

Binding and Activation of Aromatic Molecules by a Molybdenum π -Base

Scott H. Meiere, Joseph M. Keane, T. Brent Gunnoe, Michal Sabat, and W. Dean Harman*

Department of Chemistry, University of Virginia, Charlottesville, Virginia 22904-4319

Received August 6, 2002; E-mail: wdh5z@virginia.edu

Over the past decade, we have intensely explored the ability of π -bases to activate aromatic molecules toward otherwise inaccessible organic transformations.^{1,2} In contrast to electron-deficient metal fragments (e.g., $\{\text{Cr}(\text{CO})_3\}$, $\{\text{Mn}(\text{CO})_3\}^+$),³ $16e^-$ metal fragments such as $\{\text{Os}(\text{NH}_3)_5\}^{2+}$ and $\{\text{TpRe}(\text{CO})(\text{MeIm})\}$ (Tp = hydridotris(pyrazolyl)borate; MeIm = 1-methylimidazole) bind aromatic molecules across only two atoms of the aromatic system. Such coordination results in a localization of π -bonds in the uncoordinated portion of the aromatic ring,⁴ and this feature in concert with a strong π -back-bonding interaction renders the bound aromatic molecule highly nucleophilic.^{2,5} Thus, a broad range of carbon electrophiles including acetals, Michael acceptors, nitrilium salts, anhydrides, and methyl triflate have been added to arenes and aromatic heterocycles with a high degree of stereocontrol. The resulting cationic ligands are stabilized by the π -base, and their subsequent treatment with a nucleophile followed by oxidative decomplexation results in dearomatized organic products.^{2,5,6} In principle, this approach could significantly expand the range of organic transformations available for aromatic molecules. However, the high cost associated with stoichiometric use of rhenium and osmium has limited the proliferation of this methodology. The activation of aromatic molecules using π -bases (i.e., η^2 -binding) has until now been demonstrated only with these two heavy metals.

Although rare, examples of thermally stable dihapto-coordinated arenes have been reported with second (e.g., Rh^I ,⁷ $\text{Ru}^{0,8,9}$) and first-row (e.g., Ni^0 ,^{10,11} $\text{Cu}^{I,12}$) transition metals. However, these electron-rich d^8 and d^{10} metals are coordinatively unsaturated, a feature that likely makes them incompatible with strong electrophiles. Rhenium(I) successors to pentaammineosmium(II) were ultimately discovered by adjusting the ligand set of the rhenium such that the metal d^5/d^6 reduction potential closely matched that of the osmium. Specifically, we found that the reduction potential of pentaammineosmium(II) could be approximated using Re^I by replacement of a single ammine with the π -acid CO (Figure 1; N_L = ammonia or nitrogen heterocycle).¹³ We rationalized that a Mo^0 -based system analogous to the known dearomatization fragment $\{\text{TpRe}^I(\text{CO})(\text{MeIm})\}$ would have to include a more π -acidic ligand than CO (Figure 1). According to a comparison of the d^5/d^6 reduction potentials for $[\text{TpMo}(\text{CO})_3]^-$ (0.00 V, NHE), and $\text{TpMo}(\text{CO})_2(\text{NO})$ ($E_{p,a} = 1.12$ V at 100 mV/s),¹⁴ replacement of CO with NO^+ raises the complex potential by > 1 V. Furthermore, comparing the reduction potentials of $\text{Re}(\text{CO})_2(\text{dmppe})_2^+$ (1.66 V)¹⁵ and $\text{Mo}(\text{CO})_2(\text{dmppe})_2$ (0.22 V)¹⁶ suggests that replacement of Re^I with Mo^0 decreases the d^5/d^6 reduction potential by a similar amount. We hypothesized that a metal fragment of the form $\{\text{TpMo}^0(\text{NO})(\text{MeIm})\}$, which is isosteric to $\{\text{TpRe}^I(\text{CO})(\text{MeIm})\}$, might form stable, isolable complexes with arenes that could be employed in the type of electrophilic addition reactions that have been the hallmark of the Os^{II} and Re^I systems described above.

