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Mechanistic Studies of the Facile Four-Electron Reduction of Azobenzene at a Single Tungsten Metal Center

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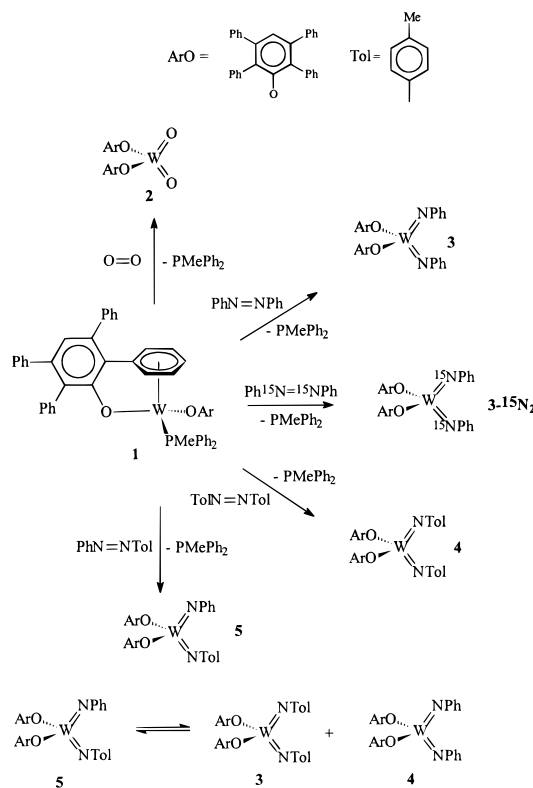
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Although the reduction of dioxygen and isoelectronic diazo compounds can be achieved by a plethora of metal-based systems, evidence presently is lacking concerning the direct four-electron reduction of these substrates at a single metal site.^{1–5} We communicate here our studies of the reaction of a mononuclear tungsten aryloxo compound with O₂ and RN=NR molecules to produce the corresponding bis(oxo) and bis(imido) derivatives. Mechanistic studies conclusively prove that reduction of the diazo compound occurs at a single metal center.

The emerald green complex [W(OC₆HPh₃-η⁶-C₆H₅)(OAr)(PMePh₂)] **1** (OAr = 2,3,5,6-tetraphenylphenoxide) formally contains a d⁴-W(II) metal center stabilized by an η⁶-interaction with the *o*-phenyl ring of one of the aryloxo ligands (Scheme 1).⁶ This thermally stable 16-electron species will react with a wide variety of substrates in hydrocarbon solvents. Exposure to oxygen results in rapid formation of the dioxo complex **2** along with free PMePh₂ (Scheme 1),^{7,8} while reaction with azobenzene produces the corresponding bis(phenylimido) derivative **3** which has been characterized by

Scheme 1^a



^a ArO = C₆HPh₄O. Tol = 4-MeC₆H₄.

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(1) (a) Brown, S. N.; Mayer, J. M. *Inorg. Chem.* **1992**, *31*, 4091 and references therein. (b) Hall, K. A.; Mayer, J. M. *J. Am. Chem. Soc.* **1992**, *114*, 10402. (c) *Oxygen Complexes and Oxygen Activation by Transition Metals*; Martell, A. E.; Wawyer, D. T., Eds.; Plenum: New York, 1988. (d) Nugent, W. A.; Mayer, J. A. *Metal-Ligand Multiple Bonds*; Wiley-Interscience: New York, 1988. (e) Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401. (f) Holm, R. H. *Coord. Chem. Rev.* **1990**, *100*, 183. (g) Wigley, D. E. *Prog. Inorg. Chem.* **1994**, *42*, 239.

(2) The bimetallic cleavage of azobenzene by transition metal systems (typically d²) has precedence; see, for example: (a) Cotton, F. A.; Duraj, S. A.; Roth, W. J. *J. Am. Chem. Soc.* **1984**, *106*, 4749. (b) Hill, J. E.; Profflet, R. D.; Fanwick, P. E.; Rothwell, I. P. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 664. (c) Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Inorg. Chem.* **1991**, *30*, 1143.

(3) The intra- and intermolecular cleavage of 1,2-diphenylhydrazine to generate phenylimido ligands has been reported; see: (a) Arney, D. S. J.; Burns, C. J. *J. Am. Chem. Soc.* **1995**, *117*, 9448. (b) Zambrano, C. H.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1994**, *13*, 1174.

(4) Organic azides are a common substrate for the synthesis of metal imido complexes; see: (a) Hillhouse, G. L.; Haymore, B. L. *J. Am. Chem. Soc.* **1982**, *104*, 1537. (b) Proulx, G.; Bergman, R. G. *J. Am. Chem. Soc.* **1995**, *117*, 6382. (c) Fickes, M. G.; Davis, W. M.; Cummins, C. C. *J. Am. Chem. Soc.* **1995**, *117*, 6384.

