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A Promising New Dearomatization Agent: Crystal Structure, Synthesis, and Exchange Reactions of the Versatile Complex TpRe(CO)(1-methylimidazole)(η^2-benzene) (Tp = Hydridotris(pyrazolyl)borate)

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Summary: The π-basic metal fragment {TpRe(CO)(MeIm)} (MeIm = 1-methylimidazole; Tp = hydridotris(pyrazolyl)borate) binds a variety of aromatic molecules, including benzene, 2,6-lutidine, and 1-methylpyrrole, in an η^2 fashion. Although TpRe(CO)(MeIm)(η^2-benzene) as a solid shows no decomposition over several months at 25 °C under a nitrogen atmosphere, the complex has proven to be a valuable precursor to a variety of other aromatic complexes through ligand exchange reactions in solution.

Two complementary strategies have been developed for the transition-metal-based dearomatization of aromatic molecules. Metal fragments that form η^6 complexes with arenes (e.g., $\{Cr(CO)_3\}$,[1] $\{Mn(CO)_3\}^+$,[2,3] $\{CpFe\}^+$, and $\{CpRu\}^+$ [4−6]) withdraw electron density from the aromatic ring and facilitate nucleophilic addition or deprotonation of the arene ligand.[7,8] In contrast, coordination of the arene with an electron-rich metal fragment such as $\{\eta^2\text{-}Os(NH_3)_5\}^{2+}$ or $\{\eta^4\text{-}Mn(CO)_3\}^-$ activates the aromatic system toward addition of electrophiles.[9−11] Although other η^2-arene complexes are known,[12−16] the exceptional thermal stability and tolerance toward electrophiles make the pentaammineosmium(II) fragment unique in its utility as a synthetic dearomatization agent.[9] For the past decade, we have actively sought alternatives to the osmium(II) system capable of forming thermally stable η^2-arene complexes. Recently, we discovered that the metal fragment $\{TpRe(CO)(PMe_3)\}$ (Tp = hydridotris(pyrazolyl)borate) formed stable η^2-coordinated complexes with furan, thiophene, and naphthalene.[17,18] Unfortunately, benzenes and nitrogen-containing heterocycles eluded complexation. By utilizing a more strongly σ-donating and less sterically demanding ligand in place of the PMe_3 moiety, we hoped to increase the binding affinity for these aromatic ligands.

The synthesis of $TpRe(PMe_3)Br_2$, the Re(III) precursor to complexes of the type $TpRe(CO)(PMe_3)(L_\pi)$ (where L_π is a η^2-coordinated ligand) is readily modified to accommodate the replacement of PMe_3 with other ligands. Thus, a variety of fragments of the general formula $TpRe(L)Br_2$ have been synthesized, including those where L = ${}^tBuNC$, pyridine (py), 1-methylimidazole (MeIm), or NH_3. As expected, moving from PMe_3 to py, MeIm, and NH_3 yields a more electron-rich metal center and decreases the amount of steric bulk cis to the coordination site. Reduction of the these compounds in the presence of CO and an aromatic ligand results in complexes of the form $TpRe(CO)(L)(L_\pi)$. The remainder of this preliminary report will focus on the most promising of these systems where L = MeIm.

The complex $TpRe(MeIm)(Br)_2$ (**1**) was synthesized via a preparation similar to that reported by Mayer for the py analog[19] with minor modifications (bromide derivative, 5 equiv of 1-methylimidazole, and reflux for 4 h). Reduction of $TpRe(MeIm)(Br)_2$ with sodium amalgam (1 wt %) in benzene under a CO atmosphere (1 atm) for 48 h at 20 °C produces the complex TpRe(CO)(MeIm)(η^2-benzene) (**2a**) in 40−45% isolated yield after chromatography (Scheme 1).[20] This complex exhibits a carbonyl stretching frequency ν_{CO} 1794 cm^{-1} (horizontal attenuated total reflectance), which is indicative of an extraordinarily electron-rich metal. A cyclic voltammogram of **2a** features an irreversible oxidation at $E_{p,a} = -0.16$ V (vs NHE; II/I; *N*,*N*-dimethylacetamide (DMAc)

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Scheme 1. Synthesis of TpRe(CO)(MeIm)(L_π)