An attractive precursor to our target was the compound $\text{TpMo}(\text{NO})\text{Br}_2$ similar to that reported by McCleverty et al.¹⁷ Reduction of $\text{TpMo}(\text{NO})\text{Br}_2$ (0.125 g, 0.25 mmol) with sodium amalgam (1%,

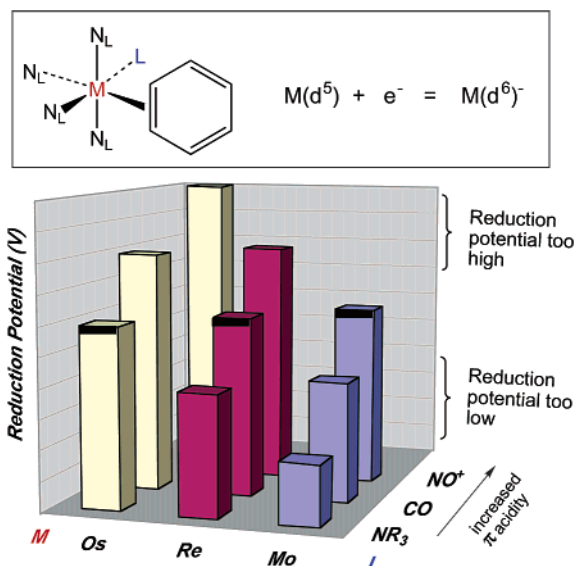


Figure 1. Matching reduction potentials for d^6 metal π -bases. (Black indicates kinetically stable arene complex isolated.)

11 g, 4.8 mmol) in the presence of 1.5 equiv of 1-methylimidazole (MeIm; 0.029 g) and an excess of cyclohexene (1.45 g 17.6 mmol) produces a new compound (**1**) identified as the molybdenum(0) alkene complex $\text{TpMo}(\text{NO})(\text{MeIm})(\text{cyclohexene})$. A cyclic voltammogram of **1** was chemically irreversible at 100 mV/s, with $E_{p,a} = -0.11$ V. This value is almost identical to that of the $\text{TpRe}(\text{CO})(\text{MeIm})$ analogue ($E_{1/2} = -0.05$ V), except that the latter compound shows reversible behavior at this scan rate.

We next repeated the reduction of $\text{TpMo}(\text{NO})\text{Br}_2$ in the presence of MeIm with a series of aromatic molecules including anisole, 1-methylpyrrole, naphthalene, furan, and thiophene. While the reactions with anisole and 1-methylpyrrole did not yield identifiable products, stable Mo^0 complexes of naphthalene (**2**; 41%), furan (**3**; 38%), and thiophene (**4**; 35%, 90% pure) were successfully isolated. Of note, **3** and **4** represent the first examples of η^2 -thiophene or furan complexes not involving a heavy metal.

The structure of **2** was confirmed by single-crystal X-ray diffraction. For comparison, the crystal structure of $\text{TpRe}(\text{CO})(\text{MeIm})(\eta^2\text{-naphthalene})$ (**2R**) was also determined.⁵ An ORTEP diagram for the naphthalene complex **2** shown in Figure 2 is virtually identical to that of its rhenium analogue, save the metal–ligand bond lengths, which are longer than those observed for **2R**. The bond distances for the bound naphthalene rings are identical within experimental error and show an isolated C3–C4 double bond of 1.32 Å (cf. **2R**, 1.34 Å).

The diastereoselectivity for compounds **2–4** is only moderate at 20 °C, showing ratios very similar to those of the rhenium analogues (Scheme 1). Assignments for diastereomers were made on the basis of chemical shift trends observed for $\text{TpRe}(\text{CO})(\text{L})$ analogues.⁴ Compounds **2–4** showed no evidence of decomposition

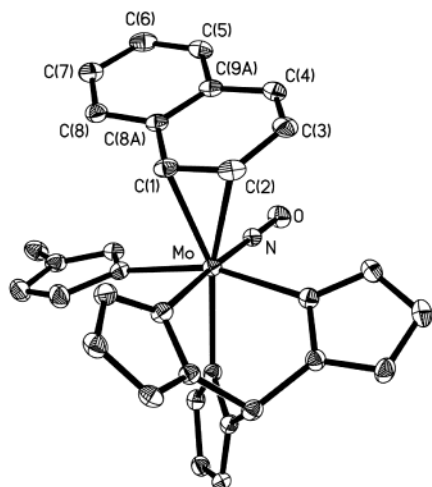
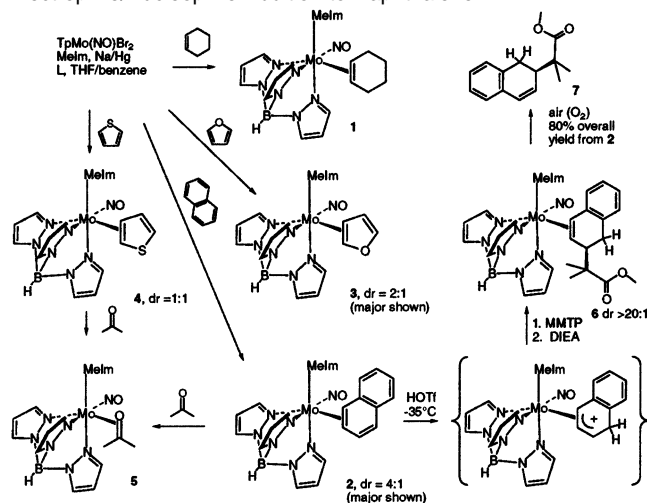