(5) Many elegant strategies for the bimetallic rupture of multiple bonds to oxygen and nitrogen have been developed; for recent examples, see: (a) Bryan, J. C.; Mayer, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 2298. (b) Laplaza, C. E.; Cummins, C. C. *Science* **1995**, *268*, 861. (c) Laplaza, C. E.; Odom, A. L.; Davis, W. M.; Cummins, C. C.; Protasiewicz, J. D. *J. Am. Chem. Soc.* **1995**, *117*, 4999 and references therein. (d) Legzdins, P.; Young, M. A.; Batchelor, R. J.; Einstein, F. W. B. *J. Am. Chem. Soc.* **1995**, *117*, 8798. (e) Lee, S. Y.; Bergman, R. G. *J. Am. Chem. Soc.* **1995**, *117*, 5877.

(6) Lockwood, M. A.; Fanwick, P. E.; Rothwell, I. P. *Polyhedron* **1995**, *14*, 3363.

(7) (a) Addition of O₂ to [Mo(OR)₄] has been shown to yield [(O)₂Mo(OR)₂] along with alkoxy radicals: Chisholm, M. H.; Folting, K.; Huffman, J. C.; Kirkpatrick, C. C. *Inorg. Chem.* **1984**, *23*, 1021. (b) It is interesting to contrast the facile cleavage of O₂ by this W(II) aryloxo system and the stability of species such as [(H₂O)₅Cr(O₂)]²⁺; see: Bakac, A.; Scott, S. L.; Espenson, J. H.; Rodgers, K. R. *J. Am. Chem. Soc.* **1995**, *117*, 6483 and references therein.

(8) The ¹H NMR spectrum of **2** in C₆D₆ shows only a complex pattern from δ 6.9 to 7.5 ppm. The observed and calculated FAB mass spectra of **2** are contained in the supporting information.

X-ray diffraction.⁹ This latter reaction can be readily monitored in C₆D₆ solvent by following changes in the aromatic region of the ¹H NMR spectrum. Kinetic studies show that the formation of **3** is inhibited, but not reversed, by the addition of PMePh₂ to the initial reaction mixture of **1** and PhN=NPh. The reactivity of **1** can be exploited (Scheme 1) for the synthesis of the isotopically labeled compounds [(ArO)₂W(=¹⁵NPh)₂] **3-¹⁵N₂** and [(ArO)₂W(NC₆D₅)₂] **3-²H₁₀**. The reaction of **1** with Ph¹⁵N=¹⁵NPh can be monitored by ¹⁵N NMR spectroscopy and shows that all of the ¹⁵N label is cleanly converted into **3-¹⁵N₂** with no detectable intermediates or minor products.¹⁰

Important mechanistic insights into this reactivity are gained by utilizing the symmetric and asymmetric substrates C₆H₅-N=NC₆H₅, 4-MeC₆H₄N=NC₆H₄-4-Me, and C₆H₅N=NC₆H₄-4-Me (Scheme 1).¹¹ The 500 MHz ¹H NMR spectra of the crude reaction mixtures show that three distinct products are produced. An important observation is that the asymmetric diazo substrate initially produces only the mixed imido product **5** with no detectable amounts of **3** or **4** (Figure 1). Interestingly, this solution of **5** in C₆D₆ converts slowly over days to a 1:2:1 mixture of **3**:**5**:**4** (Figure 1). A similar mixture can be obtained after several days by combining solutions of **3** and **4** in C₆D₆.

(9) Crystal data at 213 K for WO₂N₂C₇₂H₅₂ **3**: *a* = 11.361(6) Å, *b* = 20.414(6) Å, *c* = 26.125(5) Å, α = 110.97°, β = 91.40(3)°, γ = 100.97(3)°, and *Z* = 4 in space group P1 bar. Two independent molecules with almost identical structural parameters were present in the unit cell; selected interatomic distances (Å) and angles (deg) for molecules 1 [2] are W–O, 1.897(6) [1.900(6)], 1.929(6) [1.942(6)]; W–N, 1.702(7) [1.777(5)], 1.778(5) [1.697(7)]; O–W–O, 118.8(2) [120.7(2)]; N–W–N, 108.3(3) [108.2(3)]. An ORTEP view of **3** is contained in the supporting information. There are many examples of molecules containing the d⁰ [W(=NR)₂] function; see Table XXX of ref 1g.

(10) ¹⁵N NMR data (50.66 MHz, C₆D₆) for **3-¹⁵N₂**: δ (relative to nitromethane) 101.87, ¹*J*(¹⁸³W–¹⁵N) = 136 Hz. We have been unable to resolve separate signals for [(ArO)₂W(=¹⁵NPh)₂] and [(ArO)₂W(=¹⁵NPh)(=¹⁴NTol)] in a solution formed by mixing **3-¹⁵N₂** with **4**.

(11) (a) Bigelow, H. E.; Robinson, D. B. *Org. Synth.* **1955**, *3*, 103. (b) Ayyangar, N. R.; Naik, S. N.; Srinivasan, K. V. *Tetrahedron Lett.* **1989**, *30*, 7253.

