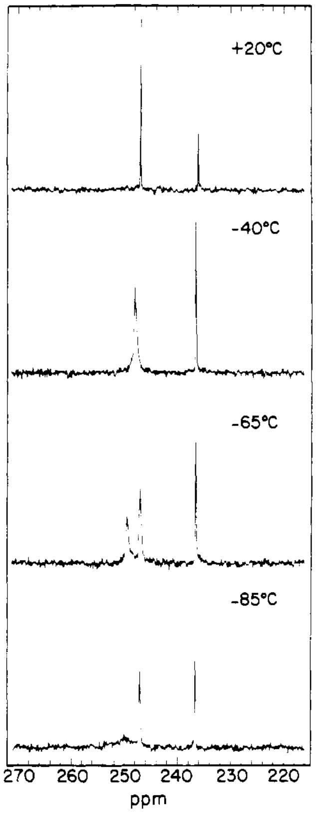
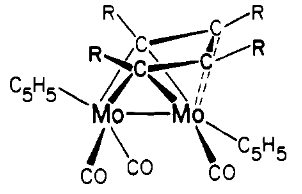


Figure 1. CO ^{13}C DNMR spectra for $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_3(C_{12}H_{20})$ in a toluene solution.

Metallacycles of structural form **1** have a metal–metal bond of formal bond order 3; crystallographic data,[2,3] which established short metal–metal bond distances, support this characterization. We have explored the reactivity of this type of multiple bond for the metallacycle derived from 3-hexyne. Carbon monoxide rapidly converted the bridged monocarbonyl to the metal–metal singly bonded species $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_3(C_{12}H_{20})$, with two terminal carbonyl groups on one molybdenum atom and one terminal carbonyl on the other (see below); this reaction was thermally reversible. Analogous was the facile addition of two *tert*-butyl isocyanide ligands at 25 °C to give $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)[CNC(CH_3)_3]_2(C_{12}H_{20})$. In sharp contrast, neither triethylphosphine nor trimethyl phosphite reacted with the metallacycle. Molecular models clearly suggest that this lack of reaction is steric in origin. There is insufficient room to allow addition of bulky ligands without a large increase in the molybdenum–molybdenum separation. Protonation of the metal–metal triply bonded metallacycle did proceed rapidly to give the dimer $(\eta^5\text{-}C_5H_5)(H)_2Mo(\eta^5\text{-}C_5H_5)Mo(CO)(C_{12}H_{20})^{2+}$.

The tricarbonyl derived from **1** should have structure **2** with essentially a Mo–Mo formal bond order of 1. The infrared spectrum of a solution of **2** showed that all the carbonyls were terminal. All three CO environments should be differentiable by NMR barring dynamic processes that equilibrate CO sites. At ~-65 °C, the ^{13}C spectrum of **2** consisted of a three-line pattern consistent with the proposed structure (Figure 1). At higher temperatures, two of the three CO ligands underwent selective site exchange. These are assigned to CO ligands bonded to the same molybdenum atom.[6] Below -65 °C, one of the terminal CO resonances underwent extensive broadening; we propose no specific explanation for the broadening (either another dynamic process or a selective relaxation effect may be extant).



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The proton NMR spectrum of the isocyanide derivative, $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)[CNC(CH_3)_3]_2(C_{12}H_{20})$, which should be isostructural with **2**, showed the presence of two $(CH_3)_3C$ proton resonances of nearly equal intensity. Irrespective of whether the isocyanide ligands are on the same or different molybdenum atoms, there would be two isocyanide ligand environments; hence, the NMR data do not establish which isomer predominates in solution. Because of overlap of some methylene and methyl (metallacycle) resonances, there was no obvious and unique interpretation of all the ^1H NMR resonances; note that all ethyl groups should be inequivalent and the protons in each CH_2 group should be diastereotopic, irregardless of the isocyanide ligand placement. The structure of the hydride derived from **1** by protonation was not defined by the spectroscopic data.

Acknowledgment. This research was supported by a grant from the National Science Foundation. We especially thank Dr. Mamoru Tachikawa for critical comments.

Registry No. $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)(C_6H_{10})_2$, 76136-86-2; $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_3(C_6H_{10})_2$, 76136-87-3; $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)[CNC(CH_3)_3]_2(C_{12}H_{20})$, 76282-00-3; $(\eta^5\text{-}C_5H_5)(H)_2Mo(\eta^5\text{-}C_5H_5)Mo(CO)(C_{12}H_{20})^{2+}(F_3CSO_3^-)_2$, 76282-02-5; $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(C_2H_5C_2C_2H_5)$, 61373-51-1.

