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Synthesis, Characterization and Reactivity of the Dinuclear Tungsten Complexes $[Et_4N]_2[W_2(CO)_8(SR)_2]$

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The new complexes $[Et_4N]_2[W_2(CO)_8(SR)_2]$ (R = Ph, t-Bu) (**1**) have been prepared from reaction of $W(CO)_6$ with $(Et_4N)(SR)$ in MeCN and characterized by standard analytical, spectroscopic, and electrochemical techniques. Like its Mo analogs, **1** undergoes pseudoreversible two-electron oxidation in a single step, behavior attributed to metal–metal bond formation accompanied by structural rearrangement in the known W(I) product $W_2(CO)_8(SR)_2$ (**2**). **2** reacts with MeCN to yield $W_2(CO)_6(MeCN)_2(SR)_2$ (**3**) which in turn reconverts to **2** on treatment with CO. The new dinuclear complex $[Et_4N]_2[W_2(CO)_8(SH)_2]$ was prepared by reaction of $W(CO)_6$ with $(Et_4N)(SH)$ in THF using a procedure similar to that for the known $[PPN][W(CO)_5(SH)]$.

Recently we reported [1] preparation of the new species $[Mo_2(CO)_8(SR)_2]^{2-}$ (R = Ph, t-Bu) and described their two electron chemical and electrochemical oxidations to the known complexes [2] $[Mo_2(CO)_8(SR)_2]$. A particularly interesting property of these compounds in the *simultaneous* transfer of two electrons at the same potential, which we attribute to the presence of a metal–metal bond in the oxidized complex and the lack thereof in the reduced species. We have now extended this chemistry to the analogous tungsten compounds and herein report preliminary results describing some aspects of the syntheses, reactivity and electrochemistry of the complexes $[Et_4N]_2[W_2(CO)_8(SR)_2]$ (R = Ph, t-Bu). In addition, we report preparation of the hydrogen sulfide analog, $[Et_4N]_2[W_2(CO)_8(SH)_2]$, and compare the synthetic method for this new compound to that for the well-studied [3] mononuclear species, $[PPN][W(CO)_5SH]$.

In a procedure similar to that for the molybdenum complexes [1], $W(CO)_6$ was reacted with one equivalent of $(Et_4N)(SR)$ (R = Ph, t-Bu) in refluxing (~80 °C) MeCN for 5 h. The yellow brown reaction mixture was filtered, the filtrate concentrated, and i-PrOH added to precipitate the bright yellow solid products. The conditions necessary for complete reaction are somewhat harsher than for the molybdenum system (4 h at 50 °C), not a surprising result since tungsten carbonyls are generally more inert to substitution reactions[‡]. Elemental analyses[+] are consistent with the empirical formula $[Et_4N][W(CO)_4(SR)]$, and plots of equivalent conductivity versus the square root of concentration are linear with slopes of *ca.* −600 units consistent with that for 2:1 electrolytes [1, 4, 5]. These data and the presence of four strong CO bands in the infrared spectra (Table I) indicate that the products should be formulated as $[Et_4N]_2[W(CO)_8(SR)_2]$ (**1**). It is surprising that these simple tungsten species have not been reported previously. Photochemical reaction of thiols with $W(CO)_6$ in toluene [6] produces the dinuclear W(I) complexes, $[W_2(CO)_8(SR)_2]$, which we have prepared by a different method (*vide infra*), but the W(O) dimers apparently do not form in significant yields under these conditions.

Oxidation of **1** (R = Ph, t-Bu) with one mole of I_2 in toluene under CO yields the known [6] complexes $[W_2(CO)_8(SR)_2]$ (**2**) as evidenced by elemental analytical[ǂ] and spectral data. In MeCN, I_2 oxidation of **1** (R = Ph, t-Bu) yields[#] $W_2(CO)_6(MeCN)_2(SR)_2$ (**3**). These reactions are fully analogous to those reported [1] for the $[Mo_2(CO)_8(SR)_2]^{2-/0}$ system, as is the interconversion of **2** and **3** by treatment of **2** with MeCN and **3** with CO in toluene. Spectral data for all complexes are given in Table I.

The tungsten dimers **1** and **2** exhibit interesting electrochemical behavior. The cyclic voltammo-

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[‡] However, as Gingerich and Angelici [3a] point out, reaction of SH^- with $W(CO)_6$ to form $[W(CO)_5(SH)]^{1-}$ is too rapid to involve simple rate-determining dissociation of CO. A similar, although as yet unknown, mechanism may be involved in our reactions yielding the dinuclear thiolate-bridged species.

[+] $[Et_4N][W(CO)_4(SPh)]$. Calcd. for $C_{18}H_{25}NO_2SW$: C, 40.37; H, 4.67; N, 2.62. Found: C, 40.50; H, 4.89; N, 2.27. $[Et_4N][W(CO)_4(S\text{-}t\text{-}Bu)$. Calcd. for $C_{16}H_{29}NO_4SW$: C, 37.28; H, 5.63; N, 2.72. Found: C, 36.88; H, 5.80; N, 2.99.