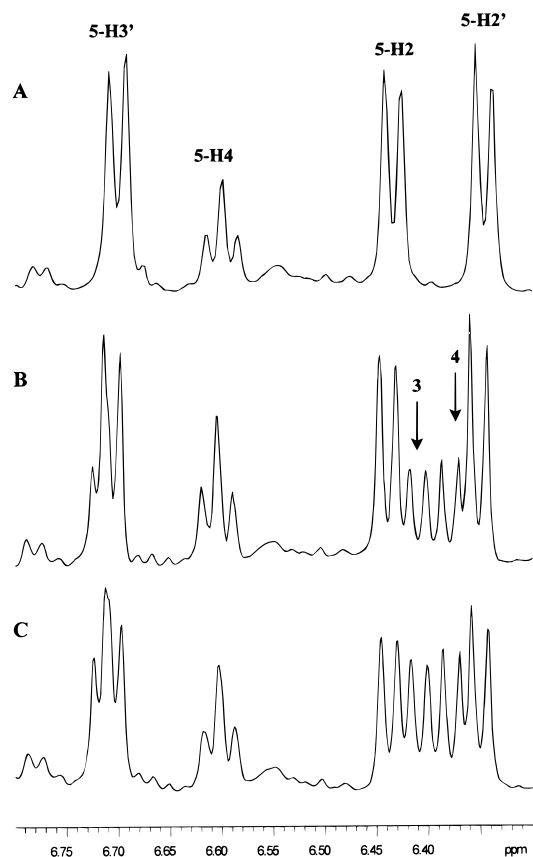


Figure 1. ^1H NMR (500 MHz, C_6D_6) spectra of the aromatic region of the reaction of **1** with excess $\text{PhN}=\text{NTol}$: (A) initial spectrum showing **5**; (B) and (C) same sample after 24 and 72 h at room temperature showing equilibration between **3**, **4**, and **5**. Protons **5-H2** and **5-H2'** are the ortho protons of the NPh and NTol groups in compound **5**, respectively.

The pathway that leads to exchange can be shown *not* to involve overall metathesis of diazo compounds.¹² Hence

(12) (a) Mayer, K. E.; Walsh, P. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1995**, *117*, 974. (b) The metathesis of P–P double bonds has recently been reported; see: Dillon, K. B.; Gibson, V. C.; Sequeira, L. J. *J. Chem. Soc., Chem. Commun.* **1995**, 2429.

formation of **3** and **4** from **5** in the presence of excess $\text{C}_6\text{H}_5\text{N}=\text{NC}_6\text{H}_4\text{-4-Me}$ does not produce any detectable (NMR/GC) amounts of either of the symmetric diazo compounds. This is confirmed by the addition of $\text{Ph}^{15}\text{N}=\text{N}^{15}\text{Ph}$ to **3** which fails to produce (^{15}N NMR) any detectable amounts of ^{15}N -labeled **3** over weeks at 25 °C.

Previous theoretical analysis of the single metal center reduction of O_2 by Mayer et al.^{1a} has shown that a concerted opening of a d^2 -metal peroxo species to the corresponding d^0 -metal dioxo product is symmetry disallowed. A preliminary orbital analysis of the azobenzene reaction uncovered here shows that the concerted coordination and cleavage of *cis*-azobenzene by a bent d^4 - $[\text{W}(\text{OAr})_2]$ unit is feasible (see the supporting information).¹³

We can, therefore, conclude that the facile, four-electron reduction of diazo compounds occurs at these mononuclear tungsten metal centers to produce the corresponding bis(imido) derivatives. The exchange of imido groups between tungsten centers can occur, but azobenzene metathesis does not account for this ligand exchange reaction. Further mechanistic and theoretical studies of these and related reactions are underway.

Acknowledgment. We thank the National Science Foundation for financial support of this research.

Supporting Information Available: Experimental procedures and supporting spectroscopic data, ORTEP view and crystallographic study of $[(\text{ArO})_2\text{W}(\text{NPh})_2]$ **3**, kinetic data for the reaction of **1** with azobenzene, and orbital analysis of the interaction of a *cis*-diazo substrate with a bent $[\text{W}(\text{OAr})_2]$ fragment (53 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(13) Although orbital analysis shows that concerted cleavage of a *cis*-diazo substrate is feasible, the actual pathway for cleavage at a single tungsten metal center may involve undetected intermediates containing η^1 - or η^2 -diazo ligands; for η^1 -diazo coordination to tungsten, see: Cheng, T.-Y.; Peters, J. C.; Hillhouse, G. L. *J. Am. Chem. Soc.* **1994**, *116*, 204 and references therein. For η^2 -diazo coordination to tungsten metal centers, see: Glassman, T. E.; Vale, M. G.; Schrock, R. R. *Inorg. Chem.* **1992**, *31*, 1985 and references therein. Diazo ligands bridging two Group 6 metals have been characterized; for a recent review of diazo complexes, see: Sutton, D. *Chem. Rev.* **1993**, *93*, 995.