4364 *Organometallics* **2003,** *22,* 4364−4366

Dearomatization of Benzene, Deamidization of *N,N*-Dimethylformamide, and a Versatile New Tungsten π Base

Peter M. Graham, Scott H. Meiere, Michal Sabat, and W. Dean Harman*

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

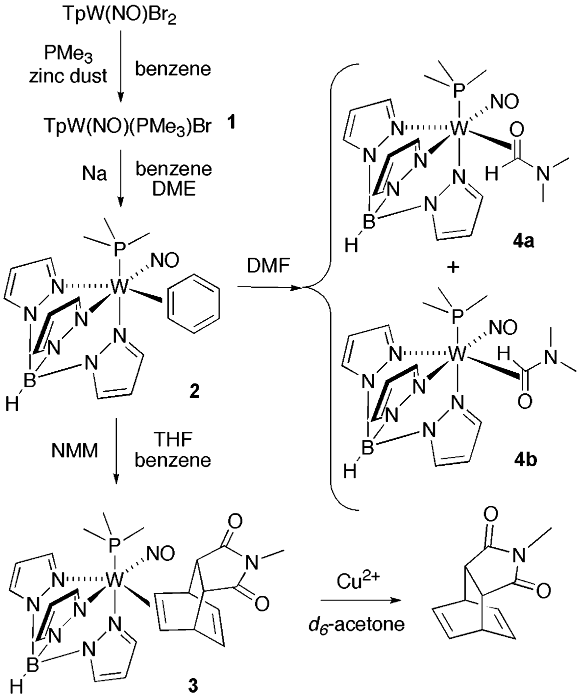
Received July 30, 2003

Summary: The first group VI η^2-coordinated benzene complex, TpW(NO)(PMe$_3$)(η^2-benzene), is reported. The bound arene is activated toward Diels−Alder cycloaddition, and substitution of the arene with DMF yields a rare example of a η^2-coordinated amide.

Over the past decade, we have endeavored to develop π-basic metal fragments with the ability to bind aromatic molecules and activate them toward otherwise inaccessible organic transformations, with the ultimate goal of expanding the array of reactions available for this ubiquitous class of molecules.[1−3] These electron-rich transition-metal fragments such as $\{Os(NH_3)_5\}^{2+}$ and {TpRe(CO)(MeIm)} (Tp = hydridotris(pyrazolyl)-borate, MeIm = 1-methylimidazole) coordinate aromatic molecules across only two atoms of the aromatic ring and thereby localize the π-bonds of the uncoordinated portion, rendering the molecule highly nucleophilic.[2,4,5] Recently, the first group VI dearomatization fragment, {TpMo(NO)(MeIm)}, was synthesized[6] by using a strategy of matching d^5/d^6 reduction potentials with previously developed rhenium(I) and osmium(II) systems. Although this complex forms stable η^2 complexes with naphthalene and furan, complexes of benzene or pyrrole could not be isolated. We hypothesized that a heavy-metal analogue of the form $\{TpW^0(NO)(L)\}$ could more effectively back-bond with aromatic molecules, thereby strengthening the metal−arene bond to the point that a full range of complexes with aromatic molecules could be isolated and characterized.

The difference in d^5/d^6 reduction potentials between $TpRe(CO)_3$[7] and $TpW(NO)(CO)_2$[8] suggests that the fragment {TpW(NO)} is approximately 300 mV more reducing than {TpRe(CO)}.[9] This observation, along with a comparison of electrochemical data for the series of complexes {TpRe(CO)(L)} (L = NH$_3$, MeIm, py, PMe$_3$, t-BuNC)),[10] pointed to the target TpW(NO)(PMe$_3$)(η^2-benzene) (**2**) as being a close electrochemical match to the known complex TpRe(CO)(MeIm)(η^2-benzene).

