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Synthesis, reactivity and two-electron electrochemistry of the dinuclear molybdenum(0) complexes [Et4N]2[Mo2(CO)8(SR)2] (R = tert-Bu, Ph)

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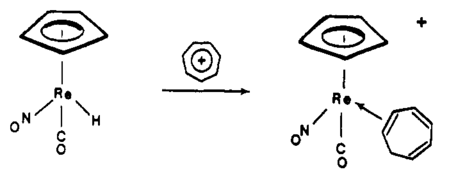

(10)

CpRe(NO)(CO)H, then undergoes hydride abstraction with $C_7H_7^+$ to afford the final d^6 product $CpRe(CO)_2(\eta^2\text{-}1,2\text{-}C_7H_8)$. This proposed mechanism provides another example of how the H reactivities in $CpML_nH$ complexes are influenced to give electronically stabilized d^6 three-legged piano stool products. Another closely related example is the compound $CpRe(CO)_2(CH_3)H$, prepared by methylation of $CpRe(CO)_2H^-$. In a scheme proposed by Yang and Bergman,[9] this hydride also behaves as a proton donor affording the d^6 three-legged piano stool product $CpRe(CO)_2(CH_3)^-$.

It is interesting to note that all 18-electron three-legged piano stool hydrides are formally d^6 species while all 18-electron four-legged hydrides are d^4 complexes. In order to form d^6 three-legged piano stool products, three-legged piano stool hydrides (in the presence of a 2-electron donor ligand) must function as hydride donors and four-legged hydrides must behave as proton donors. Hence, we expect the reactivity patterns shown in eq 11 and 12. In addition

$$\text{hydridic}\quad (\eta^n\text{-}C_nH_n)ML_2H \xrightarrow{L'} (\eta^n\text{-}C_nH_n)ML_2L'^+ + H^- \qquad (11)$$

$$n = 5$$

$$\text{acidic}\quad (\eta^n\text{-}C_nH_n)ML_3H \rightarrow (\eta^n\text{-}C_nH_n)ML_3^- + H^+ \qquad (12)$$

$$n = 5, 6$$

to the complexes examined here, all other characterized three- and four-legged piano stool complexes, tabulated in Table I, appear to support this generalization. Two other silyl hydride complexes,[15] the d^4 $(\eta^6\text{-}C_6H_6)Cr(CO)_2(SiCl_3)H$ and the d^6 $CpCo(CO)(SiCl_3)H$, have not been included in Table I since their acid–base properties have not yet been determined. Our reasoning, however, would predict acidic character for the former and hydridic behavior for the latter.

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Synthesis, Reactivity, and Two-Electron Electrochemistry of the Dinuclear Molybdenum(0) Complexes $[Et_4N]_2[Mo_2(CO)_8(SR)_2]$ (R = *t*-Bu, Ph)[†]

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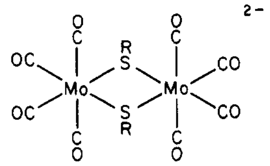
Summary: New dinuclear Mo(0) complexes $[Et_4N]_2[Mo_2(CO)_8(SR)_2]$ (R = Ph, *t*-Bu) (**1**), prepared by reaction of $Mo(CO)_6$ with $[Et_4N]SR$ in MeCN, undergo chemically reversible two-electron oxidation in a single step. This behavior is attributed to metal–metal bond formation accompanied by structural rearrangement in the Mo(I) product $Mo_2(CO)_8(SR)_2$ (**2**). **1** and **2** may be interconverted chemically or electrochemically and exhibit markedly different reactivities with solvent (MeCN, DMF) and CO.

Current interest in molybdenum thiolate complexes[2–7] arises from the known presence of Mo–S bonding in a variety of molybdoenzymes, among them nitrogenase. Our efforts to model the Fe–Mo–S cluster[8] at the molybdenum site of this enzyme led us to initiate synthetic studies of low-valent molybdenum complexes via reactions of $Mo(CO)_6$ with monodentate thiolates. Herein we report some initial results that reflect the rich chemistry and electrochemistry of compounds prepared by such reactions.

