

Figure 1. (A) UV-visible absorption spectra in acetonitrile under argon (0.1-cm path length cell) for 0.5 mM AQ (—), for the combination of 0.5 mM AQ and 1.5 mM (Bu₄N)OH (in MeOH) at -20 °C (---), and for the latter solution after it was warmed to 25 °C (···). (B) Initial rates of formation of AQ^{••} from the reaction of AQ with (Bu₄N)OH in MeCN under argon at 25 ± 1 °C. The ordinate is the initial rate of appearance for AQ^{••} (mM s⁻¹) as monitored spectrophotometrically at 543 (ε 12 mM⁻¹ cm⁻¹) in a 1-cm cell. The solid curve was calculated from eq 6 with K₁ = 4.3 × 10⁴ M⁻¹ s⁻¹ and k₂ = 1.2 M⁻¹ s⁻¹.

system is via reaction 3. Any O₂ formed reacts with AQ^{••} to form O₂^{•-}.¹⁹



Combination of reaction 1 with material balance relations for AQ and OH⁻ and the expression for the rate of formation of AQ^{••} via Reaction 2 gives an expression for the initial rate

$$\left(\frac{d[\text{AQ}^{\bullet\bullet}]}{dt} \right)_{t=0} = k_2[\text{AQ}(\text{OH})^{\bullet-}][\text{AQ}] = k_2(C_{\text{AQ}} - C_{\text{OH}^-} + [\text{OH}^-]) \left(\frac{C_{\text{AQ}}K_1[\text{OH}^-]}{1 + K_1[\text{OH}^-]} \right) \quad (6)$$

with C_{AQ} and C_{OH⁻} the initial concentrations of AQ and OH⁻. The parameters K₁ and k₂ have been determined by adjusting their values to give the best fit to the initial-rate data (Figure 1B). The respective values of K₁ and k₂ for AQ are (4.3 ± 0.5) × 10⁴ M⁻¹ and 1.2 ± 0.1 M⁻¹ s⁻¹ and for 2-EtAQ are 4 × 10⁴ M⁻¹ and 4.2 M⁻¹ s⁻¹. The solid curve of Figure 1B results from the best-fit parameters for AQ in eq 6; the maximum at [OH⁻]/[AQ] = 0.5 is consistent with the proposed reaction sequence (eq 1 and 2).

The fate of the AQ(OH)[•] species that results from electron transfer to AQ from the adduct [AQ(OH)[•]] is not clear. However, the results indicate a rapid dimerization of AQ(OH)[•] followed by decomposition to AQ and H₂O₂. With excess base H₂O₂ is unstable and can disproportionate to O₂ and H₂O,¹⁶ react with MeCN, and oxidize AQ^{••}. Thus, the combination of OH⁻ and AQ in aprotic solvents results in a significant yield of radicals (AQ^{••}) and dioxygen species (H₂O₂, O₂, and O₂^{•-}). Such chemistry is likely to occur in biomembranes that contain the primary reactants and may represent one path for the apparent toxicity of natural quinones.¹²

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Registry No. AQ, 84-65-1; AQ^{••}, 3426-73-1; AQ(OH)[•], 96914-49-7; AQ(OH)[•], 96914-50-0; EtAQ(OH)[•], 96914-51-1; 2-EtAQ, 84-51-5; OH⁻, 14280-30-9; H₂O₂, 7722-84-1; CH₃CN, 75-05-8; Bu₄NOH, 2052-49-5; NaOH, 1310-73-2; O₂, 7782-44-7.

(19) The reversible redox potentials for the AQ/AQ^{••} (-0.58 V vs. NHE) and O₂/O₂^{•-} (0.63 V) couples in MeCN provide a measure of K₅ (log K = ΔE/0.059).

Preparation of an Unsubstituted Hydrazido(1-) Complex and an Authentic High Oxidation State Tungsten Dinitrogen Complex

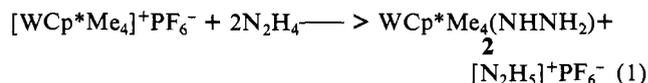
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Although at least one end of dinitrogen is believed to bind to molybdenum (perhaps Mo(IV)) in nitrogenase in order to be reduced to ammonia,¹ no dinitrogen complex of tungsten(IV) or molybdenum(IV) has ever been reported. There is good reason to expect that at least μ-N₂ complexes containing two M(IV) (d²) metals might be prepared since Zr(II),² Nb(III),³ and Ta(III)³ complexes of this type are known and a recent W₂(μ-N₂) complex (formally W(II) if N₂ and diphenylacetylene are assumed to be neutral ligands) prepared from hydrazine⁴ shows the relatively long N-N bond (1.292 (16) Å) characteristic of a highly reduced N₂ (N₂⁴⁻) ligand first observed in the Nb and Ta complexes.³ Here we show that a ditungsten(IV) μ-N₂ complex can be prepared from hydrazine, that NHNH₂¹⁻ and NNH₂²⁻ intermediates can be isolated, and that the μ-N₂ complex also can be prepared by reducing a W(V) complex in the presence of molecular nitrogen.