Scheme 1. Synthesis of 1−4



The synthesis of TpW(NO)(PMe$_3$)(η^2-benzene) (**2**) is outlined in Scheme 1. Its precursor, TpW(NO)Br$_2$, was prepared from W(CO)$_6$ in three steps (overall 70% yield) using a procedure similar to that described by Deane and Lalor[11] and McCleverty.[12] The 17e complex TpW(NO)(PMe$_3$)Br (**1**) was then synthesized by stirring TpW(NO)Br$_2$ in the presence of PMe$_3$ and Zn dust. Finally, **1** was stirred for 24 h in benzene/DME (0.5 vol % DME) in the presence of Na pieces, generating TpW(NO)(PMe$_3$)(η^2-benzene) (**2**; 35%), the first example of an isolable mononuclear η^2-benzene complex formed from a group VI or earlier transition metal.[13−15] Complex **2** can also be formed directly from the W(II) precursor by a two-stage reduction process (Supporting Information) in 38% yield. A cyclic voltammogram of **2** features an irreversible oxidation at $E_{p,a} = -0.13$ V (NHE; I/0; *N,N*-dimethylacetamide (DMA)), a value that

---

(1) Smith, P. L.; Chordia, M. D.; Harman, W. D. *Tetrahedron* **2001**, 8203.

(2) Harman, W. D. *Chem. Rev.* **1997**, *97*, 1953.

(3) Chordia, M. D.; Smith, P. L.; Meiere, S. H.; Sabat, M.; Harman, W. D. *J. Am. Chem. Soc.* **2001**, *123*, 10756.

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

(5) Valahovic, M. T.; Gunnoe, T. B.; Sabat, M.; Harman, W. D. *J. Am. Chem. Soc.* **2002**, *124*, 3309.

(6) Meiere, S. H.; Keane, J. M.; Gunnoe, T. B.; Sabat, M.; Harman, W. D. *J. Am. Chem. Soc.* **2003**, *125*, 2024−2025.

(7) Gunnoe, T. B.; Sabat, M.; Harman, W. D. *J. Am. Chem. Soc.* **1998**, *120*, 8747.

(8) Trofimenko, S. *Inorg. Chem.* **1969**, *8*, 2675.

(9) Unpublished results.

(10) Meiere, S. H.; Brooks, B. C.; Gunnoe, T. B.; Carrig, E. H.; Sabat, M.; Harman, W. D. *Organometallics* **2001**, *20*, 3661.

(11) Deane, M. E.; Lalor, F. J. *J. Organomet. Chem.* **1974**, *67*, C19.

(12) McCleverty, J. A.; Rae, A. E.; Wolochowicz, I.; Bailey, N. A.; Smith, J. M. A. *J. Chem. Soc., Dalton Trans.* **1982**, 429−438.

(13) Reinartz, S.; White, P. S.; Brookhart, M.; Templeton, J. L. *J. Am. Chem. Soc.* **2001**, *123*, 12724.

(14) Tagge, C. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1996**, *118*, 6908.

(15) Chin, R. M.; Dong, L.; Duckett, S. B.; Partridge, M. G.; Jones, W. D.; Perutz, R. N. *J. Am. Chem. Soc.* **1993**, *115*, 7685.

10.1021/om030560h CCC: $25.00 © 2003 American Chemical Society
Publication on Web 09/30/2003