Reaction of $Mo(CO)_6$ with one equivalent of $[Et_4N][SR]$ (R = *t*-Bu, Ph) in MeCN for 4 h at 45 °C gave a yellow-brown reaction mixture which, after concentration and addition of *i*-PrOH, deposited a bright yellow solid product. Elemental analyses[9] were consistent with the empirical formula $[Et_4N][Mo(CO)_4(SR)]$, and plots of equivalent conductivity vs. the square root of concentration were linear with slopes of ca. −615 units. This value is consistent with that for 2:1 electrolytes[10,11] and suggests a formulation of $[Et_4N]_2[Mo_2(CO)_8(SR)_2]$ (1) for the products. The presence of four strong bands in the CO stretching region (1750–2050 cm^{-1}) of these complexes (Table I) also is consistent with this formulation. In light of these data, the most reasonable structure for the complex anions consists of two $Mo(CO)_4$ fragments bridged by two μ-SR moieties. Remarkably, we have been unable to find any mention of these relatively simple dinuclear species in the literature, although the chemistry of several related monomeric systems has been reported.[5,7,12]



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Our preliminary studies of the chemical reactivity of the dimeric anions are summarized in Scheme I. Oxidation of 1 with 1 equiv of I_2 in CO-saturated toluene yields the

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(9) $[Et_4N][Mo(CO)_4(SPh)]$. Calcd for $C_{18}H_{25}NMoO_4S$: C, 48.32; H, 5.59; N, 3.13. Found: C, 48.20; H, 5.80; N, 3.08. $[Et_4N][Mo(CO)_4(S\text{-}t\text{-}Bu)]$. Calcd for $C_{16}H_{29}NMoO_4S$: C, 44.96; H, 6.79; N, 3.28. Found: C, 44.75; H, 7.04; N, 3.06.
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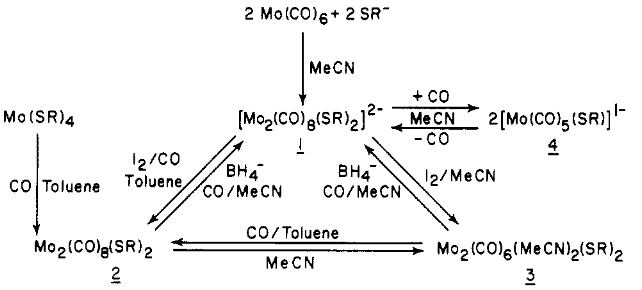
Table I. Infrared and Electronic Spectral Data

complex	IR[a]	UV/vis[b]
1 (R = Ph)	2000 m, 1920 s, 1860 s, 1790 s	375 (2720)[c]
1 (R = *t*-Bu)	2000 m, 1900 s, 1850 s, 1790 s	385 (2180)[c]
2 (R = Ph)	2020 m, 2000 s, 1980 s	345 (9130), 422 (10 100), 640 (662)[d]
2 (R = *t*-Bu)	2015 m, 2000 s, 1970 s	405 (14 100), 650 (652)[d]
3 (R = Ph)	2040 w, 1990 s, 1950 s, 1900 s	335 (18 900), 432 (10 700), 700 (758)[c]
3 (R = *t*-Bu)	2030 w, 2000 s, 1950 s, 1870 s	340 (13 100), 420 (12 000), 720 (880)[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.

Scheme I



dinuclear Mo(I) species $Mo_2(CO)_8(SR)_2$ (R = Ph, *t*-Bu) (**2**).[13] $Mo_2(CO)_8$(S-*t*-Bu)$_2$ has been prepared previously by high-pressure carbonylation of Mo(S-*t*-Bu)$_4$ and its structure determined by X-ray methods.[6] Spectral data for **2** (Table I) formed by these two routes are very similar,[14] supporting our proposed formulation of **1**. The chemically reversible nature of the redox conversion is demonstrated by the fact that reduction of **2** with $[Et_4N]BH_4$ in MeCN under CO yields **1**. Oxidation of **1** to **2** is a more general route to the Mo(I) species than the previously reported method,[6] since $Mo(SR)_4$ has been prepared[4] only for R = *t*-Bu. In our hands it is a more facile synthetic procedure and produces higher yields.