Figure 2. Crystal structure of naphthalene complex **2** (30% ellipsoids). Bond lengths (Å): Mo–C(1) 2.237(3); Mo–C(2) 2.266(3); C(1)–C(2) 1.437(5); C(2)–C(3) 1.449(5); C(3)–C(4) 1.319(5); C(4)–C(9A) 1.447(5) Å; C(9A)–C(8A) 1.413(4); C(8A)–C(1) 1.457(4).

Scheme 1. Synthesis of Complexes **1–5** and the Tandem Electrophile/Nucleophile Addition to Naphthalene



after months when stored as solids under nitrogen. However, these compounds undergo substitution of the aromatic molecule for acetone to form $\text{TpMo}(\text{NO})(\text{MeIm})(\eta^2\text{-acetone})$ **5** with half-lives ranging from 37 to 236 h at 20 °C. Compounds **1–4** readily lose the organic ligand upon exposure to oxygen (>95% after ~5 min); however, the addition of water to an acetone solution of **2** resulted in no observable change in the rate of decomposition. Pertinent to our studies are reports of the related compounds $\text{Cp}^*\text{W}(\text{NO})(\text{PMe}_3)$ -(cyclohexene),¹⁸ $\text{Cp}^*\text{W}(\text{NO})(\text{PPh}_3)(\eta^2\text{-acetone})$, and $\text{Cp}^*\text{W}(\text{NO})(\text{PPh}_3)(\eta^2\text{-ethyl acetate})$.¹⁹ The latter compound gives testament to the extraordinarily π -basic character of the $\{\text{W}(\text{NO})\}^+$ fragment in absence of other π -acids.

To test the tolerance of the molybdenum(0) aromatic complexes to electrophilic/acidic environments, a tandem addition sequence was attempted for the complex $\text{TpMo}(\text{NO})(\text{MeIm})(\eta^2\text{-naphthalene})$ (**2**). In a manner similar to that used with the $\text{TpRe}(\text{CO})(\text{MeIm})(\eta^2\text{-naphthalene})$ analogue,⁵ an acetonitrile solution (–35 °C) of **2** was exposed sequentially to triflic acid, 1-methoxy-2-methyl-1-

trimethylsilyloxypropene, and an amine base. ¹H NMR spectra of a reaction aliquot showed quantitative conversion to a single diastereomer of what we assign to be the 1,2-dihydronaphthalene complex **6**. No evidence of free naphthalene or 1,4-addition product was observed. Stirring the reaction mixture with exposure to air resulted in an 80% overall yield of 2-(1,2-dihydronaphthalen-2-yl)-2-methyl-propinoic acid methyl ester (**7**) following TLC purification. ¹H NMR spectra for this compound match those of authentic samples.⁵

Conclusions. By choosing a ligand set for Mo(0) such that the d^5/d^6 reduction potential approximates that of the known dearomatization agent $\{\text{TpRe}(\text{CO})(\text{MeIm})\}$, a group VI dearomatization agent has been developed and used in a tandem addition reaction sequence. While the kinetic stabilities of the molybdenum furan, naphthalene, and thiophene complexes are less than those of their rhenium analogues, the desired redox properties, structural characteristics, and ability to promote a stereocontrolled dearomatization reaction have been achieved. Given the low cost of molybdenum, this new family of compounds expands the practicality of a dearomatization methodology based on η^2 -coordination. More significantly, a general strategy has been developed for the design of future η^2 dearomatization agents, a synthetically valuable class of molecules which until recently consisted solely of pentaammine-osmium(II).

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Supporting Information Available: Crystallographic data of **2** and **2R** (CIF) and experimental preparations for **1–7** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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