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Articles

Coordination Chemistry and Properties of Unusually π-Basic Molybdenum Fragments

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A series of complexes of the form TpMo(NO)(L)(η^2-L$_\pi$) were synthesized, where Tp = hydridotris(pyrazolyl)borate, L = 1-methylimidazole or ammonia, and L$_\pi$ is an alkene, alkyne, ketone, polyaromatic hydrocarbon, or aromatic heterocycle. The thermal stability of the dihapto-coordinated aromatic complexes is indicative of a strong π back-bonding interaction similar to that found in the heavy metal analogues [Os(NH$_3$)$_5$(η^2-arene)]$^{2+}$, TpRe(CO)(L)(η^2-arene), and TpW(NO)(L)(η^2-arene). Several synthetic routes to these molybdenum complexes are outlined.

Introduction

Over the past decade, we have investigated the ability of low-valent, d^6 metal fragments to act as potent π-bases.[1,2] The dihapto coordination of dienes, alkynes, and aromatic molecules has been shown to activate these ligands toward reactions with electrophiles that would otherwise be inaccessible.[1,3] While the focus of our investigation has been on the d^6 heavy metals Os(II),[1,2] Re(I),[4−7] and, most recently, W(0),[8] we hoped to extend this chemistry to the second row through the use of Mo(0).[9] Group 6 η^2-carbonyl[10,11] and alkene[12] complexes are widely known. Although examples of thermally stable dihapto-coordinated arenes have been reported with both second-row (e.g., Rh(I),[13] Ru(0)[14,15]) and first-row (e.g., Ni(0)[16,17] and Cu(I)[18]) transition metals, these d^8 and d^{10} metal systems are coordinatively unsaturated and are expected to be incompatible with strong electrophiles. We sought the same ligand framework that was used successfully with the chiral {TpRe(CO)(L)} systems, but with the replacement of CO by the stronger π-acid NO$^+$ in order to stabilize the zero-valent oxidation state of the molybdenum.[9] Pertinent to our studies were Mo(I) complexes such as Tp*Mo(NO)(py)Cl[19,20] (Tp* = hydridotris(3,5-dimethylpyrazolyl)borate) due to their similarity to the d^5 analogue TpRe(CO)(L)(OTf), a precursor of the d^6 system TpRe(CO)(L)(aromatic).

Herein, we describe the syntheses and properties of a series of molybdenum(0) complexes of the form TpMo(NO)(L)(L$_\pi$), where Tp = hydridotris(pyrazolyl)borate, L = 1-methylimidazole or ammonia, and L$_\pi$ is an η^2-coordinated alkene, alkyne, ketone, polyaromatic hydrocarbon, or aromatic heterocycle. A portion of this study has been previously communicated.[9]

Results and Discussion

The complex TpMo(NO)Br$_2$[21] (**1**) has proven to be a versatile precursor to complexes of the form TpMo(NO)(MeIm)(η^2-aromatic).[9] When a THF solution of **1** is combined with 1-methylimidazole and a suitable π-ligand in the presence of a sodium/mercury amalgam or sodium dispersion, the corresponding dihapto-bound complex is

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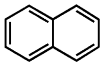
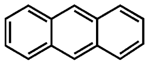
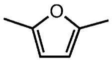
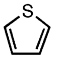
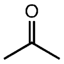
Table 1. Synthesis and Characterization Data for Complexes 4−13

Compound	Ligand (L_π)	Yield from **2** (%)	dr	$E_{p,a}$ (1/0) mV, 100 mV/s)	ν (NO; cm^{-1})
4		60	4:1	-180	1579
5		62	10:1	-109	1583
6		45	2:1	-360	1571
7		35	>20:1	-475	1565
8		60	1:1	-330	1574
9		70	>20:1	-211	1571
10		65	-	-110	1546
11		63	1.4:1	155	1557
12		20	-	41	1590
13		35	4:1	93	1546

afforded in yields ranging from 25 to 40%. Although multigram scale quantities have been produced in this manner for the naphthalene (4.1 g) and furan (3.5 g) analogues, the yield was typically less than 40%. A control reaction pointed to a potential reason for the low yields: When a THF solution of **1** is treated with 1-methylimidazole with no reducing agent present, TpMo(NO)(MeIm)Br (**2**) was isolated in 20−30% yield. This suggests the presence of a disproportionation reaction similar to that observed by Ward and McCleverty for related Tp* systems.[20]

Electrochemical data indicated that TpMo(NO)Br$_2$ undergoes a reversible one-electron reduction ($E_{1/2} = -0.24$ V at 100 mV/s in THF), so attempts were made to prereduce **1** prior to the addition of the nitrogen ligand, a strategy previously used for the Tp* analogue.[20] Once reduction to Mo(I) was complete, it was hoped that addition of MeIm would effect a substitution reaction, generating **2**, the purported precursor of the desired aromatic complexes. Thus, a THF solution of **1** was treated with 25% sodium dispersion in toluene and allowed to stir until a darkening was observed. Subsequent addition of 1 equiv of 1-methylimidazole caused an immediate color change. The resulting green solution was filtered and added to pentane to precipitate compound **2**, which after recrystallization was isolated in 65% yield. An alternate synthetic route to **2** was also explored in which the precursor to **1**, TpMo(NO)(CO)$_2$, was refluxed in xylenes in the presence of MeIm. After 2 days, TpMo(NO)(CO)(MeIm) (**3**) was afforded in 50−60% yield after recrystallization. Treatment of this complex with bromine in a methylene chloride solution resulted in **2** in 80% yield after recrystallization.

Reduction of **2** using a sodium/mercury amalgam or 25% sodium dispersion in toluene (CAUTION) in the presence of a suitable π-ligand afforded the intended dihapto-bound complex with a typical yield of 60%. Using this strategy, molybdenum(0) complexes of a broad range of unsaturated organic ligands have been prepared, as are summarized in Table 1. Attempts to isolate complexes of benzene, substituted benzenes, or pyrroles by this method have been unsuccessful.

Complexes were characterized using COSY, HSQC, NOESY, and 1D NOE data and by correlating proton and carbon NMR spectra with those of previously published rhenium-based complexes.[22] Structures for the 1-hexyne complex **13**, the diene complex **11**, the naphthalene complex **4**,[9] and the anthracene complex **5** were confirmed from single-crystal X-ray diffraction studies. In the case of **5**, however, the unit cell was too large to determine meaningful bond length or angle values. The ORTEP diagram for the hexyne complex **13** is shown in Figure 1. The bond length of the alkyne has lengthened only slightly to 1.23 Å from that of free 1-hexyne (1.21 Å). The Mo−C1 and Mo−C2 bond lengths are 2.14 and 2.17 Å, respectively, values significantly shorter than for analogous Mo-alkene or aromatic hydrocarbon complexes (cf., for **4**, 2.24, 2.27 Å).[9] The chemical shift of the bound alkyne proton appears as a triplet at 6.65 ppm ($J = 2$ Hz), nearly identical to the triplet at 6.64 ppm ($J = 2$ Hz) in the analogous rhenium system. The proton splitting arises from allylic coupling of the terminal proton to the nearest CH$_2$ group of the aliphatic chain. In the complex TpMo(NO)(MeIm)(η^2-2-butyne) (**12**) the methyl protons with chemical shifts at 1.87 ppm (away from imidazole) and 1.99 ppm (toward imidazole) are quartets in the NMR spectrum, owing to their homoallylic coupling (1.3 Hz). In the case of the thiophene complex **8**, no *S*-bound isomer could be detected.