If the I_2 oxidation of **1** (R = *t*-Bu, Ph) is carried out in MeCN instead of toluene, the products $Mo_2(CO)_6(MeCN)_2(SR)_2$ (**3**) are isolated.[15] Lack of complexity in the CO stretching patterns of these new Mo(I) species (Table I) suggests a symmetric distribution of ligands with one MeCN on each molybdenum. Reversible CO/MeCN exchange is demonstrated by bubbling CO through toluene solutions of **3** to yield **2**, whereas concentration of solutions of **2** in MeCN produces **3** (Scheme I). Prolonged treatment of **2** with MeCN gives only **3**, with no further substitution of CO by MeCN.[16]

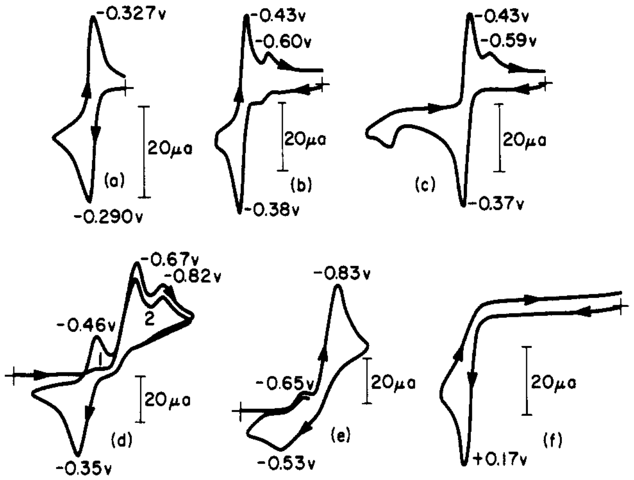


Figure 1. Cyclic voltammograms of **1**, **2**, and **3** (R = Ph): (a) 1.1 mM **1**, DMF, 25 mV s^{-1}; (b) 1.1 mM **1**, MeCN, 50 mV s^{-1}; (c) 1.1 mM **1**, MeCN, after bubbling with CO for 30 s, 50 mV s^{-1}; (d) 2.0 mM **2**, MeCN, in the presence of 1 atm CO, 50 mV s^{-1}; (e) 2.0 mM **3** (formed in situ by solvolysis of **2**), MeCN, 50 mV s^{-1}; (f) 1.1 mM **1**, MeCN, after bubbling with CO for 60 min, 50 mV s^{-1}.

The dinuclear complexes in Scheme I exhibit interesting electrochemical behavior. Figure 1a shows a cyclic voltammogram[17] of **1** (R = Ph) in DMF. Reversible oxidation of this dianion occurs at $E_{1/2} = -0.31$V vs. SCE and has a separation between anodic and cathodic peak potentials of 37 mV that is smaller than the value of 57 mV expected for a Nernstian one-electron transfer.[18] Oxidation of **1** by normal pulse voltammetry[17] results in a current parameter of $i_d/AC = 1200\ \mu A\ cm^{-2}\ mM^{-1}$ in DMF, which compares with $i_d/AC = 620\ \mu A\ cm^{-2}\ mM^{-1}$ for the known[19] one-electron oxidation of $Mo[S_2C_2(CN)_2]_4^{3-}$ in this solvent. Coulometric oxidation[20] of **1** at 0.0 V vs. SCE yields the value $n = 2.03$ for the number of electrons transferred. These results indicate that oxidation of **1** proceeds by loss of two electrons at the same potential.[21]

$$\underset{\mathbf{1}}{[Mo_2(CO)_8(SR)_2]^{2-}} \rightleftharpoons \underset{\mathbf{2}}{Mo_2(CO)_8(SR)_2} + 2e^- \qquad (1)$$

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(12) Angelici, R. J.; Gingerich, R. G. W. *Organometallics* **1983**, *2*, 89.

(13) $[Mo_2(CO)_8(SPh)_2]$. Calcd for $C_{20}H_{10}Mo_2O_8S_2$: C, 37.85; H, 1.57. Found: C, 37.74; H, 1.64. $[Mo_2(CO)_8$(S-*t*-Bu)$_2]$. Calcd for $C_{16}H_{18}Mo_2O_8S_2$. C, 32.32; H, 3.03. Found: C, 31.85; H, 3.10.

(14) Infrared spectra (hexane solution) of **2** (R = *t*-Bu) formed by oxidation of **1** (R = *t*-Bu) and by the method of Otsuka[6] are identical. However, the visible spectrum of **2** (R = *t*-Bu) from our method contained bands at 650 (ϵ 652) *and* at 405 nm (ϵ 14100). The latter band was not reported for **2** (R = *t*-Bu) formed[6] by carbonylation of Mo(S-*t*-Bu)$_4$. Because of this discrepancy, we repeated the carbonylation reaction in our laboratory and indeed obtained a product whose visible spectrum contained the 405 nm band (ϵ 14000). We therefore conclude that the report of this band was inadvertantly omitted in the previous[6] reference to this compound.