WCp*Me₄ (Cp* = η⁵-C₅Me₅)⁵ can be oxidized by [FeCp₂]⁺PF₆⁻ (Cp = η⁵-C₅H₅) in dichloromethane to give yellow [WCp*Me₄]⁺PF₆⁻ (**1**) in 90% yield as a yellow powder.⁶ We believe **1** is the only isolable cationic d⁰ alkyl complex other than [TaCp₂Me₂]⁺BF₄⁻.⁷ When **1** is added to ~2 equiv of hydrazine suspended in diethyl ether, it dissolves to give a colorless solution and a small amount of a beige and sometimes gummy precipitate. When dried thoroughly in vacuo the precipitate becomes a powder that has IR, ³¹P NMR, and ¹⁹F NMR spectra that show the presence of the PF₆⁻ ion and that can be hydrolyzed to give ~1 equiv of hydrazine.⁸ Therefore, we believe the reaction proceeds as shown in eq 1. The proposed hydrazido(1-) complex (**2**) is



a white microcrystalline material that is soluble in ether or toluene. Its ¹H NMR spectrum in C₆D₆ at 298 K shows a broad lump at 3.0 ppm that can be ascribed to the N₂H₃ protons in addition to peaks for the Cp* and three other types of methyl groups at 1.23 (Cp*), 0.44 (2 Me), 0.42 (Me), and 0.34 ppm (Me). The N₂H₃ peak at 2.7 ppm in CD₂Cl₂ splits into three broad singlets at 2.1, 2.5, and 3.5 ppm at 190 K. At the same time the two methyl groups that are equivalent at 298 K become inequivalent at 190 K. These data are consistent with the low-temperature, 18c⁻

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(6) Satisfactory elemental analyses have been obtained.

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(8) (a) Hydrazine was quantitated in the usual manner.^{8b} (b) Ball, G. W.; Chusp, J. D. *Anal. Chem.* **1952**, *24*, 2006.

(9) (a) McCleverty has good evidence for Mo[HB(Me₂p_z)₃](NO)(I)-(NHNH₂),^{9b} but only one of three NHNH₂ protons could be found in the ¹H NMR spectrum. (b) McCleverty, J. A.; Rae, A. E.; Wolochowicz, I.; Bailey, N. A.; Smith, J. M. A. *J. Chem. Soc., Dalton Trans.* **1983**, 71.

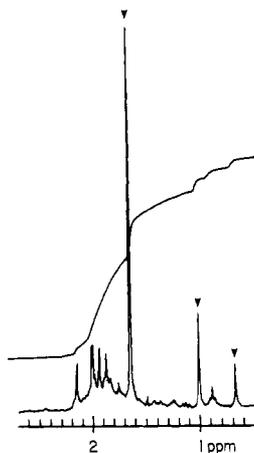
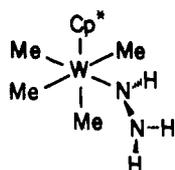


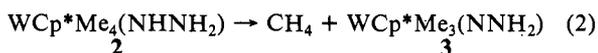
Figure 1. ^1H NMR spectrum in C_6D_6 of the crude reaction mixture produced upon reduction of $[\text{WCp}^*\text{Me}_3\text{Cl}]$ under N_2 showing $\sim 20\%$ $[\text{WCp}^*\text{Me}_3]_2(\mu\text{-N}_2)$.

structure being one in which W, N_α , H_α , N_β , H_β , and H_β' all lie in a plane that is not a molecular plane, viz.,

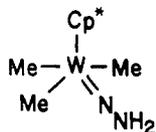


An alternative $18e^-$ structure containing an $\eta^2\text{-NHNH}_2$ ligand^{1d} is less likely for steric as well as electronic reasons. This is the least ambiguous example of a complex containing the extremely rare parent $[\text{NHNH}_2]^-$ ion.⁹ Due to the instability of **2** (see below) we have not yet been able to show whether the three protons equilibrate by an intra- or an intermolecular process. Limited stability of **2** also has prevented accurate elemental analyses. We have shown, however, that **2** is hydrolyzed rapidly by aqueous HCl to give 0.85 (5) equiv of hydrazine.

In polar solvents such as dichloromethane **2** decomposes quantitatively (by ^1H NMR) to **3** (eq 2).⁶ **3** is a fully characterized

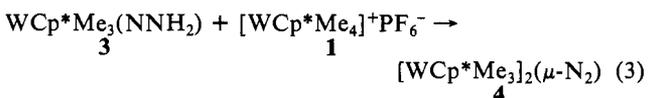


red-orange, pentane-soluble complex whose NMR spectra are consistent with a square-pyramidal structure, viz.



