{t}BuNC. K_{eq} = 1.2 (0 °C). ^{1}H NMR (acetone-d_6, −60 °C, δ): 8.40, 8.00, 7.96, 7.95, 7.93, 7.92, 7.89, 7.87, 7.85, 7.84 (12H, overlapping d, Tp 3,5), 6.42, 6.33, 6.31, 6.29, 6.21 (1:1:1:2:1, each a t, Tp 4), 7.42 (1H, dd, J = 5, 9 naphthalene 3), 7.35 (4H, m, naphthalene 5,6,7,8), 7.14 (4H, m, naphthalene 5,6,7,8), 6.57 (1H, d, J = 9, major naphthalene 4), 6.48 (1H, d, J = 9 Hz, minor naphthalene 4), 5.19 (1H, d, J = 8, major naphthalene 1), 4.80 (1H, dd, J = 5, 8, minor naphthalene 2), 3.35 (1H, d, J = 8, minor naphthalene 1), 3.08 (1H, dd, J = 5, 8, major naphthalene 2), 1.56 (9H, s, minor ^{t}BuNC), 1.41, (9H, s, major ^{t}BuNC). IR: ν_{CN} 2059 cm^{-1}, 2097 cm^{-1} (s); ν_{CO} 1847 cm^{-1} (vs). CV: $E_{1/2}$ = 0.47 V (II/I) (quasi-reversible). Anal. Calcd for $C_{25}H_{27}N_7OBRe$: C, 47.02; H, 4.26; N, 15.35. Found: C, 47.37; H, 4.47; N, 14.94.

TpRe(CO)(^{t}BuNC)(η^2-furan) (10). To a solution of TpRe(CO)(^{t}BuNC)(η^2-cyclohexene) (**8**) (0.878 g, 1.48 mmol) in DME (25 mL) was added AgOTf (0.812 g, 3.16 mmol). The mixture immediately darkened and Ag(0) precipitated. The mixture was stirred (10 min) and filtered through a fine frit. The golden yellow filtrate was then refluxed (~30 min) to give a dark purple solution. This solution was allowed to cool (20 °C), and furan (2.52 g, 36.9 mmol) and Na/Hg (17.38 g, 7.4 mmol) were added. The mixture was stirred (~1 h) and filtered. The solvent was evaporated from the filtrate under reduced pressure to give an oil. The crude product was then chromatographed on silica gel utilizing hexanes followed by 1:1 hexanes/CH_2Cl_2 to elute the orange-yellow product. The solvent was removed from the eluate under reduced pressure. The purified product was dissolved in MeOH (~25 mL) and precipitated by dropwise addition of an aqueous NH_4PF_6 solution (0.1 M). The resulting solid was filtered, washed with water (35 mL), and dried in vacuo to give 0.547 g (64%) of product. K_{eq} = 2.2 (0 °C). ^{1}H NMR (acetone-d_6, −60 °C, δ) major isomer (oxygen toward pz): 8.45, 7.97, 7.89, 7.88, 7.59 (6H, 1:1:1:2:1), each a d, Tp 3,5), 6.43, 6.28, 6.22 (3H, 1:1:1, each a t, Tp 4), 6.76 (1H, d, J = 2, α-unbound), 6.23 (1H, t, J = 2, β-unbound), 5.96 (1H, d, J = 4, α-bound), 5.15 (1H, dd, J = 2, 4, β-bound), 1.53 (9H, s, ^{t}BuNC); minor isomer (oxygen toward ^{t}BuNC): 8.36, 7.95, 7.93, 7.91, 7.84, 7.38 (6H, 1:1:1:1:1:1, each a d, Tp 3,5), 6.39, 6.15 (3H, 2:1, each a t, Tp 4), 7.80 (1H, d, J = 4, α-bound), 6.72 (1H, d, J = 2, α-unbound), 6.56 (1H, t, J = 2, β-unbound), 3.33 (1H, dd, J = 2, 4, β-bound), 1.51 (9H, s, ^{t}BuNC). IR: ν_{CN} 2094 cm^{-1}, 2047 cm^{-1} (s); ν_{CO} 1846 cm^{-1} (vs). CV: $E_{p,a}$ = 0.47 V. Anal. Calcd for $C_{19}H_{23}N_7O_2BRe$: C, 39.45; H, 4.01; N, 16.95. Found: C, 39.43; H, 4.24; N, 17.40.