(15) $[Mo_2(CO)_6(MeCN)_2(SPh)_2]$. Calcd for $C_{22}H_{16}N_2Mo_2O_6S_2$: C, 40.00; H, 2.42; N, 4.24. Found: C, 39.51; H, 2.30; N, 4.25. $[Mo_2(CO)_6(MeCN)_2$(S-*t*-Bu)$_2]$. Calcd for $C_{18}H_{24}N_2Mo_2O_6S_2$: C, 34.84; N, 3.87; N, 4.52. Found: C, 34.82; H, 4.01; N, 4.29.

(16) DMF appears to behave similarly to MeCN in reactions with **2**, but complete characterization of products has not been accomplished at this time.

(17) Cyclic voltammetry (CV) and normal pulse voltammetry (NPV) experiments were carried out in a three-electrode cell using 0.1 M $[Bu_4N]BF_4$ as the supporting electrolyte. The working electrode was a glassy carbon disk (area = 0.071 cm^2) from Bioanalytical Systems (BAS), and the reference electrode was an aqueous SCE separated from the sample solution by a salt bridge. A CV-1A potentiostat from BAS was used for CV experiments. NPV experiments were carried out with an IBM Instruments Model EC225 voltammetric analyzer using a 4 mV/s sweep rate and a 2-s pulse repetition time.

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(20) Controlled potential coulometry was carried out at a 12 cm^2 Pt foil electrode in MeCN solvent with 0.1 M $[Bu_4N]BF_4$ supporting electrolyte. A Princeton Applied Research Model 173/179 potentiostat and digital coulometer and Model 377 coulometry cell were used in these experiments. The number of electrons transferred was calculated from the coulomb reading at the time the current dropped below 1% of its initial value.

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We speculate that the two-electron character of eq 1 derives from creation of a single metal–metal bond and structural rearrangement within the binuclear unit upon forming the oxidized product. Complex **2** (R = *t*-Bu) is reported[6] to have an Mo–Mo distance of 2.98 Å and an acute Mo–S–Mo bridge angle of ca. 74°. These facts are consistent with the presence of a single metal–metal bond in $Mo_2(CO)_8(SR)_2$ to produce an 18-electron configuration about each Mo. $[Mo_2(CO)_8(SR)_2]^{2-}$ satisfies the 18-electron rule without a metal–metal bond and is expected to have a substantially different $Mo_2(SR)_2$ core structure.[22] The related 18-electron phosphido-bridged complexes $Fe_2(CO)_6(PPh_2)_2$ and $[Fe_2(CO)_6(PPh_2)_2]^{2-}$ exhibit remarkably distinct core structures,[23,24] yet undergo reversible two-electron transfer ($E_{1/2}$ = –1.26 V in MeCN).[25] We believe the $Mo_2(SR)_2$ and $Fe_2(PPh_2)_2$ complexes share a similar phenomenological explanation[23,25] of their electrochemical behavior in which formation or cleavage of a metal–metal single bond coupled with structural rearrangement in a bridged bimetallic center leads to simultaneous transfer of two electrons. This behavior is a marked contrast to the stepwise transfer of single electrons that is commonly observed in strongly coupled bi- and polynuclear complexes.[26]

Additional interesting chemistry associated with the $Mo_2(SR)_2$ centers is illustrated by the remaining voltammetric traces in Figure 1. In Figure 1b, a small oxidation wave (E_{pa} = –0.54 V) is observed prior to the major oxidation of **1** in MeCN. This wave is quenched when a voltammogram is run under CO, but the corresponding cathodic peak (E_{pc} = –0.59 V) is still apparent (Figure 1c). This cathodic peak and a more negative one (E_{pc} = –0.82 V) are observed when a voltammogram of **2** is run under CO (Figure 1d). The –0.82-V peak is assigned to reduction of $Mo_2(CO)_6(MeCN)_2(SR)_2$ based on a voltammogram of **3** in the absence of CO (Figure 1e). In keeping with the chemistry of Scheme I, we attribute these observations to successive replacement of CO by MeCN in the Mo(I) oxidation state and assign the cathodic peaks at ca. –0.4, –0.6, and –0.8 V to reduction of $Mo_2(CO)_8(SR)_2$, $Mo_2(CO)_7(MeCN)(SR)_2$, and $Mo_2(CO)_6(MeCN)_2(SR)_2$, respectively. Purging with CO in MeCN does not completely reverse these reactions (Figure 1c,d). In contrast to Mo(I), the Mo(0) species display a greater affinity for CO and are less susceptible to solvolytic reactions. The small anodic wave at –0.54 V (Figure 1b), which we attribute to oxidation of $[Mo_2(CO)_7(MeCN)(SR)_2]^{2-}$, is the only evidence of Mo(0) solvolysis; this artifact is removed by purging briefly with CO (Figure 1c). Furthermore, CV of **2** or **3** in the presence of CO (Figure 1d) exhibits no anodic waves in conjunction with the cathodic peaks at –0.6 and –0.8 V, only the reoxidation of **1** at –0.35 V. Thus, the MeCN-substituted species appear to be rapidly carbonylated upon electrochemical reduction to Mo(0).