Stereochemistry. The stereogenic molybdenum center causes complexes **4**−**9**, **11**, and **13** to be formed as mixtures of either coordination or conformational dia-

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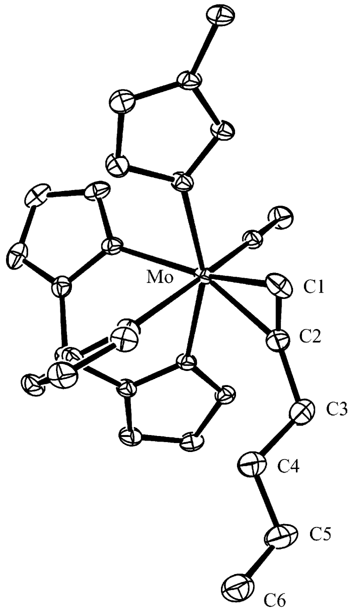

Figure 1. ORTEP diagram (30% ellipsoids) for the alkyne complex **13**.

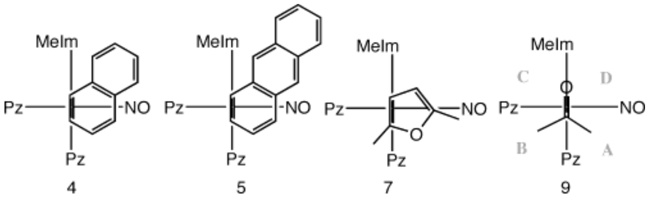

Figure 2. Dominant stereoisomers for complexes **4**, **5**, **7**, and **9**.

stereomers. In considering their stereochemistries, it is useful to describe these complexes as projections, viewed down the metal−aromatic bond (Figure 2).[23] Of the four quadrants, C is the most sterically congested.[24] As observed for the rhenium systems,[25] the coordinated π bond is oriented perpendicular to the diatomic ligand in order for a ligand π^* orbital to interact with the highest energy filled d orbital. For all complexes with cyclic ligands, crystallographic or NOE data are consistent with the uncoordinated portion of the ligand lying over the NO ligand, extending into quadrants D and A. In cases where there is a significant steric difference in the two halves of the coordinated C=C or C=O bond (naphthalene (**4**), anthracene (**5**), 2,5-dimethylfuran (**7**), or acetone (**9**)), one diastereomer dominates. In the case of **4** and **5**, the uncoordinated aromatic ring lies toward the MeIm, and in complexes **7** and **9**, the methyl groups connected to bound carbons avoid quadrant C. In contrast, where there are only minor steric differences in the two halves of the bound C=C bond, such as the thiophene (**8**), furan (**6**), and cyclohexadiene (**11**) complexes, stereoselectivity is poor. These observations are in line with what was earlier reported for rhenium.[22] The dominant conformer of the 1-hexyne complex **13** has the butyl group extending away from the MeIm ligand.

Isomerization and Ligand Substitution Kinetics. Half-lives of {TpMo(NO)(MeIm)} systems are generally shorter than those of the corresponding TpRe(CO)(MeIm) systems, but similar to other rhenium complexes we have studied.[26] The {TpMo(NO)(MeIm)} fragment does not form an isolable complex with benzene or *N*-methylpyrrole, and this is likely a consequence of the greater lability of the molybdenum system compared to rhenium. The free energy of activation for the substitution of the bound naphthalene in **4** by acetone has been estimated by determining the half-life from NMR data. This barrier can be compared directly to those previously reported for the TpRe(CO)(L)(η^2-naphthalene) complexes.[26] Complex **4** has a $\Delta G^\ddagger$ of 26.6 kcal/mol at 100 °C, a value between that for TpRe(CO)(t-BuNC)(η^2-naphthalene) (23.8 kcal/mol at 23 °C) and TpRe(CO)(py)(η^2-naphthalene) (28.1 kcal/mol at 100 °C). The molybdenum value is only about 2 kcal/mol less than that for TpRe(CO)(MeIm)(η^2-naphthalene) (28.5 kcal/mol at 100 °C), suggesting that other derivatives of Mo(0)−NO might be capable of forming an isolable benzene complex. The $\Delta G^\ddagger$ values of TpMo(NO)(MeIm)(η^2-furan) and TpMo(NO)(MeIm)(η^2-thiophene) systems are both 24.5 kcal/mol at 25 °C, which is similar to the TpRe(CO)(^{t}BuNC)(η-2-furan) analogue (24.6 kcal/mol at 25 °C).[26]

Kinetic data for the interconversion of diastereomers also provide a useful comparison between the molybdenum and rhenium systems.[26] The exchange rate for each mechanism was determined by measuring the decrease in ^{1}H NMR signal intensity for the peak in question after irradiation of its exchange partner and comparing that to the intensity of the same peak without irradiation. In addition, the observed spin−lattice relaxation times (T_1) for the various peaks observed in the spin saturation experiment were measured. From these data, the rate was calculated utilizing the Forsen−Hoffman relation.[27−29] The activation barriers were then calculated utilizing the Eyring equation.[30] The $\Delta G^\ddagger$ for both interfacial and intrafacial isomerization for the naphthalene complex **4** was found to be 20.7 ± 0.3 kcal/mol at 50 °C). These values are most similar to TpRe(CO)(py)(η^2-naphthalene) (20.3 kcal/mol at 20 °C; intrafacial) and are significantly lower than that of the TpRe(CO)(MeIm)(η^2-naphthalene) system (22.5 kcal/mol at 50 °C; intrafacial).[26] For the thiophene complex **8**, $\Delta G^\ddagger$ for interfacial isomerization is 21.0 kcal at 50°C, and that for intrafacial isomerization is 21.4 kcal/mol at 50°C.