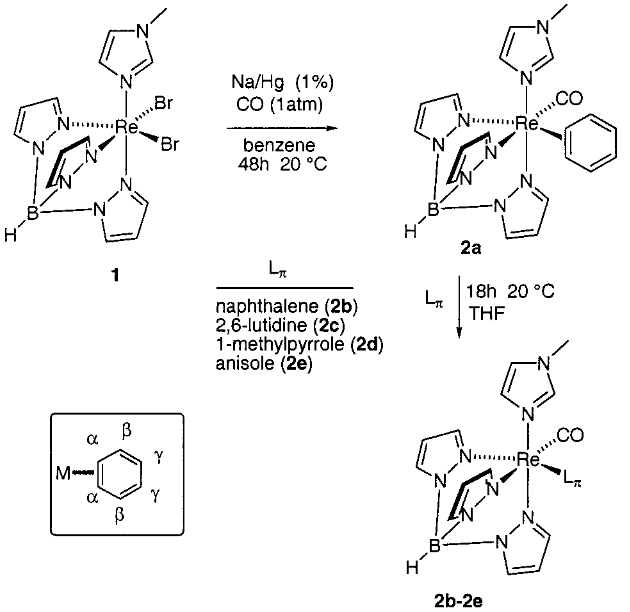

Table 1. IR, CV, and ^{13}C Data for Complexes 2a−e[a]

ligand (L_π)	ν_{CO} (cm^{-1})	$d^6 \rightarrow d^5$ (V, NHE) [Re][b]	[Os][k]	bound C[c] (ppm) [Re]	[Os]
1-methylpyrrole	1792	−0.53[f]	0.14[f]	87.2, 64.7[g]	80.6, 58.2
benzene	1794	−0.16[j]	0.15[f,h]	66.9, 64.9[d]	53.1, 49.6
anisole	1797	−0.15[j]	0.16[f,h]	65.1, 62.9	62.6. 56.7[e]
2,6-lutidine	1799	−0.14[j]	0.45[i,j]	65.8, 64.8	
naphthalene	1803	0.02[f]	0.41[b,f]	64.5, 58.6	57.2, 55.6

[a] [Re] = TpRe(CO)(MeIm)(L_π) and [Os] = $[(NH_3)_5Os(L_\pi)]^{2+}$. [b] DMA/TBAH. [c] Acetone-d_6 unless otherwise noted. [d] −20 °C. [e] CD_3CN. [f] Reported as $E_{1/2}$. [g] $T = -92$ °C. [h] 1-Methylpyrrolidinone. [i] DME/NaOTf. [j] Reported as $E_{p,a}$ for 100 mV/s. [k] Reference 9.

with tetrabutylammonium hexafluorophosphate (TBAH) at 100 mV/s), a value 310 mV more reducing than for the corresponding pentaammineosmium(II) complex (Table 1). A return wave (not initially present) with $E_{p,c} = -1.07$ V is consistent with reduction of a TpRe(CO)(MeIm) complex in which the benzene has been replaced by amide solvent. The complex **2a** as a solid shows no decomposition over several months at 25 °C under a nitrogen atmosphere. In a refluxing benzene solution the half-life for decomposition is slow ($t_{1/2} > 8$ h). When **2a** is exposed to air, the product decomposes slowly as a solid ($t_{1/2} \approx 1$ week) but quickly in solution (e.g., $t_{1/2} \approx 20$ min in acetone). Of note, under none of these conditions has the presence of a binuclear complex analogous to $\{[Os(NH_3)_5]_2((1,2\text{-}\eta^2)\text{:}(3,4\text{-}\eta^2)\text{-benzene})\}^{4+}$ been detected.[21] Most significantly, the benzene complex **2a** undergoes clean substitution of the benzene ligand with a variety of other unsaturated molecules (vide infra). The rate of ligand substitution to form TpRe(CO)(MeIm)(η^2-acetone-d_6) was measured in acetone-d_6, where $t_{1/2} = 1.6$ h at 22 °C, assuming pseudo-first-order kinetics (cf. $t_{1/2} = 8$ h at 22 °C for the pentaammineosmium(II) system).[9]

The ^{1}H NMR spectrum (acetone-d_6, 500 MHz) at 20 °C of **2a** displays sharp Tp and 1-methylimidazole resonances, but the benzene resonances are broadened to the point that they are indiscernible. This fluxionality is due to migration of the metal around the benzene moiety on the NMR time scale. When the sample is cooled to −20 °C, six resonances (dd) are clearly observed (7.1, 6.7, 6.1, 6.0, 3.9, and 3.2 ppm). The ^{13}C NMR spectrum at −20 °C shows bound carbon resonances at 66.9 and 64.9 ppm (acetone-d_6, 125 MHz).

The solid-state structural analysis of **2a** was made possible by X-ray diffraction studies.[22] A single crystal was grown from a concentrated benzene/THF solution layered with hexanes. Although crystal structures of other mononuclear η^2-benzenes have been reported, they are only for "layered structures" with copper[23,24] and silver[25] or for entirely fluorinated arenes,[26,27] which show no significant lengthening in arene bond distances. The observed bond lengths for the crystal of **2a** provide insight into the reactivity of aromatics when η^2-bound to an electron-rich metal. The distortion of the bond lengths from those of free benzene demonstrates the similarity between simple diene distances and the lengths of the uncoordinated portion of the bound benzene (Figure 1).[28] Thus, η^2-coordination *dearomatizes* the aromatic ligand in a structural as well as a reactivity sense.