[ǂ] $W_2(CO)_8(SPh)_2$. Calcd. for $C_{20}H_{10}O_8S_2W_2$: C, 29.63; H, 1.23. Found: C, 29.35; H, 1.49. $W_2(CO)_8(S\text{-}t\text{-}Bu)_2$. Calcd. for $C_{16}H_{18}O_8S_2W_2$: C, 24.94; H, 2.33. Found: C, 24.51; H, 2.39.

[#] $W_2(CO)_6(MeCN)_2(SPh)_2$. Calcd. for $C_{22}H_{16}N_2O_6S_2W_2$: C, 31.58; H, 1.91; N, 3.35. Found: C, 30.86; H, 1.77; N, 2.93. $W_2(CO)_6(MeCN)(S\text{-}t\text{-}Bu)_2$. Calcd. for $C_{18}H_{24}N_2O_6S_2W_2$: C, 27.14; H, 3.02; N, 3.52. Found: C, 26.34; H, 2.89; N, 2.69.

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TABLE I. Infrared and Electronic Spectral Data.

Complex	IR^{a}	UV/Vis^{b}
1 (R = t-Bu)	2000m, 1890m, 1845s, 1795s	388(1990)^{c}
1 (R = Ph)	2000m, 1910s, 1855s, 1790s	450sh, 410sh 388(2100)^{c}
1 (R = H)	2000m, 1900s, 1840s, 1780s	425sh,^{c} 390(2480)
2 (R = t-Bu)	2020m, 2010m, 1980s, 1950s	622(1910) 400(13,100)^{d}
2 (R = Ph)	2020m, 1980s, 1965s	612(1130), 415(10,400), 340sh
3 (R = t-Bu)	2030w, 1985s, 1935s, 1980s	690(960),^{c} 412(9220), 339(12,000)
3 (R = Ph)	2040w, 1980s, 1935s, 1885s	680(760), 426(8000), 320(1400)^{c}

^{a}Values of CO stretching frequencies in cm^{-1}. Spectra taken as KBr pellets. ^{b}Values in nm with molar absorptivities in parentheses. ^{c}MeCN solution. ^{d}Hexane solution.

gram* in Fig. 1a shows that 1 (R = t-Bu) undergoes a two-electron oxidation at -0.34 V *vs.* SCE that displays distinctly non-Nernstian character. The separation between anodic and cathodic peak potentials $E_{pa}-E_{pc}$ is 185 mV at a scan rate of 20 mV/sec and increases to 275 mV at 200 mV/sec. This degree of electrochemical irreversibility is much greater than that of the Mo complexes [1], for which $E_{pa}-E_{pc} \cong$ 40 mV under equivalent conditions. The two-electron character of the $[W_2(CO)_8(SR)_2]^{(2-/0)}$ redox couple is established from the voltammetric peak current parameters $(i_p/\nu^{1/2}AC)$ of 920 A cm $s^{1/2}$ $V^{-1/2}$ mol^{-1} for the relatively broad oxidation of 1 (R = t-Bu) and 1050 A $s^{1/2}$ $V^{-1/2}$ mol^{-1} for its slightly sharper reverse reduction in 0.1 M $[Bu_4N]BF_4$/DMF (Fig. 1a). Under identical conditions peak current parameters of 545 and 1315 A cm $s^{1/2}$ $V^{-1/2}$ mol^{-1} are observed for the one-electron oxidation of $Mo[S_2C_2(CN)_2]_4{}^{3-}$ [7] and the two-electron oxidation of $[Mo_2(CO)_8(SR)_2]^{2-}$ [1], respectively. We attribute loss of two electrons at the same potential to formation of a metal–metal bond in the oxidized product 2, which is required to maintain an 18-electron configuration about each metal atom**. The greater difference in

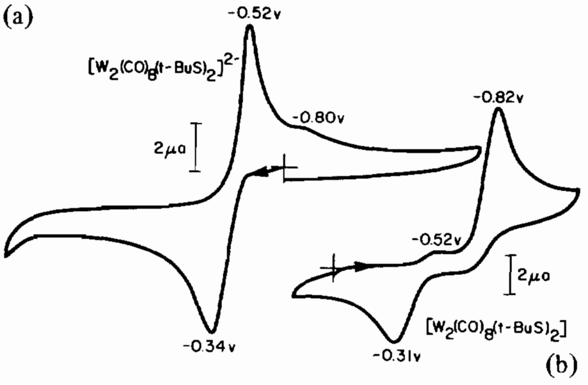

Fig. 1. Cyclic voltammograms of 1 and 2 (R = t-Bu): (a) 0.80 mM 1, DMF, 20 mV/sec; (b) 1.35 mM 2, DMF, 10 mV/sec.

$E_{pa}-E_{pc}$ for the tungsten dimers represents a larger kinetic barrier to transfer of two electrons than for the corresponding molybdenum compounds. Reasons for this difference in behavior are under investigation.