Ligand Protonation. To establish the degree to which the metal activates the ligand toward addition of electrophiles, we investigated the ability of the diene and the naphthalene complexes to undergo protonation. An acetonitrile solution (10 mL) of the complex TpMo(NO)(MeIm)(η^2-1,3-cyclohexadiene) (**11**), as a mixture of diastereomers, undergoes protonation when treated

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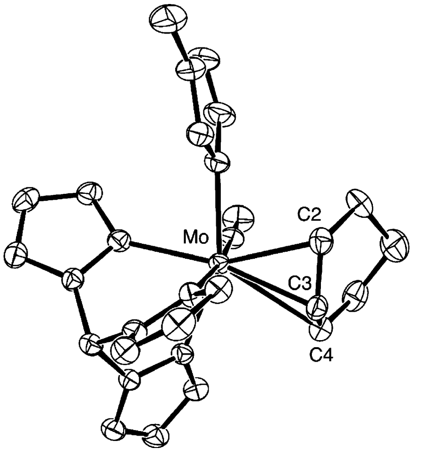
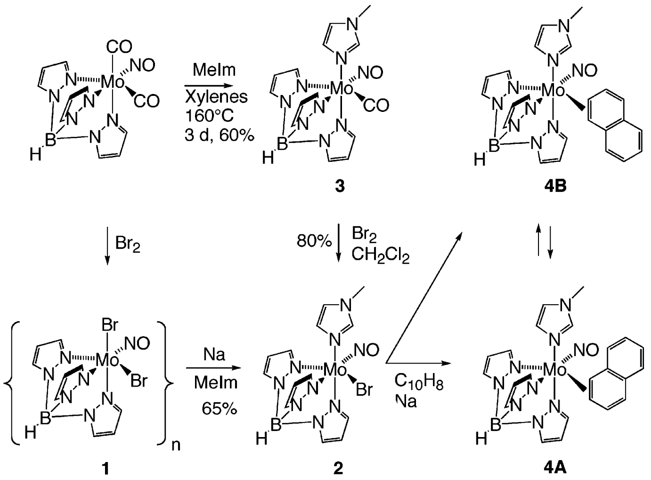


Figure 3. ORTEP diagram for the cation [TpMo(NO)(MeIm)(C_6H_9)]$^+$ (**1*H*-11**).

Scheme 1. Synthesis of TpMo(NO)(MeIm)(η^2-naphthalene) and Its Mo(I) Precursor



with 1 mL of a 10% HOTf in MeOH solution to afford complex **1*H*-11**, an η^3-1*H*-cyclohexadienium complex, in 80% yield.

Single-crystal X-ray diffraction studies were carried out on both the diene complex **11** and its conjugate acid, and the structure of the latter appears in Figure 3. The ORTEP diagram for **1*H*-11** shows an η^3-allyl complex with the bulk of the organic ligand in quadrants A and D. The average of the bond lengths taken from the two independent complexes in the asymmetric unit shows a major distortion in the allyl ligand. The average Mo−C2 and Mo−C3 bond lengths are statistically identical at 2.33 Å, whereas the Mo−C4 bond average is 2.64 Å, a value 0.31 Å longer than that determined for the other terminal allylic carbon. The carbon−carbon bond distances are also nonsymmetrical, with the average C2−C3 bond = 1.41 Å, slightly longer than that of C3−C4 = 1.37 Å. This suggests a significant contribution from a resonance contributor best described as an η^2-allyl cation, a coordinated alkene adjacent to a carbonium ion (Scheme 2). Interestingly, ^{13}C NMR data show that C4 (125.6 ppm) of the allyl fragment is significantly more downfield than C2 (109.7 ppm), further supporting the notion of partial “η^2-allyl” character for this complex. This distortion reflects the large difference in energy between the d orbital that is orthogonal to the π^* orbitals of the nitrosyl ligand and those d orbitals that overlap with the π^* orbitals of the nitrosyl ligand.[25]

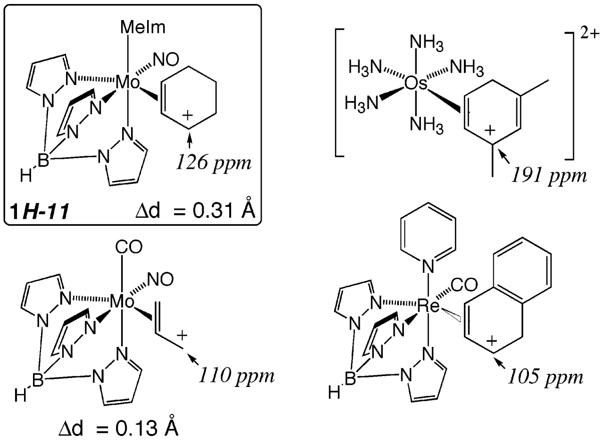
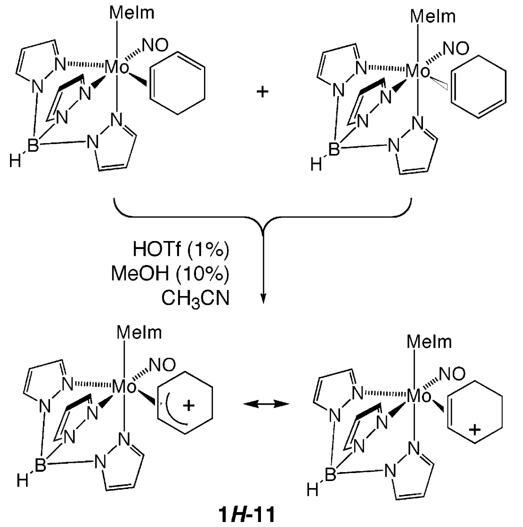


Figure 4. Examples of η^2-allyl and benzenium resonance contributors (Δd is the difference in M−C1 and M−C3 bond lengths).

Scheme 2. Synthesis of Allyl Complex 1*H*-11 from Cyclohexadiene



A similar distorted η^3-allyl species has been observed in the complex [TpMo(CO)(NO)(η^3-C_3H_5)]$^+$ [31] (where the difference in M−C bond lengths for the terminal carbons is 0.13 Å). Similar distortions have also been hypothesized in the benzenium complex [Os(NH_3)$_5$(1*H*-2,4,-dimethylbenzenium)]$^{3+}$ [32] and naphthalenium complex [TpRe(CO)(py)(1*H*-naphthalenium)]$^+$ (Figure 4).[33]

The basicity of the diene complex **11** was estimated by a series of experiments in which **11** was treated with various weak acids. Additionally, the conjugate acid **1*H*-11** was treated with several weak bases. Most pertinent were the observations that **11** can be protonated in an acetonitrile solution by 1 equiv of diphenylammonium triflate (pK_a ≈ 1), while **1*H*-11** can be deprotonated by 2,6-lutidine (pK_a ≈ 3). Several attempts were made to stereoselectively deprotonate **1*H*-11**, by varying temperature and base strength. Ratios varied from 1:1.4 to

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4:1, but in no case was one diastereomer of **11** formed exclusively.

Studies of TpMo(NO)(MeIm)(3,4-η^2-naphthalene) (**4**) and its conjugate acid (**1*H*-4**) were generally comparable to those of the {TpRe(CO)(RIm)} analogues. Protonation of **4** was accomplished using a solution of triflic acid in acetonitrile. Solvation and subsequent observation by NMR spectroscopy at −40 °C indicated the presence of a 20:1 ratio of two diastereomers, **1*H*-4A** and **1*H*-4B**. In contrast, complex **4** showed no reaction with phosphoric acid. Unlike the rhenium analogue, **1*H*-4** was not stable to isolation as a solid. It also showed a shorter half-life toward decomposition (several hours at −20 °C) than that of TpRe(CO)(BuIm)(1*H*-naphthalenium) (indefinitely stable at −20 °C).[34] When equivalent portions of [TpRe(CO)(BuIm)(2,3,4-η^3-(1*H*-naphthalenium))](OTf) and TpMo(NO)(MeIm)(3,4-η^2-naphthalene) (**4**) were combined, proton transfer was not observed after 0.5 h at −20 °C (^{1}H NMR). These experiments, together with earlier reports of [Os(NH$_3$)$_5$(η^2-naphthalene)]$^{2+}$,[1] show that the naphthalene in **4** is more basic than when it is bound to {Os(NH$_3$)$_5$}$^{2+}$, but not as basic as when it is bound to {TpRe(CO)(MeIm)} (assuming that the lack of proton transfer is not just a result of slow kinetics). In an earlier study, naphthalenium **1*H*-4** was combined with a silyl ketene acetal to generate a 2-alkyl-1,2-dihydronaphthalene in 80% yield after decomplexation, an observation that demonstrates the synthetic potential of this molybdenum-based dearomatization agent.[9]