Taking advantage of the relative lability of the benzene ligand in complex **2a**, a variety of complexes of other aromatic molecules have been synthesized (Figure 2) with isolated yields ranging from 75 to 85%.[29] Examples include complexes of naphthalene (**2b**), 2,6-lutidine (**2c**), 1-methylpyrrole (**2d**), and anisole (**2e**).

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(20) Synthesis of **2a**: 1% Na/Hg (80 g, 34.8 mmol Na) was added to a benzene (1.8 L) suspension of **1** (8.0 g, 12.4 mmol). The suspension was purged with CO (20 min) and stirred vigorously under a slow CO purge (23 °C, 48 h). The mixture was moved into a glovebox and filtered through Celite, and the filtrate was placed onto a silica column. The product was obtained with 3/2 benzene/ether as the eluent. Fractions containing ν_{CO} 1795 cm^{-1} were combined. The solvent volume was reduced by half in vacuo, hexanes were added to restore the initial volume, and the solvent was reduced by half. The previous step was repeated, the suspension was filtered, and the yellow solid was dried in vacuo. Yield: 2.93 g (40%). ^{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, 64.9 (benzene 1, 2), 34.3 (NMe). IR: ν_{CO} 1794 cm^{-1} (vs), $\nu_{BH} = 2480$ cm^{-1} (w). CV: $E_{p,a} = -0.16$ V (II/I). Anal. Calcd for $ReC_{20}H_{22}N_8BO\cdot0.75C_6H_6$: C, 45.55; H, 4.13; N, 17.34. Found: C, 45.45; H, 4.24; N, 17.13.

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(22) Crystallographic data: orange prism-like crystal (0.22 mm × 0.47 mm × 0.86 mm), Mo Kα radiation ($\lambda = 0.710\,73$ Å). A total of 10 700 reflections were collected at 148 K to a maximum 2θ angle of 50.00° (0.84 Å resolution), of which 4103 were independent. Final cell constants: $a = 10.1935(5)$ Å, $b = 18.3070(9)$ Å, $c = 12.5987(6)$ Å, $\beta = 96.299(1)°$. The structure was solved and refined using the Bruker SHELXTL software package, using the monoclinic space group $P2_1/n$, with $Z = 4$ for the formula unit $C_{23}H_{25}BN_8ORe$. The final anisotropic full-matrix least-squares refinement on F^2 converged at R1 = 3.00%, wR2 = 6.10%, and a goodness of fit of 1.042. The largest peak on the final difference map was 1.527 e/Å^3.

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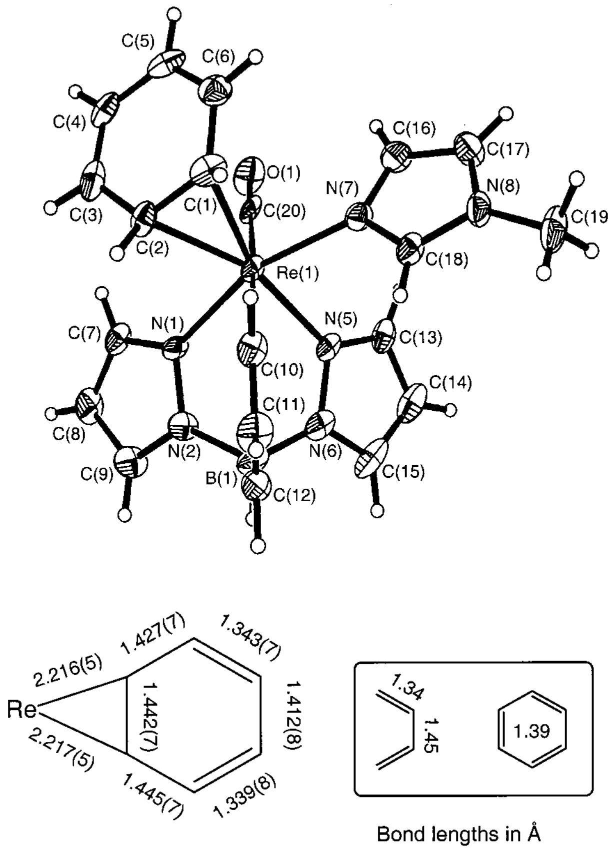
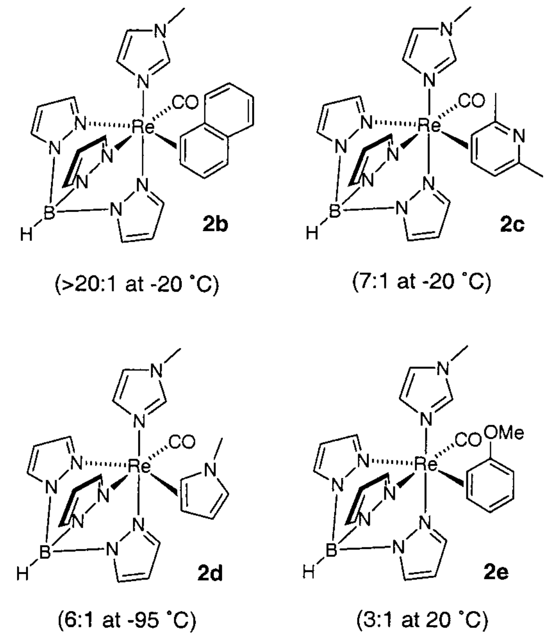