The cyclic voltammogram in Fig. 1b illustrates that complex 2 (R = t-Bu) undergoes irreversible reduction at -0.82 V and reoxidation at -0.31 V, which is the potential corresponding to oxidation of 1 (R = t-Bu). Only a small cathodic peak is observed at -0.52 V where reduction of 2 (R = t-Bu) is expected. We rationalize this behavior by assuming that, prior to electrochemistry, 2 solvolyzes almost completely to $[W_2(CO)_7(DMF)(S\text{-}t\text{-}Bu)_2]$ or $[W_2(CO)_6(DMF)_2(S\text{-}t\text{-}Bu)_2]$†. After electrochemical reduction of this solvento complex at -0.82 V, the W(O) dimer rapidly recombines with released CO to form 1, which is oxidized at -0.31 V. Scheme 1 summarizes this overall behavior. Similar effects of solvolysis, decarbonylation and recarbonylation reactions on the electrochemistry of $[Mo_2(CO)_8(SR)_2]^{(2-/0)}$ complexes have been reported [1].

$$\begin{tikzcd}
{[W_2(CO)_8(SR)_2]} \arrow[r, "DMF"] & {[W_2(CO)_{8-x}(DMF)_x(SR)_2]} \arrow[d, "+2e^-"] \\
{[W_2(CO)_8(SR)_2]^{(2-)}} \arrow[u, "-2e^-"] & {[W_2(CO)_{8-x}(DMF)_x(SR)_2]^{(2-)}} \arrow[l, "CO"']
\end{tikzcd}$$

(x = 1 or 2)

Scheme 1.

The chemistry of the $W(CO)_6/SH^-$ system differs from that of the alkyl and aryl thiolates. Reaction of $(Et_4N)(SH)$ with $W(CO)_6$ in refluxing MeCN fails to produce detectable amounts of $[Et_4N]_2[W_2(CO)_8(SH)_2]$ (1, R = H). However, reaction of equimolar

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*Cyclic voltammetry experiments were carried out with a three-electrode cell using N,N-dimethylformamide (DMF) as solvent and 0.1 M $[Bu_4N]BF_4$ as supporting electrolyte. The working electrode was a glassy carbon disk (A = 0.0707 cm^2) from Bioanalytical Systems (BAS), the reference electrode was an aqueous SCE separated from the sample solution by a salt bridge, and the potentiostat was a CV-IA unit from BAS.

**A similar explanation has been offered [1] for the 2-electron character of the $[Mo_2(CO)_8(SR)_2]^{(2-/0)}$ redox couple and that of a related $Fe_2(I)/Fe_2(O)$ system [8].

†This assumption is reasonable because 2 undergoes solvolysis/decarbonylation to produce $[W_2(CO)_6(SR)_2(MeCN)_2]$.

quantities of (Et$_4$N)(SH) (generated by the method of Gingerich and Angelici [3a]) and W(CO)$_6$ in THF yields the new μ_2-(SH)$_2$-bridged complex 2 (R = H) as evidenced by elemental analytical‡ and spectral (Table I) data. This result was unexpected, since, under these conditions, reaction of (PPN)(SH) with W(CO)$_6$ gives mononuclear [W(CO)$_5$(SH)]$^{1-}$, a species whose reactivity has been extensively studied [3]. The difference appears to be due to the insolubility of the (Et$_4$N)$^+$ salt of [W$_2$(CO)$_8$(SH)$_2$]$^{2-}$, which precipitates from THF (and is purified by recrystallization from MeCN/i-PrOH), whereas the (PPN)$^+$ salt of [W(CO)$_5$(SH)]$^{1-}$ remains in solution under the reaction conditions [3a] and must be precipitated by addition of Et$_2$O/hexane*. Studies are in progress to examine the electrochemical behavior of **1** (R = H) and its molybdenum analog which, interestingly, we have been able to prepare by reaction of (Et$_4$N)(SH) with Mo(CO)$_6$ in MeCN [9]. In this regard, it may be pertinent to note that [W$_2$(CO)$_8$(SH)$_2$], the two-electron oxidation product of **1** (R = H) has recently been prepared [10] by photolysis of [W(CO)$_5$(H$_2$S)].

Our investigation of these compounds was prompted by current interest in molybdenum thiolate complexes as probes for the structure and function of molybdoenzymes [11]. We believe these new metal–carbonyl–thiolate species may be useful as reagents for the synthesis of new multimetal complexes which might mimic certain aspects of metalloenzymes, among them the molybdenum site of nitrogenase. In addition, a study of the chemistry of the new SH bridged species [W$_2$(CO)$_8$(SH)$_2$]$^{2-}$ should complement the extensive data already available on the reactivity of [W(CO)$_5$SH]$^{1-}$ and [W(CO)$_5$]$_2$S^{2-} [3].

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‡[Et$_4$N][W$_2$(CO)$_8$(SH)$_2$]. Calcd. for C$_{24}$H$_{42}$N$_2$O$_8$S$_2$W$_2$: C, 31.37; H, 4.57; N, 3.05. Found: C, 30.86; H, 4.74; N, 3.04. The amount of CO evolved on excess Br$_2$ oxidation was 96% of that predicted.

*We find it unusual that the soluble [PPN][W(CO)$_5$(SH)] salt does not decarbonylate to dinuclear [W$_2$(CO)$_8$(SH)$_2$]$^{2-}$ under these conditions. The reasons for this behavior are not understood.