TpMo(NO)(NH$_3$)(η^2-aromatic) Complexes. A more powerful σ-donating L ligand was desired for the molybdenum system to see if enhanced π-basicity of the fragment would allow the molybdenum to bind benzenes similar to what is seen for osmium,[35] rhenium,[6] and tungsten systems.[8] Attempts to replace one carbon monoxide ligand of TpMo(NO)(CO)$_2$ with NH$_3$ failed, and an alternate pathway was formulated. Reduction of **1** with activated magnesium in an NH$_3$-saturated THF solution affords TpMo(NO)(NH$_3$)Br (**14**) in 50−55% yield after isolation from silica gel and recrystallization.

When **14** was reduced in the presence of naphthalene or furan in a manner analogous to that reported earlier for the imidazole analogue **2**, the complexes TpMo(NO)(NH$_3$)(η^2-naphthalene) (**15**) and TpMo(NO)(NH$_3$)(η^2-furan) (**16**) were isolated, but in disappointing yields (10−20%). In a typical experiment, a THF solution of **14** was reduced using a sodium/mercury amalgam in the presence of the desired aromatic for 24 h, and the resulting complex was eluted down a silica column using neat diethyl ether. Addition of pentane precipitated the yellow products. NMR chemical shifts were assigned by correlation with the molybdenum-imidazole-based complexes. Unfortunately, all attempts to isolate complexes of substituted benzenes failed.

Finally, an alternate route to the TpMo(NO)(L)X family (**2** and **14**, if X = Br) was explored starting from MoCl$_5$. This pentachloride was added to a THF solution of KTp, then placed under a slow nitric oxide purge.[36] An IR stretch correlating to the nitrosyl ligand of TpMo(NO)Cl$_2$ (**17**) was observed at 1710 cm^{-1}. The mixture was filtered, and the filtrate was then stirred with MeIm or ammonia and magnesium powder. The complexes TpMo(NO)(L)Cl (L = NH$_3$ (**18**) or MeIm (**19**)) were isolated in 22% yield. A single-crystal X-ray diffraction of the ammonia analogue **18** was obtained, but disorder between the NO and Cl moieties prevented a complete analysis. However, from the crystal structure it was clear that, on some of the molecules, the hydrogen on the boron of the Tp ligand was replaced by a chlorine atom. This was confirmed for the bulk product TpMo(NO)(NH$_3$)Cl by elemental analysis, which indicated 48% substitution. Other avenues of this reaction were explored to avoid B−H substitution, but consistently low yields eventually prompted us to abandon this approach. However, we note that the Tp$^{(B-X)}$Mo(L)(NO)Cl (X = Cl, H) product was reduced with Na/Hg amalgam in the presence of excess naphthalene to form the corresponding TpMo(NO)(L)(η^2-naphthalene) complexes, **4** and **15**, albeit in only trace amounts.

Conclusion

A variety of olefins, acetylenes, ketones, polyaromatic hydrocarbons, and aromatic heterocycles can be dihapto-coordinated to the π-basic metal fragment {TpMo(NO)(L)}. Complexation to aromatic molecules in this manner effectively dearomatizes the ring similar to that observed for rhenium and osmium π-bases. Protonation and isomerization experiments indicated that the TpMo(NO)(MeIm) system is a more effective π-base than {Os(NH$_3$)$_5$}$^{2+}$, very similar to {TpRe(CO)(py)} and {TpRe(CO)(PMe$_3$)}, but not as effective as {TpRe(CO)(MeIm)}.

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 utilizing residual ^{1}H or ^{13}C signals of the deuterated solvents as an internal standard. Coupling constants (*J*) are reported in hertz (Hz). Carbon signals associated with triflate groups were not observed for any sample. 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 BAS Epsilon EC-2000 potentiostat. Electrochemical (CV) data were recorded at 100 mV/s at ambient temperature in a standard three-electrode cell from +1.7 to −1.7 V with a glassy carbon working electrode, *N*,*N*-dimethylacetamide (DMA) solvent, and tetrabutylammonium hexaflurophosphate (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 was obtained from Atlantic Microlabs, Inc., or using a PE2400 Series II analyzer. X-ray data were collected on a Bruker SMART APEX CCD diffractometer. Unless otherwise noted, all synthetic reactions and electrochemical experiments were performed under a dry nitrogen atmosphere. CH$_2$Cl$_2$, benzene, tetrahydrofuran (THF), and hexanes were purged with nitrogen and purified by passage through a column packed with activated alumina.[37] Other solvents and liquid reagents were

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[34] Keane, J. M.; Chordia, M. D.; Mocella, C. J.; Sabat, M.; Trindle, C. O.; Harman, W. D. *J. Am. Chem. Soc.*, in press.

[35] Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1987**, *109*, 1883.

[36] A slow purge is necessary in order to avoid the significant formation of an impurity characterized by two peaks in the IR spectrum at 1792 and 1673 cm^{-1}.

[37] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

thoroughly purged with nitrogen prior to use. Deuterated solvents were used as received from Cambridge Isotopes. Diphenylammonium triflate was obtained by collecting the precipitate resulting from slow addition of triflic acid to a diethyl ether solution of diphenylamine. Compounds **1**, **4**, **5**, **6**, **8**, **9**, and **10** have been characterized previously.[9]

TpMo(NO)(MeIm)Br (2). In a 500 mL Erlenmeyer flask charged with a stir bar was placed TpMo(NO)(CO)(MeIm) (21.29 g, 0.0474 mol) and CH_2Cl_2 (100 mL). A 0.66 M CH_2Cl_2 solution (36 mL, 0.0238 mol) of Br_2 was added, upon which gas evolution was observed as well as a change from blue to a green color. The solution was stirred (5 min), at which time hexane was added (200 mL). The suspension was collected on a fine-ground frit and dried under reduced pressure. Crystals were obtained through vapor-diffusion crystallization of a saturated CH_2Cl_2 solution with diethyl ether for 3 days. The mother liquor was decanted, and the resulting emerald green crystals were washed with diethyl ether (80%). Diffraction data for complex **2** confirm that this Mo(I) complex is monomeric rather than $(TpMo(NO)(MeIm)Br)_2$. Disorder in the crystal (interchange of the NO and Br ligands) prohibited a full evaluation of the molecular structure.