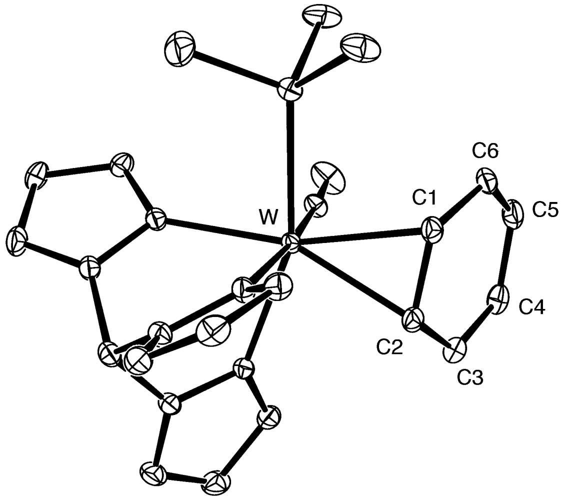


Figure 1. Solid-state molecular structure of benzene complex **2** (30% ellipsoids). Selected bond lengths (Å): W−C1, 2.272(3); W−C2, 2.237(3); C1−C2, 1.458(4); C2−C3, 1.447(4); C3−C4, 1.356(4); C4−C5, 1.435(4); C5−C6, 1.355(5); C1−C6, 1.458(4).

is within 100 mV of that observed for TpRe(CO)(MeIm)-(η^2-benzene).[16] The nitrosyl stretching frequency of **2** was measured to be 1564 cm^{-1}. At room temperature, the ^1H NMR spectrum of **2** shows a set of nine Tp resonances, a PMe_3 doublet, and six resonances corresponding to each of the benzene protons. By comparison, ^1H NMR spectra (20 °C) for the rhenium and osmium benzene complexes show severely broadened benzene features, owing to a more rapid intrafacial linkage isomerization process.

The rate of benzene dissociation for **2**, as measured in acetone-d_6, is $t_{1/2} = 1.1$ h at 22 °C, assuming pseudo-first-order kinetics. This value compares to 1.6 h for the rhenium analogue[16] and 8 h for pentaammineosmium-(II)[2] (both at 22 °C). A single crystal of **2** was grown by vapor diffusion of hexanes into a concentrated benzene solution of the complex. Structural analysis by X-ray diffraction (Figure 1) finds a benzene ligand with alternating long and short C−C bonds for the uncoordinated fragment, consistent with a localized π system.

To compare the ability of the new tungsten complex **2** to activate aromatic ligands with that of its rhenium predecessor, **2** was combined with NMM (*N*-methylmaleimide) in a cosolvent mixture of benzene and THF and stirred for 5 h at 22 °C. The expected Diels−Alder cycloadduct **3** is formed as a single diastereomer with a specific rate that is 4 times greater than for rhenium (pseudo-first-order conditions; 22 °C). The NMM olefin complex was also observed but could be minimized by increasing the concentration of NMM to enhance the rate of cycloaddition. Demetalation of the cycloadduct was achieved with addition of $Cu(OTf)_2$ in a yield of 50% (NMR).

Preliminary data indicate that the compound **2** is a suitable precursor to a number of other interesting π complexes. For example, when **2** is stirred in DMF, the benzene ligand is replaced by the solvent to form the remarkable complex TpW(NO)(PMe_3)(η^2-DMF) (**4**). The nitrosyl stretching frequency for the new complex is

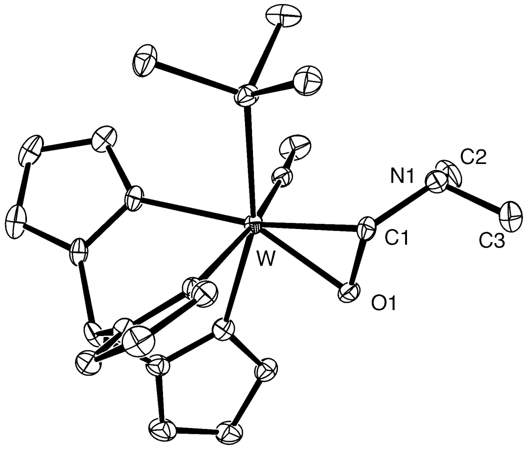


Figure 2. Solid-state molecular structure of DMF complex **4** (30% ellipsoids). Selected bond lengths (Å): W1−C1, 2.159(7); W1−O1, 2.025(5); C1−O1, 1.340(9); C1−N1, 1.446(10); N1−C2, 1.470(11); N1−C3, 1.478(10).