Its NNH_2 protons are found at δ 4.59 in C_6D_6 . In the presence of aqueous HCl **3** is hydrolyzed immediately to give 0.85 (5) equiv of hydrazine.⁸

The reaction between $[\text{WCp}^*\text{Me}_4]^+\text{PF}_6^-$ and **3** in ether produces a red-orange complex in $\sim 50\%$ yield that is physically quite similar to **3** but that has neither ν_{NH} peaks in its IR spectrum nor NH resonances in its ^1H NMR spectrum.¹⁰ We propose that it is the $\mu\text{-N}_2$ complex **4** (eq 3), with a structure related to that



of **3**.⁸ A preliminary X-ray structural study confirms that this

is the case.¹¹ Interestingly, however, **4** in ether is not readily hydrolyzed upon being shaken with 1 N NaOH overnight. Also, no hydrazine is liberated when an ether solution of **4** is treated with aqueous or gaseous HCl. A red precipitate forms that we are in the process of identifying. The stability of **4** toward hydrolysis might be ascribed to the hydrophobic coordination sphere and/or what are apparently relatively nonbasic formal electron pairs on what is believed to be essentially a $\mu\text{-N}_2^{4-}$ ligand.

An interesting question is whether **4** can be prepared by reducing $\text{WCp}^*\text{Me}_3\text{Cl}$ under molecular nitrogen. $\text{WCp}^*\text{Me}_3\text{Cl}$ is unknown. We attempted to prepare it by the conproportionation between WCp^*Me_4 (three parts) and WCp^*Cl_4 (one part) in dichloromethane for 20 h. The solvent was removed from the resulting red solution and the residue was dissolved in THF. One equivalent of sodium amalgam was added and the mixture was stirred under N_2 (40 psi) overnight. The mixture was filtered and the THF removed in vacuo to give a red semisolid whose ^1H NMR spectrum showed $\sim 20\%$ of the diamagnetic product mixture to consist of **4** (Figure 1). **4** was isolated from this mixture by recrystallization from pentane in 5-10% yield. We hesitate to suggest a mechanism for this reaction in view of the number of unknowns, but the fact that any **4** is observable, whatever the mechanism might be, is intriguing. It is possible, however, that a relatively high oxidation state complex (e.g., WCp^*Me_3) does scavenge N_2 at a rate that competes with other reactions involving the methyl groups.

We believe that these preliminary studies show that high oxidation state tungsten $\mu\text{-N}_2$ complexes can be prepared and that they are likely to have some unique properties and reactivities. We expect to encounter other examples soon.

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Registry No. 1, 96999-45-0; **2**, 96999-46-1; **3**, 96999-47-2; **4**, 96999-48-3; $\text{WCp}^*\text{Me}_3\text{Cl}$, 96999-49-4; WCp^*Me_4 , 96055-89-9; $[\text{FeCp}_2]^+\text{PF}_6^-$, 11077-24-0; WCp^*Cl_4 , 96055-85-5; N_2H_4 , 302-01-2; $[\text{N}_2\text{H}_3]^+\text{PF}_6^-$, 88186-61-2; N_2 , 7727-37-9.

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Bimetallic-Mediated Reaction of Carbon Monoxide and Dioxxygen

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The reaction of dioxxygen and carbon monoxide is slow in the absence of catalysts. The role of a single metal atom to activate CO and O_2 and to mediate their reaction has been suggested,¹ but one of the most effective homogeneous catalysts for the reaction is the $\text{Rh}_6(\text{CO})_{16}$ cluster.² Spectral studies of the reaction of CO and O_2 on Pt/SiO₂ led to a proposal of a multi metal atom mechanism involving dissociative adsorption of O_2 and subsequent reaction with coordinated CO.³ We describe experiments which provide evidence for a bimetallic-mediated pathway for the reaction of CO and O_2 .

Gaseous dioxxygen was observed not to react with $[\text{Pt}(\text{PPh}_3)_2(\text{CO})\text{Cl}]\text{BF}_4$ (**2**), but the dioxxygen complex $\text{Pt}(\text{PPh}_3)_2\text{O}_2$ (**1**) in CH_2Cl_2 reacts rapidly with **2**. The reaction proceeds with loss of $\nu(\text{CO})$ of **2** at 2115 cm^{-1} and formation of a strong IR band at 1521 cm^{-1} . Gas chromatographic assay on molecular sieves

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(10) Typically $\text{WCp}^*\text{Me}_3(\text{NNH}_2)$ (0.2 g, 0.51 mmol) and $[\text{WCp}^*\text{Me}_4]^+\text{PF}_6^-$ (0.26 g, 0.51 mmol) are stirred together in diethyl ether (15 mL) for 12 h. The mixture is then filtered and the ether removed from the filtrate in vacuo to give 0.22 g of red $[\text{WCp}^*\text{Me}_3]_2(\mu\text{-N}_2)$. $[\text{WCp}^*\text{Me}_3]_2(\mu\text{-N}_2)$ can be recrystallized from pentane.