TpRe(CO)(^{t}BuNC)(η^2-thiophene) (11). The thiophene complex was prepared in a manner similar to the furan complex **10** using TpRe(CO)(^{t}BuNC)(η^2-cyclohexene) (**8**) (0.935 g, 1.57 mmol), AgOTf (0.815 g, 3.17 mmol), thiophene (3.236 g, 6.83 mmol), and Na/Hg (15.701 g, 5.5 mmol). Following chromatography (silica gel, 1:1 hexanes/CH_2Cl_2), the purified product was precipitated from MeOH solution using aqueous NH_4PF_6 solution (0.1 M). The product was filtered, washed with water (25 mL), and dried in vacuo to give 0.550 g (59%) of the yellow product. K_{eq} = 4.3 (0 °C) for η^2-isomers. ^{1}H NMR (acetone-d_6, −60 °C, δ) major η^2 (sulfur toward pz) and η^1 isomers: 8.63, 8.00, 7.90, 7.83, 7.79, 7.75 (12H, overlapping d, Tp 3,5), 6.42, 6.27, 6.23 (6H, overlapping t, Tp 4), 7.71, 7.25 (2H, 1:1, each a m, α- and β-positions of η^1 isomer), 6.87 (1H, dd, J = 2.5, 5, β-unbound), 6.35 (1H, d, J = 5, α-unbound), 5.22 (1H, dd, J = 2.5, 6, β-bound), 4.95 (1H, d, J = 6, α-bound), 1.53 (9H, s, ^{t}BuNC of η^1 isomer), 1.40 (9H, s, ^{t}BuNC of major η^2 isomer); minor isomer (sulfur toward ^{t}BuNC): 8.38, 7.95, 7.90 (1:3:2, each a d, Tp 3,5), 6.39, 6.23 (2:1, each a t, Tp 4), 7.03 (1H, dd, J = 2.5, 5, β-unbound), 6.98 (1H, d, J = 6, α-unbound), 6.31 (1H, d, J = 5, α-bound), 3.52 (1H, dd, J = 2.5, 6, β-bound), 1.40 (9H, s, ^{t}BuNC). ^{13}C NMR (CD_2Cl_2, −60 °C, δ) major η^2 and η^1 isomers only: 198.1 (CO), 157.99, 156.4 (^{t}BuN*C*), 144.7, 139.4, 139.1, 135.2, 134.7, 130.9 (Tp 3,5), 136.4 (η^1-thiophene α), 131.9 (α-unbound), 129.0 (η^1-thiophene β), 120.9 (β-unbound), 106.1, 105.8, 105.5 (Tp 4), 66.1 (α-bound), 65.6 (β-bound), 56.7 (C, ^{t}BuNC), 31.2 (CH_3, ^{t}BuNC). IR: ν_{CN} 2052 cm^{-1}, 2101 cm^{-1} (s); ν_{CO} 1831 cm^{-1} (vs). CV: $E_{1/2}$ = 0.29 V, $E_{p,a}$ = 0.55 V. Anal. Calcd for $C_{17}H_{23}N_7OSBRe$: C, 38.39; H, 3.90; N, 16.49. Found: C, 38.13; H, 3.93; N, 16.92.

TpRe(CO)(py)(η^2-cyclohexene) (16). 16 was prepared similarly to **18**, and a beige powder was isolated. Yield: 0.32 g (74%), bound at 1,2-position (C1 toward py). ^{1}H NMR (acetone-d_6, 20 °C, δ): 8.07, 7.92, 7.77, 7.77, 7.61, 7.21 (6H, 1:1:1:1:1:1, each a d, Tp 3,5), 6.36, 6.21, 6.08 (3H, 1:1:1, each a t, Tp 4), 8.54 (2H, br s, py 2,6), 7.82 (1H, t, J = 7, py 4), 7.26 (2H, t, J = 7, py 3,5), 2.90, 2.80, 2.68, 2.56, 2.30, 1.82, 1.40 (10H, 1:2:1:1:1:2:2, each a m, cyclohexene). ^{13}C NMR (acetone-d_6, 20 °C, δ): 200.1 (CO), 156.1 (py 2,6), 145.0, 143.1, 139.2, 136.7, 136.4, 136.2, 135.6 (py 4, Tp 3,5), 125.9 (py 3,5) 106.9, 106.8, 106.4 (Tp 4), 60.7 (cyclohexene 1), 56.1 (cyclohexene 2), 31.2, 30.2, 25.3, 24.1 (cyclohexene 3, 4, 5, 6). IR: ν_{CO} 1783 cm^{-1} (vs), ν_{BH} 2479 cm^{-1} (w, br). CV: $E_{1/2}$ = 0.11 V (II/I).

TpRe(CO)(py)(η^2-naphthalene) (17). A 1 L round-bottom flask was charged with a stir bar and TpRe(py)(Br)$_2$ (**5**, 4.01 g, 6.28 mmol). Toluene (0.5 L), naphthalene (20.01 g, 156 mmol), and Na/Hg (150 g, 65 mmol Na) were added. A septum was fitted, the flask was placed in an oil bath (40 °C), and the suspension was purged with CO (10 min). Stirring was commenced and the reaction was allowed to proceed for 20 h under a slow CO purge. The suspension was filtered through a small Celite plug (350 mL coarse frit). The Celite was washed with toluene until the filtrate was practically colorless. The filtrate was then flash chromatographed (silica gel, 350 mL coarse frit). Once toluene was passed through, the product was eluted with CH_2Cl_2. The solution was reduced to an orange oil under reduced pressure. The oil was redissolved in a minimal amount of CH_2Cl_2, and the solution was transferred to a 250 mL round-bottom flask containing a stir bar. Hexanes (~100 mL) were added. The total solvent volume was reduced