Alternate Synthesis. In a 250 mL round-bottom flask charged with a stir bar was placed $TpMo(NO)Br_2$ (5.30 g, 10.6 mmol) and 200 mL of THF, and the mixture was stirred to dissolution. A 25% sodium dispersion in toluene (1.01 g, 10.9 mmol) was added, and the mixture was stirred vigorously. Over the course of 10 min the solution turned from red to a dark color. 1-Methylimidazole (1.75 g, 21.3 mmol) was added, upon which an instant color change to green was observed. The solution was decanted through a Celite plug on a 150 mL medium-porosity fritted glass disk and washed with THF. The eluent was reduced to 50 mL, and pentanes (150 mL) were added to precipitate a green solid. Crystals were obtained in the same manner as above.

Paramagnetic compound: CV (DMAc) $E_{1/2}$ −1.33V (NHE), $E_{p,a} = +0.86$ V (NHE). IR (HATR, glaze): ν(BH) = 2510 cm^{-1}, ν(NO) = 1610 cm^{-1}. Typical yields: 60−65%. Anal. Calcd for $C_{13}H_{16}BBrMoN_9O$: C, 31.17; H, 3.22; N, 25.16. Found: C, 31.34; H, 2.98; N, 25.29.

TpMo(NO)(CO)(MeIm) (3). In a dry round-bottom flask charged with a stir bar was placed $TpMo(NO)(CO)_2$ (51.6 g, 0.131 mol), xylenes (500 mL), 1-methylimidazole (72.1 g, 0.879 mol), and CaH_2 (0.050 g, 0.0012 mol). The mixture was refluxed under a dinitrogen atmosphere for 2 days, over which time a darkening was observed. The resulting mixture was poured onto a 5 cm plug of silica in a 350 mL frit, and the xylenes were eluted through. The plug was first washed with diethyl ether and then with CH_2Cl_2, and the product band was collected. The solvent was removed in vacuo. The residue was dissolved in a minimal amount of CH_2Cl_2, and crystals were obtained through vapor diffusion with diethyl ether for 4 days. The mother liquor was decanted, and the resulting dark blue crystals were washed with diethyl ether. Typical yields: 50−60%.

CV (DMAc) $E_{p,a} = +0.22$ V (NHE). IR (HATR, glaze): ν(BH) = 2483 cm^{-1} ν(NO) = 1583 cm^{-1}, ν(CO) = 1865 cm^{-1}. ^{1}H NMR (300 MHz) ($CDCl_3$) (22 °C): δ 7.73, 7.71, 7.67, 7.41, 7.30 (1H, each 1:1:1:2:1, each a d, Tp 3,5), 6.19, 6.18, 6.11 (1H each, 1:1:1, each a t, Tp 4), 7.57 (1H, s, Im), 6.79, 6.63 (1:1, each a t, J = 1.3 Hz, 1.10 Hz, Im), 3.69 (3H, s, NMe). Anal. Calcd for $C_{14}H_{16}BMoN_9O_2$: C, 37.44; H, 3.59; N, 28.07. Found: C, 37.63; H, 3.49; N, 28.19.

TpMo(NO)(MeIm)(3,4-η^2-anthracene) (5). A THF solution (125 mL) of TpMo(NO)(MeIm)Br (0.942 g, 1.89 mmol) and anthracene (4.60 g, 25.8 mmol) was prepared in a dry 250 mL round-bottom flask charged with a stir bar. To this solution was added 1.03% sodium/mercury amalgam (28.7 g), and the mixture was stirred for 24 h. The solution was decanted away from the mercury amalgam, and the solvent was removed under reduced pressure. The residue was dissolved in a minimal amount of THF and subjected to flash chromatography first with diethyl ether and then with 1:3 THF−diethyl ether (product elution). The solvent was removed in vacuo to 10 mL, and pentane (100 mL) was added to afford an orange solid precipitate. The solid was collected and dried in vacuo. Typical yields: 60−65%.

CV (DMAc) $E_{p,a} = -109$ mV (NHE). IR (HATR, glaze): ν(BH) = 2475 cm^{-1}, ν(NO) = 1583 cm^{-1}. ^{1}H NMR of major diastereomer (300 MHz) (acetone-d_6) (22 °C): δ 8.15, 8.01, 7.93, 7.85, 7.79, 7.03 (1H each, 1:1:1:1:1:1, each a d (Tp 3 or 5)), 6.40, 6.365, 6.04 (1H each, 1:1:1, each a t (Tp 4)), 6.60, 7.29 (1H each, 1:1, each a t (Im), 6.77 (1H, s, (Im)), 3.61 (3H, s, (N-Me)), 8.08 (1H, d), 8.07 (1H, d, anthracene), 8.05 (1H, d, anthracene), 8.05 (1H, d, anthracene), 7.57 (1H, s, anthracene H10), 6.35 (1H, s, anthracene H9), 3.73 (1H, d, J = 8.1 Hz, anthracene H4), 3.07 (1H, dd, J = 8.1 Hz, anthracene H3), 7.09 (1H, ddd, J = 9.23 Hz, anthracene H2), 6.58 (1H, br d, J = 9.0 Hz, anthracene H1). ^{13}C NMR (300 MHz) (acetone-d_6) (22 °C): δ 106.5, 106.3, 106.0 (Tp 4), 34.7 (N-Me), 74.3, 68.0 (anthracene C1, C2), 143.6, 142.4, 141.9, 138.8, 137.4, 136.8, 136.2, 135.5, 132.6, 129.0, 128.9, 127.9, 126.9, 126.7, 126.2, 124.5, 123.8, 123.0, 122.1, 121.0, 118.4. Anal. Calcd for $C_{27}H_{26}BMoN_9O$: C, 54.11; H, 4.37; N, 21.03. Found: C, 53.99; H, 4.20; N, 21.00.

TpMo(NO)(MeIm)(2,3-η^2-2,5-dimethylfuran) (7). A THF solution (125 mL) of TpMo(NO)(MeIm)Br (0.560 g, 0.00112 mol) and 2,5-dimethylfuran(2.47 g, 0.0257 mol) was prepared in a dry 250 mL round-bottom flask charged with a stir bar. To this solution was added 1.03% sodium/mercury amalgam (8.00 g), and the mixture was stirred for 24 h. The solution was decanted away from the mercury amalgam, and the solvent was removed in vacuo. The residue was dissolved in a minimal amount of THF and was subjected to flash chromatography first with diethyl ether and then with 1:3 THF−diethyl ether (product elution). The solvent was removed under reduced pressure to 10 mL, and pentane (100 mL) was added to afford a yellow solid precipitate. The solid was collected and dried in vacuo. Typical yields: 40−50%.