Finally, we note that continued purging of **1** with CO results in complete loss of the reversible couple at –0.40 V and generation of an irreversible oxidation wave at +0.17 V (Figure 1c,f). When the solution in Figure 1f is bubbled with N_2, the original CV (Figure 1b) is restored. This behavior is attributed to the reversible formation of two equivalents of $[Mo(CO)_5(SR)]^-$ (**4**) (Scheme I), whose irreversible oxidation occurs at +0.17 V. We have not isolated salts of these pentacarbonyl anions, but their existence is reasonable because $[Mo(CO)_5(SH)]^-$ is a well-characterized species.[7] It is interesting that the SH species apparently[7] does not decarbonylate to $[Mo_2(CO)_8(SH)_2]^{2-}$, whereas the SR derivatives readily convert to **1** upon purging with inert gas.

Acknowledgment. This research was supported by grants from the USDA/SEA Competitive Research Grants Office (59-2394-1-1-675-0) to J.W.M. and W.E.N. and the National Science Foundation (CHE-8211694) to F.A.S.

Registry No. **1** (R = *t*-Bu), 90029-14-4; **1** (R = Ph), 90029-16-6; **2** (R = *t*-Bu), 77593-56-7; **2** (R = Ph), 90029-17-7; **3** (R = *t*-Bu), 90029-18-8; **3** (R = Ph), 90029-19-9; **4** (R = *t*-Bu), 90029-20-2; **4** (R = Ph), 90029-21-3; $Mo(CO)_6$, 13939-06-5; $Mo_2(CO)_7(MeCn)(SBu\text{-}t)_2$, 90029-22-4; $Mo_2(CO)_7(MeCn)(SPh)_2$, 90029-23-5; $[Mo_2(CO)_7(MeCN)(SBu\text{-}t)_2]^{2-}$, 90029-24-6; $[Mo_2(CO)_7(MeCn)(SPh)_2]^{2-}$, 90029-25-7; I_2, 7553-56-2; $[Et_4N]BH_4$, 17083-85-1.

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[22] Structural characterization of **1** is planned to determine the Mo–Mo distance and other appropriate dimensions in the $Mo_2(SR)_2$ core.

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[24] The neutral complex contains a single metal–metal bond with Fe–Fe = 2.623 Å and an Fe–P–Fe bridge angle of 72°, whereas the dianion exhibits a nonbonding Fe–Fe distance of 3.630 Å and an Fe–P–Fe angle of 106°.

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Transfer and Coupling of Zirconocene-Bound Alkenyl Ligands. An Alternative Route to (*s-trans*-η^4-Conjugated diene)$ZrCp_2$ Complexes

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Summary: Dibenzylzirconocene (**3a**) and (*s-trans*-η^4-*trans,trans*-1,4-diphenylbutadiene)zirconocene (**5**) are formed rapidly upon irradiation of benzyl(β-styryl)zirconocene (**2a**) in benzene at ambient temperature. Trapping and crossover experiments using benzyl chloride and (β-styryl)zirconocene chloride and the kinetic influence of added "moderators" trimethyl phosphite and triphenylphosphine in addition to ESR experiments point to a radical reaction mechanism for alkenyl group transfer. Transfer and coupling of alkenyl ligands can also be initiated in a dark reaction when starting from methyl(β-styryl)zirconocene (**2b**).

The synthetic procedures presently applied for the preparation of the unique (*s-trans*-η^4-conjugated diene) group 4 metallocene complexes **5** have in common that they use an intact 1,3-diene as a starting component.[2,3b] We have now found an example where the preparation of **5** is achieved in a rather different fashion. The compound

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[1] (a) Ruhr-Universität Bochum. (b) Universität Essen, ESR experiments.