by 25%, then hexanes were added to restore the initial volume. The previous step was repeated three times, and the orange precipitate was isolated by filtration (fine frit). The orange powder was washed with cold hexanes (2 × 10 mL) and dried in vacuo. Yield: 1.75 g (46%). Assignments made with naphthalene bound at the 1,2 position. $K_{eq} = 3.0$ (22 °C). ^{1}H NMR (acetone-d_6, 20 °C, δ) major diastereomer (β ring toward py): 8.24, 8.04, 7.86, 7.82, 7.80, 6.85 (6H, 1:1:1:1:1:1, each a d, Tp 3,5), 6.46, 6.30, 6.01 (3H, 1:1:1, each a t, Tp 4), 7.96, 7.8 (2H, 1:1, both br, py 2,6), 7.85 (1H, tt, $J = 1.5, 7.5$, py 4), 7.16 (2H, br t, isochronous py 3,5), 7.38 (1H, dd, $J = 1.5, 6.8$, naphthalene 5), 7.32 (1H, dd, $J = 5.1, 9.0$, naphthalene 3), 7.02 (1H, td, $J = 1.5, 6.8$, naphthalene 6), 6.89 (1H, td, $J = 1.5, 6.8$, naphthalene 7), 6.53 (1H, d, $J = 9.0$, naphthalene 4), 6.09 (1H, dd, $J = 1.5, 6.8$, naphthalene 8), 4.32 (1H, d, $J = 8.1$, naphthalene 1), 3.47 (1H, dd, 5.1, 8.1, naphthalene 2); select minor resonances (β ring toward pz): 6.44, 6.16, 6.02 (3H, 1:1:1, each a t, Tp 4), 6.52 (d, $J = 9.0$, naphthalene 4), 4.05 (br dd, $J = 5, 8$, naphthalene 2), 3.73 (br d, $J = 8$, naphthalene 1). ^{13}C NMR (acetone-d_6, 20 °C, δ): 195.9 (CO), 159.6, 152.9, 145.9, 145.6, 143.5, 140.0, 139.8, 138.4, 137.1, 136.9, 136.7, 136.6, 136.3, 135.8 (Tp 3,5, 2 py 3,5, 2 unbound naphthalene), 144.8, 132.4 (naphthalene 9, 10), 129.4, 127.8, 127.0, 126.6, 126.5, 126.0, 125.2, 124.5, 124.2, 124.1, 121.1, 120.3 (10 naphthalene unbound, 2 py 4), 107.3, 106.9, 106.7, 105.8 (Tp 4), 67.2 (major naphthalene 1), 64.1 (minor naphthalene 2), 62.6 (minor naphthalene 1), 60.6 (major naphthalene 2). IR: ν_{CO} 1812 cm^{-1} (vs), ν_{BH} 2481 cm^{-1} (w). CV: $E_{p,a}$= 0.20 V (II/I). Anal. Calcd for $ReC_{25}H_{23}N_7BO$: C, 47.32; H, 3.65; N, 15.45. Found: C, 47.11; H, 3.90; N, 15.32.

TpRe(CO)(py)(η^2-furan) (18). A solution of **17** (0.50 g, 0.80 mmol) in DME (65 mL) was added to a 100 mL round-bottom flask charged with a stir bar. A DME (10 mL) solution of AgOTf (0.22 g, 0.87 mmol) was added dropwise (~30 s) to the stirring solution, and an immediate darkening was observed. After 15 min, Na/Hg (18 g, 7.8 mmol Na) and furan (5.3 g, 78 mmol) were added and stirring was continued (~1 h). The suspension was filtered, and the filtrate was reduced to an oil. The oil was dissolved in a minimal amount of ether, and the solution was poured down a small silica plug (150 mL coarse frit). The yellow band was reduced to an oil and redissolved in a minimal amount of CH_2Cl_2. After transferring the solution to a 100 mL round-bottom flask containing a stir bar, hexanes were added (~50 mL). The total solvent volume was reduced by 25%, then hexanes were added to restore the initial volume. The previous step was repeated twice, the solvent volume was reduced by 75%, and the suspension was filtered through a fine frit. The orange-yellow solid was dried in vacuo. Yield: 0.28 g (61%). Major isomer orients oxygen toward pz. $K_{eq} = 1.6$ (22 °C). ^{1}H NMR (acetone-d_6, 20 °C): 8.33, 8.16, 7.34, 7.04, 7.01 (5H, 1:1:1:1:1, each a d, Tp 3,5), 8.3 (2H, br, 2 py 2 or 6), 7.26−7.18 (6H, Tp 3,5, py 3,5, minor α-bound), 7.94−7.80 (10H, 6 Tp 3,5, 2 py 2 or 6, 2 py 4), 6.31−6.26 (4H, overlapping t, Tp 4), 6.14−6.12 (2H, overlapping t, Tp 4), 6.72 (1H, d, $J = 2.3$, major α-unbound), 6.63 (1H, d, $J = 4.1$, major α-bound), 6.20 (1H, t, $J = 2.5$, major β-bound), 4.43 (1H, dd, $J = 2.6, 4.1$, major β-bound), 7.25 (1H, buried d, minor α-bound), 6.68 (1H, d, $J = 2.3$, minor α-unbound), 6.34 (1H, t, $J = 2.5$, minor β-unbound), 3.69 (1H, dd, $J = 2.5, 4.1$, minor β-bound). ^{13}C NMR (acetone-d_6, 20 °C, δ): 198.4 (CO), 155.5, 145.5, 145.1, 144.0, 142.4, 141.8, 140.6, 140.4, 136.8, 136.5, 136.4, 136.3, 135.9, 135.9, 135.8, 135.7 (Tp 3,5, 2 furan unbound, 2 py 3,5), 125.6, 125.3 (2 py 4), 115.0, 113.2 (α-bound), 110.0, 109.8 (β-unbound), 107.1, 107.0, 106.9, 106.7 (Tp 4), 59.5 (β-bound major), 58.4 (β-bound minor). IR: ν_{CO} 1810 cm^{-1} (vs), ν_{BH} 2485 cm^{-1} (w). CV: $E_{p,a} = 0.16$ V (II/I). Anal. Calcd for $ReC_{19}H_{19}N_7BO_2$: C, 39.73; H, 3.33; N, 17.07. Found: C, 39.34; H, 3.42; N, 17.19.