CV (DMAc) $E_{p,a} = -475$ mV (NHE). IR (HATR, glaze): ν(BH) = 2479 cm^{-1}, ν(NO) = 1565 cm^{-1}. ^{1}H NMR (300 MHz) (acetone-d_6) (22 °C): δ 8.26, 7.89, 7.87, 7.76, 7.69, 7.07 (1H each, 1:1:1:1:1:1, each a d (Tp 3 or 5)), 6.36, 6.24, 6.08 (1H each, 1:1:1, each a t (Tp 4)), 6.77, 7.38 (1H each, 1:1, each a t (Im)), 7.20 (1H, d, (Im)), 3.87 (3H, s, (N-Me)), 0.89 (3H, s, (C5-Me)), 2.10 (3H, s, (C2-Me)), 5.62 (1H, br s, (C3)), 2.97 (1H, br s, (C4)). ^{13}C NMR (300 MHz) (acetone-d_6) (22 °C): δ 106.8, 106.3, 105.4 (Tp 4), 121.5, 129.6 (Im), 143.5, 143.3, 142.9, 142.2, 140.8, 136.8, 135.9 (Tp 3 or 5 or Im), 34.4 (N-Me), 21.3 (CCH_3), 13.3 (CCH_3), 150.7 (C2, unbound) 68.7 (C4, bound), 108.9 (furan 3 or 5), 105.9 (furan 3 or 5). Anal. Calcd for $C_{19}H_{24}BMoN_9O_2$: C, 44.12; H, 4.68; N, 24.37. Found: C, 43.99; H, 4.61; N, 24.45.

TpMo(NO)(MeIm)(1,2-η^2-1,3-cyclohexadiene) (11). To a solution of 0.929 g (1.85 mmol) of TpMo(NO)(MeIm)Br in 100 mL in a 250 mL round-botton flask were added 3.11 g (38.8 mmol) of cyclohexadiene and 31.2 g of 1.05% Na/Hg amalgam. The mixture quickly turned from green to purple and was allowed to stir for 24 h. The THF solution was decanted away from the amalgam, and the solvent was removed in vacuo. The residue was dissolved in a minimal amount of THF and pipetted onto a 2 in. silica gel plug in a 60 mL coarse fritted-glass funnel. The beige product band was collected by elution with a 1:3 THF−diethyl ether solution. The eluent was stripped of solvent to 10 mL, at which time pentane (100 mL) was added to precipitate a beige solid, which was subsequently collected on a fine fritted-glass disk. The solid was dried under reduced pressure. Typical yields: 65−70%.

CV (DMAc) $E_{p,a} = +0.155$ V (NHE). IR (HATR, glaze): ν(BH) = 2479 cm^{-1}, ν(NO) = 1557 cm^{-1}. ^{1}H NMR of both diasteromers (300 MHz) (d_3-acetonitrile) (22 °C) δ 7.96, 7.86, 7.85, 7.82, 7.80, 7.73, 7.72, 7.71, 7.60, 7.47, 7.26, 7.17 (1H each,

each a d, Tp 3,5), 6.33, 6.13, 6.11 (1H each, 1:1:1, each a t, Tp 4), 6.27 (3H, m, Tp 4), 7.66, 7.52, 7.34, 7.05, 7.01, 6.63 (1H each, each a br s, Im), 3.65 (3H, s, NMe). 2.47 (1H, br dt, $J = 9$ Hz, C1), 1.93 (1H, br dt, $J = 9$ Hz, C1′), 2.31 (1H, dd, $J = 9$, 5 Hz, C2), 2.50 (1H, dd, $J = 9$, 5 Hz, C2′), 6.33 (1H, ddd, $J = 10$, 6, 3 Hz, C3), 5.98 (1H, ddd, $J = 10$, 6, 3 Hz, C3′), 5.17 (1H, ddd overlapping, $J = 19$, 4, 2 Hz, C4), 5.15 (1H, ddd overlapping, $J = 19$, 4, 2 Hz, C4′), 2.44 (2H, m, C5/C5′), 1.78 (2H, m, C5/C5′), 2.68 (1H, tdd, $J = 14$, 7, 4 Hz, C6), 1.82 (1H, ddt, $J = 14$, 7 Hz, C6), 2.61 (1H, tdd, $J = 14$, 7, 4 Hz, C6′), 1.99 (1H, ddt, $J = 14$, 7, 4 Hz, C6′). ^{13}C NMR (300 MHz) (d_3-acetonitrile) (22 °C): δ 145.0, 143.0, 142.5, 142.1, 142.0, 141.9, 139.1, 138.6, 137.6, 137.2, 136.8, 135.9, 135.8, 133.1, 132.9 (12 Tp 3, 5, 2 Im, 2 unbound CH), 129.8, 129.3, 122.9, 122.4 (4 Im), 118.6, 118.1 (2 unbound CH), 106.7, 106.6, 106.4, 106.5 (4 Tp 4), 71.9, 66.5, 63.9, 60.3 (4 bound CH), 34.8, 34.7 (2 Im CH_3), 27.0, 26.9, 24.3, 23.8 (4 CH_2). Anal. Calcd for $C_{19}H_{24}BMoN_9O$: C, 45.53; H, 4.83; N, 25.15. Found: C, 45.39; H, 4.81; N, 25.09.

TpMo(NO)(MeIm)(2,3,4-η^3-1-*H*-cyclohexadienyl) Triflate (1*H*-11). To a solution of TpMo(NO)(MeIm)(η^2-1,2-cyclohexadiene) (0.385 g, 0.768 mmol) in acetonitrile (10 mL) in a 125 mL flask was added dropwise 1.24 g (0.855 mmol) of 10.3% (wt/wt) triflic acid in methanol with stirring. The solution instantly changed from a light yellow to an orange color. The solution was stirred for 5 min, and the solvent was removed in vacuo. The resulting residue was dissolved in 5 mL of THF, and pentane (75 mL) was added to afford a yellow-orange precipitate, which was collected on a fine-porosity fritted-glass disk. The solid was dried in vacuo. Typical yield: 80%.

CV (MeCN) (TBAH) (100 mV/s) $E_{p,c} = -0.781$ V, $E_{p,a} = +0.027$ V (NHE). IR (HATR, glaze): ν(BH) = 2500 cm^{-1}, ν(NO) = 1657 cm^{-1}. ^{1}H NMR (300 MHz) (d_3-acetonitrile) (22 °C): δ 8.01, 7.99, 7.91, 7.90, 7.74, 7.49, 7.35 (1H each, each a d, 6 Tp 3,5, 1 Im), 7.10, 6.56 (1H each, each a t, Im), 6.50, 6.40, 6.18 (1H each, each a t, Tp 4), 5.93 (1H, dd, $J = 6$, 2.5 Hz, C3), 5.69 (1H, dd, $J = 7.5$, 1.5 Hz, C1), 4.97 (1H, t, $J = 7$ Hz, C2), 1.47 (1H, m, C5), 1.73 (1H, m, C5′), 3.24 (1H, m, C4), 3.10 (1H, m, C6), 2.79 (1H, m, C4′), 2.72 (1H, m, C6′). ^{13}C NMR (300 MHz) (CD_2Cl_2) (22 °C): δ 146.1, 142.9, 142.3, 138.6, 138.4, 138.2, 135.7 (6 Tp 3,5, 1 Im), 128.3, 123.5 (2 Im), 107.9, 107.2, 106.9 (3 Tp 4), 125.6 (C3), 109.7 (C1), 103.5 (C2), 35.4 (Im CH_3), 26.5 (C4), 26.4 (C6), 19.7 (C5). Anal. Calcd for $C_{20}H_{25}BF_3MoN_9O_4S$: C, 36.88; H, 3.87; N, 19.36. Found: C, 36.80; H, 3.88; N, 19.41.