Figure 1. ORTEP diagram of TpRe(CO)(MeIm)(η^2-benzene) (**2a**) (50% thermal ellipsoids). N(3) and N(4) are not shown. Select bond distances (Å) and angles (deg): Re(1)–C(1), 2.216(5); Re(1)–C(2), 2.217(5); Re(1)–C(20), 1.839(6); Re(1)–N(1), 2.139(4); Re(1)–(N3), 2.221(4); Re(1)–N(5), 2.141(4); Re(1)–N(7), 2.150(4); C(1)–C(2), 1.442(7); C(2)–C(3), 1.445(7); C(3)–C(4), 1.339(8); C(4)–C(5), 1.412(8); C(5)–C(6), 1.343(7); C(20)–O(1), 1.181(6); C(1)–Re(1)–C(2), 37.96(19); C(1)–Re(1)–C(20), 94.3(2); C(2)–Re(1)–C(20), 95.2(2); N(1)–Re(1)–C(20), 91.69(19); N(3)–Re(1)–C(20), 175.96(19); N(7)–Re(1)–C(20), 93.5(2); N(1)–Re(1)–N(3), 84.57(15); N(1)–Re(1)–N(7), 161.17(15); N(3)–Re(1)–N(5), 85.55(16).

Table 1 lists infrared spectroscopic (IR), cyclic voltammetric (CV), and ^{13}C NMR data for these complexes.

With the bound olefin bond oriented perpendicular to the metal carbonyl bond in order to optimize back-bonding,[17] any substituents at a β-carbon (see Scheme 1) of the bound ring prefer to orient toward the MeIm moiety. Although pyrazole and imidazole are similar in size, the rigidity of a Tp pyrazole creates a more sterically encumbering environment for substituents at the β-carbon. The uncoordinated ring of naphthalene, for example, lies toward the imidazole ring for the thermally preferred isomer. In contrast, the analogous PMe_3 system prefers to orient the unbound ring of naphthalene in the opposite direction of the auxiliary ligand.



2b

(>20:1 at -20 °C)

2c

(7:1 at -20 °C)

2d

(6:1 at -95 °C)

2e

(3:1 at 20 °C)

Figure 2. Diastereomeric selectivity of **2b**–**e** (major isomer shown).

The naphthalene compound **2b** exhibits a diastereomeric ratio (dr) of 5:1 at 20 °C and >20:1 at −20 °C. The NMR spectrum of the lutidine complex **2c** is slightly broadened at 20 °C; however, a dr of 7:1 was determined at −20 °C. The 1-methylpyrrole resonances of **2d** are broad at 20 °C but sharpen at lower temperature, exhibiting a dr of 6:1 at −95 °C, where the methyl group is oriented toward the imidazole ligand. Finally, the anisole compound **2e** is present in a 3:1 ratio at 20 °C with a similar ratio at −20 °C.

In conclusion, the {TpRe(CO)(MeIm)} fragment represents a viable alternative to the $\{Os(NH_3)_5\}^{2+}$ system by providing a route to a variety of thermally stable η^2-aromatic systems. In addition, the rhenium system provides the potential for selective binding of a prochiral aromatic molecule to a chiral metal center. Studies on organic transformations with these systems are currently underway.

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Supporting Information Available: Text and tables giving synthetic procedures and full characterization data for complexes **1** and **2a**–**e** as well as details of the X-ray diffraction study. This material is available free of charge via the Internet at http://pubs.acs.org.

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(29) To a 100 mL round-bottom flask was added **2a** (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 (18 h, 23 °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. Products were isolated as yellow or beige powders. Yields: 75–85%.