TpRe(CO)(py)(η^2-thiophene) (19). 19 was synthesized in the same manner as **18**. An orange-yellow powder was isolated. Yield: 0.33 g (74%). $K_{eq} = 1.2$ (22 °C). ^{1}H NMR (acetone-d_6, 20 °C): 8.56, 8.16, 7.98, 7.85, 7.82, 7.52, 7.45, 7.00, 6.96 (12H, each a d (some overlapping), Tp 3,5), 6.36, 6.28, 6.10 (3H, 1:1:1, each a t, Tp 4), 8.4 (2H, br s, 2 py 2 or 6), 7.88 (1H, br tt, $J = 7.5$, py 4), 7.29 (2H, br t, $J = 7$, py 3,5), 6.95 (1H, dd, $J = 2.8, 5.3$, β-unbound S toward py), 6.20 (1H, dd, $J = 1.3, 5.4$, α-unbound S toward py), 5.18 (1H, dd, $J = 1.0, 6.4$, α-bound S toward py), 4.00 (1H, dd, $J = 2.8, 6.4$, β-bound S toward py), 6.72 (1H, dd, $J = 2.5, 5.1$, β-unbound S toward pz), 6.32 (1H, dd, $J = 1.3, 5.2$, α-unbound S toward pz), 4.54 (1H, dd, $J = <1, 6.6$, α-bound S toward pz), 4.58 (1H, dd, $J = 2.3, 6.8$, β-bound S toward pz). ^{13}C NMR (acetone-d_6, 20 °C, δ): 197.5, 197.2 (CO), 155.8, 154.7, 145.9, 143.7, 141.5, 140.0, 136.9, 136.7, 136.4, 136.2, 135.8 (Tp 3,5, py 3,5), 133.1, 131.2 (α-unbound), 125.9, 125.8 (py 4), 120.6, 118.8 (β-unbound), 107.2, 107.1, 107.1, 106.9, 106.4 (Tp 4), 73.7, 71.5, 71.0, 69.4 (α-bound, β-bound). IR: ν_{CO} 1809 cm^{-1} (vs), ν_{BH} 2484 cm^{-1} (w). CV: $E_{p,a} = 0.11$ V (II/I). Anal. Calcd for $ReC_{19}H_{19}N_7BOS$: C**,** 38.65; H, 3.24; N, 16.06. Found: C, 38.91; H, 3.17; N, 16.19.

TpRe(CO)(MeIm)(η^2-cyclohexene) (20). To a 100 mL round-bottom flask was added **24** (0.10 g, 0.17 mmol) and a stir bar. THF (5 mL) and cyclohexene (0.42 g, 5.0 mmol) were added, and the solution was stirred (16 h, 20 °C). Hexanes (75 mL) were added, 40 mL of solvent was removed in vacuo, and the suspension was filtered on a 30 mL frit (medium porosity). The precipitate was washed with hexanes (2 × 15 mL) and dried in vacuo; 0.081 g (81%) of a light beige powder was isolated, bound at the 1,2 position (C1 toward Im). ^{1}H NMR (acetone-d_6, 20 °C, δ): 8.05, 7.84, 7.69, 7.74, 7.61, 7.37 (6H, 1:1:1:1:1:1, each a d, Tp 3,5), 6.30, 6.18, 6.05 (3H, 1:1:1, each a t, Tp 4), 7.76 (1H, br t, Im), 7.01 (1H, t, $J = 1.5$, Im), 6.72 (1H, t, $J = 1.5$, Im), 3.82 (3H, s, NMe), 2.65 (1H, td, $J = 2, 6$, cyclohexene), 2.78, 2.36, 2.24, 1.80, 1.33 (9H, 3:1:1:2:2, each a m, cyclohexene). ^{13}C NMR (CD_2Cl_2, 20 °C, δ): 200.1 (CO), 144.4, 142.5, 140.6, 138.7, 135.7, 135.6, 134.4 (Im, Tp 3,5), 131.9, 121.0 (Im) 105.9, 105.8 (Tp 4), 57.5 (cyclohexene 1), 53.8 (cyclohexene 2), 31.0, 30.4, 24.8, 24.1 (cyclohexene 3, 4, 5, 6), 34.4 (MeIm). IR: ν_{CO} 1775 cm^{-1} (vs), ν_{BH} 2481 cm^{-1} (w). CV: $E_{1/2} = -0.05$ V (II/I). Anal. Calcd for $ReC_{20}H_{26}N_8BO$: C**,** 40.61; H, 4.44; N, 18.95. Found: C, 40.54; H, 4.43; N, 19.04.

TpRe(CO)(MeIm)(L_π) (21−23, 25−28). To a 100 mL round-bottom flask was added **24** (0.10 g, 0.17 mmol) and a stir bar. THF (5 mL) and L_π (5.0 mmol) were added, and the solution was stirred (16 h, 25 °C). Hexanes (75 mL) were added, 40 mL of solvent was removed under reduced pressure, and the suspension was filtered on a 30 mL medium frit. The precipitate was washed with hexanes (2 × 15 mL) and dried in vacuo. Yields were 75−85% unless otherwise noted.