1547 cm^{-1}, 20 cm^{-1} lower than that observed for the benzene complex and similar to what Legzdins et al. report for Cp*W(NO)(PMe_3)(η^2-ethyl acetate).[17] The ^1H NMR spectrum of **4** at 22 °C appears as a single set of resonances. However, upon cooling of the sample to −60 °C, resonances broaden and split into two sets of signals corresponding to two isomers (**4a**,**b**; Scheme 1), most probably coordination diastereomers, present in a 2:1 ratio that favors isomer **4b**. Of particular interest are the two signals corresponding to the formyl protons at 4.01 and 5.31 ppm, the latter of which shows a J_{HP} value of 12.2 Hz. As observed for TpRe(CO)(PMe_3)(ethene), the bound sp^2 carbon that extends toward the PMe_3, as well its associated protons, strongly couples with the phosphorus. A coalescence temperature of 0 °C (±5 °C) was determined for the two formyl signals corresponding to a k value of 1.5×10^3 s^{-1} ($\Delta G^\ddagger = 12 \pm 0.2$ kcal/mol) for the interconversion of diastereomers. Almost certainly the mechanism for this interconversion involves η^1 coordination of the oxygen. By comparison, $\Delta G^\ddagger$ for η^2−η^1 isomerization is 17 kcal/mol for the complex [Os-$(NH_3)_5$(η^2-acetone)]$^{2+}$.[18] While it is possible that the two species observed by NMR are related by a metal−ligand bond rotation (rotamers), this scenario would be inconsistent with the steric profile developed for the TpReCO system.[4]

A crystal of **4** was obtained by vapor diffusion of hexanes into a concentrated DME solution containing a few drops of DMF. The ORTEP diagram of **4**, which we believe to be the first structurally characterized example of an η^2 amide complex, is shown in Figure 2. Of particular interest, the nitrogen has pyramidal geometry, indicating that the nitrogen lone pair no longer interacts with the C=O bond. Consistent with this, the C1−N1 bond has been lengthened upon coordination by 0.11 Å (from 1.341(6) Å[19] to 1.446(10) Å). Treatment of the bound amide complex with pyridinium triflate ($pK_a \approx 5$) results in protonation of the nitrogen,

---

(16) Meiere, S. H.; Brooks, B. C.; Gunnoe, T. B.; Sabat, M.; Harman, W. D. *Organometallics* **2001**, *20*, 1038.

(17) Burkey, D. J.; Debad, J. D.; Legzdins, P. *J. Am. Chem. Soc.* **1997**, *119*, 1139.

(18) Harman, W. D.; Sekine, M.; Taube, H. *J. Am. Chem. Soc.* **1988**, *110*, 2439.

(19) Borrmann, H.; Persson, I.; Sandstrom, M.; Stalhandske, M. V. *J. Chem. Soc., Perkin Trans. 2* **2000**, 393−402.

indicating that the basicity of the bound amide is significantly greater than that of a typical organic amide (p$K_a \approx -1$).[20]

The development of a tungsten dearomatization fragment represents a significant advance in metal-mediated dearomatization chemistry. In practical terms, the cost of preparation of bound aromatics is well below that of the similar rhenium or osmium systems, and they can be routinely prepared on an 8 g scale. Furthermore, {TpW(NO)(PMe_3)} promises to bind an even greater range of possible π ligands than its rhenium and osmium counterparts, as well as offer greater ability to activate these ligands toward the addition of electrophilic reagents.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. This work was also supported by the NSF (Grant Nos. CHE0111558 and 9974875) and the NIH (NIGMS: Grant No. R01-GM49236).

Supporting Information Available: Crystallographic data of **2** and **4**, as CIF files, as well as text giving experimental preparations and characterization data for **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM030560H

---

[20] Zabicky, J., Ed. *The Chemistry of Amides*; Interscience: London, 1970.