TpMo(NO)(MeIm)(2,3-η^2-2-butyne) (12). A THF solution (125 mL) of TpMo(NO)(MeIm)Br (1.02 g, 2.04 mmol) and 2-butyne (1.15 g, 21.3 mmol) was prepared in a dry 250 mL round-bottom flask charged with a stir bar. To this solution was added 1.02% sodium/mercury amalgam (34.5 g), and the mixture was stirred for 24 h. The solution was decanted away from the mercury amalgam, and the solvent was removed in vacuo. The residue was dissolved in a minimal amount of THF and was subjected to flash chromatography first with diethyl ether and then with 1:3 THF−diethyl ether (product elution). The solvent was removed under reduced pressure to 10 mL, and pentane (100 mL) was added to afford a beige solid precipitate. The solid was collected and dried in vacuo. Typical yields: 10−20%.

CV (DMAc) $E_{p,a} = 41$ mV (NHE). IR (HATR, glaze): ν(BH) = 2481 cm^{-1}, ν(NO) = 1590 cm^{-1}, ν(CC) = 1867 cm^{-1}. ^{1}H NMR (300 MHz) (acetone-d_6) (22 °C): δ 7.84, 7.83, 7.81, 7.74, 7.72, 7.24 (1H each, 1:1:1:1:1:1, each a d (Tp 3 or 5)), 6.307, 6.111, 6.100 (1H each, 1:1:1, each a t (Tp 4)), 6.73, 7.22 (1H each, 1:1, each a t (Im)), 7.10 (1H, d, (Im)), 3.88 (3H, s, (N-Me)), 1.87 (3H, q, $J = 1.3$ Hz (alkyne Me away from Im)), 1.99 (3H, q, $J = 1.3$ Hz (alkyne Me toward Im)). ^{13}C NMR (300 MHz) (acetone-d_6) (22 °C): δ 105.9, 105.7, 105.4 (Tp 4), 145.6, 141.9, 139.8, 136.2, 135.3, 135.1, 142.3 (Tp 3 or 5 or Im), 122.3, 130.3 (Im), 34.4 (N-Me), 124.1, 123.6 (alkyne 2 or 3), 13.1 (alkyne Me away from Im), ∼30 (buried, alkyne Me toward Im). Anal. Calcd for $C_{17}H_{22}BMoN_9O$: C, 42.97; H, 4.67; N, 26.53. Found: C, 43.19; H, 4.66; N, 26.49.

TpMo(NO)(MeIm)(1,2-η^2-1-hexyne) (13). A THF solution (125 mL) of TpMo(NO)(MeIm)Br (0.906 g, 1.81 mmol) and 1-hexyne (2.96 g, 36.1 mmol) was prepared in a dry 250 mL round-bottom flask charged with a stir bar. To this solution was added 1.02% sodium/mercury amalgam (15.3 g), and the mixture was stirred for 24 h. The solution was decanted away from the mercury amalgam, and the solvent was removed in vacuo. The residue was dissolved in a minimal amount of THF and was subjected to flash chromatography first with diethyl ether and then with 1:3 THF−diethyl ether (product elution). The solvent was removed under reduced pressure to 10 mL, and pentane (100 mL) was added to afford a beige solid precipitate. The solid was collected and dried in vacuo. Typical yields: 30−35%.

CV (DMAc) $E_{p,a} = 93$mV (NHE). IR (HATR, glaze): ν(BH) = 2476 cm^{-1}, ν(NO) = 1537 cm^{-1}, ν(CC) = 1769 cm^{-1}. ^{1}H NMR of major diasteromer (300 MHz) (acetone-d_6) (22 °C): δ 7.86, 7.82, 7.77, 7.73, 7.67, 7.61 (1H each, 1:1:1:1:1:1, each a d (Tp 3 or 5)), 6.31, 6.13, 6.09 (1H each, 1:1:1, each a t (Tp 4)), =7.30, 7.10 (1H each, 1:1, each a t (Im)), 7.16 (1H, d, (Im)), 3.85 (3H, s, (N-Me)), 6.65 (1H, t, $J = 1.3$ Hz, C1), 2.55 (2H, m, C3), 1.59 (2H, m, C4), 1.44 (2H, m, C5), 0.88 (3H, t, C6). ^{13}C NMR (300 MHz) (acetone-d_6) (22 °C): δ 105.8, 106.1, 105.2 (Tp 4), 135.2, 145.4, 143.1, 142.1, 140.2, 135.4, 136.3 (Tp 3 or 5 or Im), 122.0, 130.7 (Im), 33.6 (N-Me), 105.2 (C1, buried), 119.7 (C2), 29.0 (C3, buried), 33.6 (C4), 23.0 (C5), 14.2 (C6). Anal. Calcd for $C_{19}H_{26}BMoN_9O$: C, 45.35; H, 5.21; N, 25.05. Found: C, 45.37; H, 5.29; N, 25.30.

TpMo(NO)(NH_3)Br (14). In a dry 1 L round-bottom flask charged with a stir bar, TpMo(NO)Br_2 (30.5 g, 0.061 mol), activated magnesium dust (13.3 g, 0.547 mol), and freshly saturated NH_3 in THF (450 mL) were added. The mixture was stirred for 90 min, upon which the dark red solution turned green. The mixture was poured over 2 cm of sand in an extra-course-ground glass frit and washed with THF. The collected solution was eluted over 5 cm of silica gel in a medium-ground glass filter, which was then washed with THF. The solvent was removed in vacuo to 100 mL of solution, and pentane (300 mL) was added to precipitate a green solid. The solid was collected and recrystalized from a solution in CH_2Cl_2 using vapor diffusion with diethyl ether. Typical yields: 50−55%.

CV (DMAc) (TBAH) (100 mV/s) $E_{1/2}$ −1.33V (NHE), $E_{p,a} = +0.86$ V (NHE). IR (HATR, glaze): ν(BH) = 2487 cm^{-1}, ν(NO) = 1589 cm^{-1}. Anal. Calcd for $C_9H_{13}BBrMoN_8O$: C, 24.80; H, 3.01; N, 25.71. Found: C, 25.11; H, 3.19; N, 25.95.

TpMo(NO)(NH_3)(1,2-η^2-naphthalene) (15). A THF solution (125 mL) of TpMo(NO)(NH_3)Br (1.09 g, 0.00250 mol) and naphthalene (6.41 g, 0.0501 mol) was prepared in a dry 250 mL round-bottom flask charged with a stir bar. To this solution was added 1.07% sodium/mercury amalgam (17.21 g), and the mixture was stirred for 24 h. The solution was decanted away from the mercury amalgam, and the solvent was removed under reduced pressure. The residue was dissolved in a minimal amount of THF and was subjected to flash chromatography first with pentane and then with 1:1 pentane−diethyl ether (yellow product elution). The solvent was removed under reduced pressure to 10 mL, and pentane (100 mL) was added to afford a yellow precipitate. The solid was collected and dried in vacuo. Typical yields: 10−15%.