L_π = naphthalene (21): yellow solid; major isomer reported (β ring toward MeIm). Assignments were made considering naphthalene bound at the 1,2 position. $K_{eq} = 5.0$ (22 °C), >20 (−20 °C). ^{1}H NMR (acetone-d_6, 20 °C, δ): 8.22, 7.97, 7.82, 7.77, 7.52, 7.11 (6H, 1:1:1:1:1:1, each a d, Tp 3,5), 6.41, 6.27, 6.01 (3H, 1:1:1, each a t, Tp 4), 6.93, (1H, buried, Im), 7.09, 6.52 (2H, 1:1, each a t, $J = 1.5$, Im), 7.28 (1H, dd, $J = 8, 2$, naphthalene 5), 7.26 (1H, dd, $J = 8, 5$, naphthalene 3), 6.93 (2H, isochronous td, $J = 2, 8$, naphthalene 6, 7), 6.39 (1H, d, $J = 8$, naphthalene 4), 6.03 (1H, dd, $J = 8, 2$, naphthalene 8), 4.00 (1H, d, $J = 8$, naphthalene 1), 3.15 (1H, dd, $J = 5, 8$, naphthalene 2), 3.79 (3H, s, NMe). ^{13}C NMR (CD_2Cl_2, 20 °C, δ): 195.7 (CO), 144.7, 142.8, 142.2, 139.2, 139,0, 135.9, 135.5, 134.5 (Tp 3,5, naphthalene 3,5), 145.2, 131.6 (naphthalene 9,-10), 125.9, 125.7, 123.6, 123.2, 120.9, 118.9 (Im, naphthalene 4,6,7,8), 130.0 (Im), 106.0 (2 isochronous Tp 4) 105.7 (Tp 4), 64.0 (naphthalene 1), 58.2 (naphthalene 2) 34.5 (NMe). IR: ν_{CO} 1803 cm^{-1} (vs), ν_{BH} 2479 cm^{-1} (w). CV: $E_{1/2}$ (quasi-reversible) = 0.02 V (II/I). Anal. Calcd for $ReC_{24}H_{24}N_8BO$: C, 45.22; H, 3.79; N, 17.58. Found: C, 44.94; H, 3.50; N, 17.58.

L_π = furan (22): beige solid; major isomer orients oxygen toward MeIm. $K_{eq} = 1.4$ (22 °C). ^{1}H NMR (acetone-d_6, 20 °C, δ): 8.30, 8.14, 7.30, 7.17, 7.16, 7.13, 7.79 (7H, 1:1:1:1:1:1:1,

each a d, Tp 3,5) 7.86 (2H, 2 isochronous Tp 3,5), 7.77 (3H, 3 isochronous Tp 3,5), 6.24 (4H, 4 isochronous Tp 4) 6.10 (2H, 2 isochronous Tp 4) 7.66, 7.59 (2H, 1:1, each a br t, Im), 7.07, 7.03 (2H, 1:1, each a t, $J = 1.5$, Im), 6.59, 6.44 (2H, 1:1, each a t, $J = 1.5$, Im), 3.84 (3H, s, NMe, minor), 3.83 (3H, s, NMe, major), 7.02 (1H, d, $J = 4.2$, major α-bound), 6.51 (1H, d, $J = 1.5$, major α-unbound), 6.21 (1H, t, $J = 2.4$, major β-unbound), 3.38 (1H, dd, $J = 2.4, 4.2$, major β-bound), 6.56 (1H, d, $J = 1.8$, minor α-unbound), 6.39 (1H, d, $J = 4.2$, minor α-bound), 6.04 (1H, t, $J = 2.4$, minor β-unbound), 4.10 (1H, br d, $J = 2.4, 4.2$, minor β-bound). ^{13}C NMR (CD_2Cl_2, 20 °C, δ): 198.6 (CO), 144.6, 144.3, 143.6, 143.5, 141.1, 141.0, 140.6, 139.9, 139.7 (Tp 3,5, α-bound), 135.7, 135.5, 135.2, 134.6, 134.5, 132.2, 131.9 (Tp 3,5, Im), 121.2, 120.9 (Im), 114.7, 113.9 (α-bound), 109.6, 108.6 (β-unbound), 106.1 (4 isochronous Tp 4), 105.8, 105.7 (Tp 4), 56.6, 55.8 (β-bound), 34.4 (NMe). IR: ν_{CO} 1798 cm^{-1} (vs), ν_{BH} 2483 cm^{-1} (w). CV: $E_{p,a} = -0.02$ V (II/I). Anal. Calcd for $ReC_{18}H_{20}N_8BO_2$: C, 37.44; H, 3.49; N, 19.41. Found: C, 37.70; H, 3.38; N, 19.03.

L_π = thiophene (23): beige solid. $K_{eq} = 1.0$ (22 °C). ^{1}H NMR (acetone-d_6, 20 °C, δ): 8.57, 8.15, 7.90, 7.48, 7.41, 7.14, 7.11, 7.83, 7.79, 7.77 (12H, 1:1:2:1:1:1:1:1:1:2, each a d, Tp 3,5), 6.30, 6.25, 6.07 (6H, 1:1:1, each 2 isochronous t, Tp 4), 7.74, 7.63 (2H, 1:1, each a br t, Im), 7.09, 7.06, 6.6 (4H, 1:1:2, each a t, $J = 1.5$, Im), 6.83 (1H, dd, $J = 2.5, 5.0$, β-unbound S toward Im), 6.06 (1H, dd partially buried, $J = 1.5$, α-unbound S toward Im), 4.94 (1H, dd, $J = 2.0, 6.5$, α-bound S toward Im), 3.68 (1H, dd, $J = 3.0, 7.0$, β-bound S toward Im), 6.62 (1H, dd, $J = 2.5, 5.0$, β-unbound S toward pz), 6.08 (1H, dd partially buried, $J = 1.5$, α-unbound S toward pz), 4.27 (1H, dd, $J = 2.5, 6.5$, β-bound S toward pz), 4.21 (1H, dd, $J = 1.0, 6.0$, α-bound S toward pz), 3.86, 3.84 (6H, 1:1, each a s, NMe). ^{13}C NMR (CD_2Cl_2, 20 °C, δ): 197.8, 197.5 (CO), 144.9, 143.2, 143.1, 140.7, 139.6, 139.6, 139.3, 139.3, 135.7, 135.6, 135.4, 134.6, 133.1, 132.1, 130.6 (12 Tp 3,5, 4 Im, 2 α-unbound (3 resonances buried), 121.4, 121.2, 118.5, 117.8 (2 Im, 2 β-unbound), 106.2, 106.0, 106.0, 105.9, 105.8, 105.7 (Tp 4), 71.3, 69.4, 68.7, 67.0 (α, β-bound), 34.5 (2 NMe). IR: ν_{CO} 1804 cm^{-1} (vs), ν_{BH} 2482 cm^{-1} (w). CV: $E_{p,a} = -0.03$ V(II/I), $E_{1/2} = -1.33$ V. Anal. Calcd for $ReC_{18}H_{20}N_8BOS \cdot 0.5\ C_6H_6$ (note: product recrystalized in benzene/hexane for X-ray structure analysis): C, 39.88; H, 3.67; N, 17.71. Found: C, 39.96; H, 3.70; N, 17.52.

L_π = anisole (25): yellow solid. Assignments were made considering bound at the 2,3 position. $K_{eq} = 3.0$ (22 °C). ^{1}H NMR (acetone-d_6, 20 °C, δ) major isomer (oxygen toward MeIm): 8.15, 7.93, 7.81, 7.74, 7.53, 7.12 (6H, 1:1:1:1:1:1, each a d, Tp 3,5), 6.35, 6.22, 6.01 (3H, 1:1:1, each a t, Tp 4), 7.70, 7.00, 6.72 (3H, each a broad t, Im), 3.86 (3H, s, NMe), 3.53 (3H, s, OMe), 6.61 (1H, dd, $J = 5, 8$, anisole 4), 5.96 (1H, dd, $J = 7, 8$, anisole 5), 5.21 (1H, d, $J = 7$, anisole 6), 3.80 (1H, d, $J = 8$, anisole 2), 3.37 (1H, dd, $J = 5, 8$, anisole 3); select minor diastereomer resonances (OMe toward pz): 3.85 (NMe), 3.59 (OMe), 6.27 (anisole 4), 5.89 (anisole 5), 5.26 (anisole 6), 3.98 (anisole 3), 3.28 (anisole 2). ^{13}C NMR (CD_2Cl_2, 20 °C, δ) major isomer: 196.6 (CO), 143.7, 142.9, 141.4, 139.3, 135.8, 135.6, 134.5 (Tp 3,5, Im), 131.5, 128.3, 120.7, 118.3 (anisole 4,5 and Im), 106.3 (Tp 4), 105.8 (2 isochronous Tp), 90.6 (anisole 6), 65.1 (anisole 2), 62.9 (anisole 3), 34.5 (NMe), ~54 (OMe, buried); select minor diastereomer resonances: 67.0 (anisole 3) 61.2 (anisole 2). IR: ν_{CO} 1797 cm^{-1} (vs), ν_{BH} 2474 cm^{-1} (w). CV: $E_{p,a} = -0.15$ V (II/I). Anal. Calcd for $ReC_{21}H_{24}N_8BO_2$: C, 40.85; H, 3.92; N, 18.15. Found: C, 40.75; H, 4.16; N, 17.81.

L_π = *N*-methylpyrrole (26): orange solid. $K_{eq} = 6.0$ (−95 °C). ^{1}H NMR (acetone-d_6, 20 °C, δ): 8.15 (1H, br s, Tp 3,5) 7.82, 7.75, 7.70, 7.32 (4H, 1:1:1:1, each a d, Tp 3,5), 7.68, 7.21, 6.89, 7.07 (4H, 1:1:1:1, each a br s, Tp 3,5 and Im) 6.23, 6.22, 6.03 (3H, 1:1:1, each a t, Tp 4), 3.82 (3H, s, MeIm), 3.12 (3H, br s, Me pyrrole). ^{1}H NMR (acetone-d_6, −95 °C, δ), only *N*-methylpyrrole resonances for major diastereomer are reported: 6.16, 6.15 (2H, 1:1, br s, α- and β-unbound) 5.66 (1H, br s, α-bound) 3.54 (1H, br dd, β-bound) 3.10 (3H, s, Me). ^{13}C NMR (acetone-d_6, −92 °C, δ): 198.6 (CO), 142.5, 142.3, 139.9, 135.9, 135.2, 135.1, 130.4 (Tp 3,5, Im), 121.6, 117.9 (Im), 106.5 (Tp 4), 106.2 (2 isochronous Tp 4), 108.3, 107.9 (α, β-unbound), 87.4 (α-bound), 64.9 (β-bound) 34.0 (MeIm), ~29.8 (buried Me pyrrole). IR: ν_{CO} 1793 cm^{-1} (br, vs), ν_{BH} 2480 cm^{-1} (w). CV: $E_{1/2} = -0.53$ V(II/I) (quasi-reversible).

L_π = 2,6-lutidine (27): greenish-yellow solid. Assignments were made considering bound at the 3,4 position. $K_{eq} = 7.0$ (−20 °C). ^{1}H NMR (acetone-d_6, 20 °C, δ), only one isomer was observed due to broadening of the other diastereomer (nitrogen toward MeIm): 8.17, 7.93, 7.74, 7.72, 7.28 (5H, 1:1:1:1:1, each a br d, Tp 3,5), 7.81 (1H, d, Tp 3,5), 6.36, 6.25 (2H, 1:1, each a br t, Tp 4), 6.02 (1H, t, Tp 4), 7.86, 7.13, 6.89 (3H, 1:1:1, each a broad t, Im), 6.48 (1H, br d, lutidine 5), 3.93 (1H, br d, lutidine 3), 3.23 (1H, br dd, lutidine 4), 3.85 (3H, s, NMe), 2.47 (3H, br s, lutidine 6-Me), 1.63 (3H, br s, lutidine 2-Me). ^{13}C NMR (CD_2Cl_2, 20 °C, δ): 195.7 (CO), 175.2, 140.5 (lutidine 2,6) 143.8, 142.5, 141.7, 139.1, 136.0, 135.6, 134.7 (Tp 3,5, Im), 132.0 (Im), 122.0, 121.6 (Im, lutidine 5), 106.1 (Tp 4), 105.9 (2 isochronous Tp 4), 65.8 (lutidine 3), 64.8 (lutidine 4), 34.6 (NMe), 27.1 (lutidine 2-Me), 22.8 (lutidine 6-Me). IR: ν_{CO} 1799 cm^{-1} (vs), ν_{BH} 2481 cm^{-1} (w). CV: $E_{p,a} = -0.14$ V (II/I).