CV (DMAc) $E_{p,a} = -234$ mV (NHE). IR (HATR, glaze): ν(BH) = 2479 cm^{-1}, ν(NO) = 1556 cm^{-1}. ^{1}H NMR of major isomer (300 MHz) (acetone-d_6) (22 °C): δ 8.11, 7.91, 7.86, 7.69, 6.95 (1H each, 1:1:1:1:1:1, each a d (Tp 3 or 5)), 6.33, 6.27, 6.26 (1H each, 1:1:1, each a t (Tp 4)), 2.93 (3H, br s, NH_3) 3.78 (1H, d, $J = 8.3$ Hz, naphthalene 1), 2.95 (1H, dd, $J = 8.6$ Hz, naphthalene 2) 7.10 (1H dd, $J = 1.3$ Hz, naphthalene 3), 6.44 (1H, d, $J = 9.0$ Hz, naphthalene 4) 7.19 (1H, dd, $J = 7.7$ Hz, naphthalene 5), 6.95 (2H, m (overlapping), naphthalene 6 and 7), 6.92 (1H, d, $J = 1.3$ Hz, naphthalene 8). ^{13}C NMR (300

MHz) (acetone-d_6) (22 °C): δ 106.1, 105.6, 105.4 (Tp 4), 143.9, 143.5, 142.3, 142.1, 140.9, 140.6 (Tp 3 or 5), 71.4, 68.6 (naphthalene C1 and C2), 136.5, 136.3, 135.4, 134.5, 133.4, 131.1, 127.7, 125.9 (naphthalene 3−10).

TpMo(NO)(NH$_3$)(2,3-η^2-furan) (16). A THF solution (125 mL) of TpMo(NO)(NH$_3$)Br (1.125 g, 0.00258 mol) and furan (3.51 g, 0.0516 mol) was prepared in a dry 250 mL round-bottom flask charged with a stir bar. To this solution was added 1.07% sodium/mercury amalgam (15.85 g), and the mixture was stirred for 24 h. The solution was decanted away from the mercury amalgam, and the solvent was removed under reduced pressure. The residue was dissolved in a minimal amount of THF and was subjected to flash chromatography first with pentane and then with diethyl ether (yellow product elution). The solvent was removed in vacuo to 10 mL, and pentane (100 mL) was added to afford a beige precipitate. The solid was collected and dried in vacuo. Typical yields: 10−12%.

CV (DMAc) $E_{p,a}$ = −381 mV (NHE). IR (HATR, glaze): ν(BH) = 2484 cm^{-1}, ν(NO) = 1560 cm^{-1}. ^{1}H NMR of major isomer (300 MHz) (acetone-d_6) (22 °C): δ 8.409, 7.946, 7.857, 7.789, 7.586, 7.113 (1H each, 1:1:1:1:1:1, each a d (Tp 3 or 5)), 6.423, 6.259, 6.142 (1H each, 1:1:1, each a t (Tp 4)), 3.87 (3H, br s, (NH$_3$)) 3.763 (1H, J = 4.6 Hz, dd, C3), 5.629 (1H, J = 4.3 Hz, d, C2), 6.019 (1H, J = 4.1 Hz, dd, C4), 6.476 (1H, J = 4.6 Hz, d, C5).

TpMo(NO)(Cl)$_2$ (17) (not obtained pure in bulk; see Discussion). Methylene chloride (400 mL) was saturated with NO$_{(g)}$. To this solution was added 2.2 g of KTp (8.78 mmol, 1.2 equiv) and 2.0 g of MoCl$_5$ (7.32 mmol, 1.0 equiv). The solution was stirred for 18 h and then filtered. The filtrate was reduced to 100 mL and then treated with ether (400 mL). This solution was reduced to 350 mL and treated with 100 mL of hexanes, inducing precipitation. A red-brown solid (773 mg) was isolated, which was found to contain **17** (60%) and an unknown compound (40%; thought to be the Cl-substituted analogue; vide infra), which could not be separated by chromatography. Compound **17**: ^{1}H NMR (acetone-d_6): δ 8.44 (2H, d, J = 2.4 Hz, Tp-3,5-B), 8.23 (1H, d, J = 2.4 Hz, Tp-3,5-B), 8.20 (2H, d, J = 2.4 Hz, Tp-3,5-A), 8.17 (2H, d, J = 2.2 Hz, Tp-3,5-B), 8.05 (2H, d, J = 2.2 Hz, Tp-3,5-A), 7.96 (1H, d, J = 2.4 Hz, Tp-3,5-A), 7.85 (1H, d, J = 2.4 Hz, Tp-3,5-B), 7.75 (1H, d, J = 2.0 Hz, Tp-3,5-A), 6.69 (2H, t, J = 2.2, 2.2 Hz, Tp-4-B), 6.60 (2H, t, J = 2.4, 2.2 Hz, Tp-4-A), 6.46 (1H, t, J = 2.2, 2.4 Hz, Tp-4-B), 6.37 (1H, t, J = 2.4, 2.2 Hz, Tp-4-A). CV: $E_{1/2}$ = 612, 208, −204 mV. IR: NO = 1710 cm^{-1}.

TpMo(NO)(NH$_3$)(Cl) (18) (not obtained pure in bulk; see Discussion). Under an inert atmosphere, 200 mL of THF and 1.1 g of KTp (4.4 mmol, 1.2 equiv) were added to a round-bottom flask and stirred. To this mixture was slowly added 1.0 g of Mo(Cl)$_5$ (3.7 mmol, 1.0 equiv). After stirring for 30 min, the solution was slowly purged with nitric oxide (1 bubble every 3 to 5 s), and the reaction was monitored by IR. The solution turned bright yellow-green, and a strong IR stretch appeared at 1710 cm^{-1}. Once a peak at 1667 cm^{-1} began to appear, the nitric oxide purge was stopped and the solution was purged vigorously with N$_2$ for 60 min. Then the solution was filtered through a 60 mL medium frit, and the solid was washed with two 30 mL portions of THF. The solution was evaporated to dryness. The resulting solid was dissolved in 200 mL of THF and placed in a round-bottom flask with 1.84 g of activated magnesium (20 equiv), and the mixture was purged with NH$_3$ for 5 min. The solution was placed on a 2 in. silica plug in a 150 mL frit and washed with a 3:1 benzene−ether solution. A green band was eluted with THF and evaporated to dryness. The solid was then reprecipitated from THF with hexanes. The solid was recrystallized by vapor diffusion in methylene chloride and pentane. Bright green crystals were obtained (310 mg, 22% yield). CV: $E_{1/2}$ = −1819 mV, E_{pa} = 491 mV. IR: (HATR) NO = 1600 cm^{-1}.

TpMo(NO)(MeIm)(Cl) (19) (not obtained pure in bulk; see Discussion). This compound was prepared in the same manor as compound **18**. After the addition of the activated magnesium, 1.50 g of MeIm (0.018 mol) was added to the solution and this mixture was stirred for 1.5 h. The product was isolated in the same fashion as **18** (bright green crystals; 22% yield). CV: $E_{1/2}$ = −1673 mV, E_{pa} = 496 mV. IR: (HATR) NO = 1610 cm^{-1}.

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Supporting Information Available: Crystallographic data for **4**, **5**, **11**, and **1*H*-11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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