L_π = *N*-ethylaniline (28): orange solid. Yield: 30%. Assignments were made considering bound at 2,3 position. $K_{eq} = 3.0$ (22 °C). ^{1}H NMR (acetone-d_6, 20 °C, δ) major isomer (nitrogen toward MeIm): 8.24, 7.91, 7.79, 7.72, 7.17 (6H, 1:1:2:1, each a d, Tp 3,5), 6.34, 6.21, 6.01 (3H, 1:1:1, each a t, Tp 4), 7.78 (1H, buried, Im), 7.10 (1H, br s, Im), 6.80 (1H, br s, Im), 6.38 (1H, dd, $J = 9, 6$, aniline 4), 5.96 (1H, dd, $J = 9, 8$, aniline 5), 4.89 (1H, d, $J = 7$, aniline 6), 3.78 (1H, d, $J = 9$, aniline 2), 3.47 (1H, dd, $J = 10, 6$, aniline 3), 2.88 (2H, q, $J = 8$, NEt CH_2), 1.05 (3H, t, $J = 8$, NEt CH_3), 3.86 (3H, s, NMe); select minor resonances: 5.87 (1H, br dd, aniline 5), 4.93 (1H, br d, aniline 6), 4.01 (1H, br, aniline 3), 3.85 (3H, s, NMe). ^{13}C NMR (CD_2Cl_2, 20 °C, δ): 196.8 (CO), 157.0 (aniline 1) 143.4, 142.5, 141.4, 139.1, 135.7, 135.4, 134.4 (Tp 3,5, Im), 131.5 (Im), 123.0, 121.0, 119.9 (aniline 4,5, Im), 105.9, 105.7, 105.6 (Tp 4), 89.6 (aniline 6), 65.3 (aniline 2), 64.4 (aniline 3), 38.1 (NEt CH_2), 14.8 (NEt CH_3), 34.4 (NMe); select minor resonances: 89.3 (aniline 6), 66.5 (aniline 3), 62.6 (aniline 2). IR: ν_{CO} 1793 cm^{-1} (vs), ν_{BH} 2478 (w). CV: $E_{p,a} = -0.32$ V (II/I).

TpRe(CO)(MeIm)(η^2-benzene) (24). Benzene (2.8 L) was placed into a dry 3 L round-bottom flask with an egg-shaped stir bar and purged with nitrogen (20 min) and then CO (20 min). Compound **6** (6.0 g, 9.4 mmol) was added and then Na/Hg (60 g, 26.1 mmol Na). The suspension was purged with CO (20 min) and stirred vigorously under a static CO atmosphere (1 atm, 20 °C, 72 h). After purging the solution with nitrogen (15 min), the mixture was moved into a glovebox and filtered through Celite (350 mL frit, 3 cm plug). The residue on the Celite was washed with benzene until the filtrate lightened in color (~300 mL). The filtrate was passed through silica (350 mL frit, 4 cm plug, pretreated with benzene). Flash chromatography was performed, eluting first with 10% Et_2O in benzene (~1 L) and then 20% Et_2O in benzene (~1.2 L) to recover product (golden yellow solution, ν_{CO} 1795). Fractions containing ν_{CO} 1795 cm^{-1} (~1.2 L) were combined in a 2 L round-bottom flask. A third of the solvent was removed in vacuo, and then hexanes (1 L) were added. The solvent volume was reduced by half, hexanes were added to restore the original volume, and the solvent volume was reduced by half once more. The suspension was filtered on a 150 mL frit (medium porosity). The precipitate was washed with hexanes (3 × 20 mL) and dried overnight in vacuo to yield a yellow powder (3.22 g, 59%). Assignments were made considering benzene bound at the 1,2 position with C2 toward MeIm. ^{1}H NMR (acetone-d_6, 20 °C, δ): 8.10, 7.94, 7.82, 7.76, 7.47, 7.05 (6H, 1:1:1:1:1:1, each a d, Tp 3,5), 6.34, 6.23, 6.01 (3H, 1:1:1, each a t, Tp 4), 7.64, (1H, broad t, Im), 7.09, 6.72 (2H, 1:1, each a t, $J = 1.5$, Im) 3.85 (3H, s, NMe). ^{1}H NMR (acetone-d_6, −60 °C, δ), only benzene resonances reported: 7.08 (1H, dd, J

= 9, 5, benzene 6), 6.75 (1H, dd, J = 9, 5, benzene 3), 6.06 (1H, dd, J = 9, 7, benzene 5), 5.98 (1H, dd, J = 9, 7, benzene 4), 3.87 (1H, dd, J = 9, 5, benzene 2), 3.23 (1H, dd, J = 9, 5, benzene 1). ^{13}C NMR (acetone-d_6, −20 °C, δ): 196.0 (CO), 143.7, 143.1, 141.3, 139.7, 136.4, 136.0, 135.0 (Tp 3, 5, Im), 131.6 (Im), 122.3 (Im), 106.7, 106.5, 106.3 (Tp 4), 138.4, 137.1, 129.2, 118.2 (benzene 3,4,5,6), 66.9 (benzene 2), 64.9 (benzene 1), 34.3 (NMe). IR: ν_{CO} 1794 cm^{-1} (vs), ν_{BH} 2480 cm^{-1} (w). CV: $E_{p,a}$ = −0.16 V (II/I). Anal. Calcd for $ReC_{20}H_{22}N_8BO\cdot 0.75$ mol C_6H_6 (benzene amount observed in NMR; also, shown by X-ray to crystallize with benzene): C, 45.55; H, 4.13; N, 17.34. Found: C, 45.45; H, 4.24; N, 17.13.

TpRe(CO)(NH$_3$)(η^2-cyclopentene) (29). $TpRe(NH_3)(Br)_2$ (**7**) (2.14 g, 3.72 mmol) was placed in a two-neck round-bottom flask along with benzene (500 mL), cyclopentene (6.50 g, 95.4 mmol), and Na/Hg (41.67 g, 18.1 mmol). The mixture was stirred at 20 °C under a purge of CO (18 h) and was filtered through a frit containing Celite. The benzene was removed from the filtrate under reduced pressure. The crude material was chromatographed on silica gel utilizing CH_2Cl_2 followed by 1:1 ether/CH_2Cl_2 to elute the light brown product. The solvent was removed from the eluate under reduced pressure to give a beige residue. The material was dissolved in MeOH (100 mL). Aqueous NH_4PF_6 solution (0.1 M) was added dropwise with an addition funnel to precipitate the purified product as a beige solid. The solid was filtered, washed with water (25 mL), and dried in vacuo to give 0.701 g (37% yield). ^{1}H NMR (acetone-d_6, δ): 8.00, 7.78, 7.71, 7.67 (each 1H or 2H, each a d, Tp 3,5), 6.23, 6.22, 6.16 (each 1H, each a t, Tp 4), 3.32 (1H, m, cyclopentene), 3.24 (3H, br s, NH3), 3.12 (1H, m, cyclopentene), 2.62 (2H, m, cyclopentene), 2.46 (2H, m, cyclopentene), 2.25 (1H, m, cyclopentene), 1.45 (1H, m, cyclopentene) ^{13}C NMR (acetone-d_6, δ): 199.6 (CO), 144.4, 144.1, 139.6, 135.9, 135.7, 135.2 (Tp 3,5), 106.9, 106.1, 105.8 (Tp 4) 63.5 (CH, bound cyclopentene), 62.11 (CH, bound cyclopentene), 36.0, 35.8, 23.8 (each a CH_2, cyclopentene methylenes). IR: ν_{CO} 1776 cm^{-1} (vs). CV: $E_{1/2}$ = 0.00 V (II/I). Anal. Calcd for $C_{15}H_{21}N_7OBRe$: C, 35.10; H, 4.13; N, 19.13. Found: C, 35.48; H, 3.84; N, 18.76.

TpRe(CO)(NH$_3$)(η^2-naphthalene) (30). To a solution of **29** (0.33 g, 0.64 mmol) in DME (25 mL) was added AgOTf (0.32 g, 1.24 mmol). The mixture was filtered, and the resulting filtrate was refluxed (∼2 h) to give the Re(II) triflato complex. Upon cooling, naphthalene (1.82 g, 14.2 mmol) and Na/Hg (7.00 g, 3.00 mmol) were added, and the mixture was stirred (1 h). The mixture was filtered, and the residue was chromatographed on silica gel using CH_2Cl_2 followed by 1:1 CH_2Cl_2/ether. The resulting beige band was collected, and the solvent was removed under reduced pressure. The purified product was precipitated from MeOH solution using aqueous NH_4PF_6 solution (0.1 M). The product was filtered, washed with water (25 mL), and dried in vacuo to give 0.188 g (51%) of the yellow product. K_{eq} = 4.0 (22 °C). ^{1}H NMR (acetone-d_6, 22 °C, δ), only one isomer was observed due to broadening of one diastereomer (β ring toward NH_3): 8.00, 7.78, 7.71, 7.67 (each 1H or 2H, each a d, Tp 3,5), 6.30, 6.25, 6.23 (each 1H, each a t, Tp 4), 7.42 (1H, dd, J = 5, 9, naphthalene 3), 7.29 (2H, overlapping dd, naphthalene 3 and 5), 7.13, 6.97 (each 1H, td, J = 1, 8, naphthalene 6 and 7), 6.97 (1H, dd, naphthalene 8), 6.39 (1H, d, J = 9, naphthalene 4), 4.15 (1H, d, J = 8, naphthalene 1), 3.09 (1H, dd, J = 5, 8, naphthalene 2), 3.40 (3H, br s, NH_3). ^{13}C NMR (acetone-d_6, −60 °C, δ), two isomers were observed in the carbon spectrum with a ratio of approximately 4:1; major isomer (β ring toward NH_3): 194.5 (CO), 145.1, 144.6, 139.8, 139.6, 136.4, 136.1 (Tp 3,5), 107.0, 106.4, 106.3 (Tp 4), 137.7, 128.5 (naphthalene 9, 10), 135.6, 127.0, 125.3, 124.7, 123.7, 119.1 (naphthalene 3, 4, 5, 6, 7, 8), 60.7 (naphthalene 1), 57.2 (naphthalene 2). IR: ν_{CO} 1796 cm^{-1} (vs). CV: $E_{1/2}$ = 0.02 V (quasi-reversible).

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Supporting Information Available: Details of the X-ray diffraction studies including ORTEP diagrams of **6**, **8**, **11**, **17**, **18**, **23**, and **29** and NMR spectra for **26**−**28** and **30**. This material is available free of charge via the Internet at http://pubs.acs.org.

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