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[6] These assignments are based on several considerations. First, the ^{13}C chemical shift of the two CO ligands involved in the low-temperature exchange have very similar chemical shifts—a feature that might be expected for the two CO ligands on the same molybdenum atom (in a formal sense, the oxidation states of the two molybdenum atoms are different). Second, an intermetal (intramolecular) exchange should tend to involve all three CO ligands. CO exchange localized at a single metal site is a fairly common low-energy process in polynuclear complexes.[7]

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Contribution from the Department of Chemistry,
Purdue University, West Lafayette, Indiana 47907

One-Electron Oxidations of Quadruply Bonded Molybdenum Dimers[1]

Thomas C. Zietlow,[2] Douglas D. Klendworth, Tayseer Nimry, Dennis J. Salmon,[3] and Richard A. Walton*

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The molybdenum(II) dimers $Mo_2(O_2CR)_4$ (R = alkyl or aryl) and $[Mo_2(SO_4)_4]^{4-}$ may be oxidized reversibly, both chemically and electrochemically, to $[Mo_2(O_2CR)_4]^+$ and $[Mo_2(SO_4)_4]^{3-}$.[4-9] These oxidations correspond to a change

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(1) Part 28 of the series entitled "Complex Halides of the Transition Metals".

(2) Undergraduate research participant from Kalamazoo College, Kalamazoo, Mich. 49001.

(3) Postdoctoral research associate, 1977–1978.

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Table I. $E_{1/2}$ Values for Molybdenum(II) Halide and Isothiocyanate Complexes in Dichloromethane[a]

complex	$E_{1/2}$-(Ox)[b]	$E_{1/2}$-(Red)[b]	$E_{1/2}$-(Red)[b]
$Mo_2Cl_4(PEt_3)_4$ (I)	+0.35		
$Mo_2Cl_4(P\text{-}n\text{-}Pr_3)_4$ (II)	+0.38		
$Mo_2Cl_4(dppe)_2$ (III)	+0.52		
$Mo_2Br_4(dppe)_2$ (IV)	+0.54		
$Mo_2(NCS)_4(PEt_3)_4$ (V)	+0.80	−1.17	
$Mo_2(NCS)_4(dppe)_2$ (VI)	+0.74[c]	−0.85	−1.58
$Mo_2(NCS)_4(dppm)_2$ (VII)	+0.84[c]	−0.80	−1.60[d]

[a] With 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. [b] Volts vs. SCE with a Pt-bead working electrode. [c] Oxidation irreversible, with $i_{p,c}/i_{p,a} < 1$; $E_{p,a}$ is quoted rather than $E_{1/2}$. [d] $E_{p,c}$.

in electronic configuration from $(\sigma)^2(\pi)^4(\delta)^2$ to $(\sigma)^2(\pi)^4(\delta)^1$ and therefore to a decrease in the metal–metal bond order from 4 to 3.5. On the other hand, with the exception of the reduction of $Mo_2(O_2CCF_3)_4$ to $[Mo_2(O_2CCF_3)_4]^-$ by pulse radiolysis,[10] neither $Mo_2(O_2CR)_4$ nor $[Mo_2(SO_4)_4]^{4-}$ exhibits any simple reversible reduction chemistry. In contrast, the redox chemistry of the analogous rhenium dimers which contain rhenium–rhenium quadruple bonds, e.g., $Re_2(O_2CR)_4X_2$ (X = Cl, Br, or I), is that of one-electron reductions to species (i.e., $[Re_2(O_2CR)_4X_2]^-$) which possess the $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^1$ electronic configuration and thus also contain metal–metal bonds of order 3.5[11,12] In summary, with oxygen-containing anionic bridging ligands such as carboxylates and sulfate, the most significant *reversible* redox chemistry of complexes containing the Mo_2^{4+} core is that of oxidation to Mo_2^{5+}, while for isoelectronic Re_2^{6+} reduction to Re_2^{5+} is much more accessible.

This behavior is also in accord with the electrochemistry of the mixed halide–tertiary phosphine dimers $Re_2X_6(PR_3)_2$ (X = Cl or Br), where reduction to $[Re_2X_6(PR_3)_2]^-$, is well documented.[13] In the case of the dimers $Mo_2X_4(PR_3)_4$, there is to date little information as to their redox chemistry, although we had noted in an earlier report that the chemical oxidation of $Mo_2Cl_4(PR_3)_4$ (R = Et or *n*-Pr) to $(R_3PCl)_3Mo_2Cl_9$ is accomplished by use of refluxing carbon tetrachloride.[14] To ascertain whether the expected one-electron oxidation to $[Mo_2X_4(PR_3)_4]^+$ is indeed possible, we have carried out an electrochemical study on several molecules of the type $Mo_2X_4(PR_3)_4$, and we now report the salient features of this investigation.

Results and Discussion

As in previous studies,[11,13,15] we have carried out the electrochemical measurements on dichloromethane solutions of the complexes. Voltammetric half-wave potentials vs. SCE for the molybdenum(II) dimers $Mo_2Cl_4(PR_3)_4$ (R = Et or *n*-Pr) and $Mo_2X_4(dppe)_2$ (X = Cl or Br, dppe = 1,2-bis(diphenylphosphino)ethane) are presented in Table I, and the cyclic voltammogram of $Mo_2Cl_4(P\text{-}n\text{-}Pr_3)_4$ is shown in Figure 1a. In all instances the complexes exhibit a single oxidation, $Mo_2X_4L_4 \rightarrow Mo_2X_4L_4^+ + e^-$. For complexes I, II, and IV, $i_{p,c}/i_{p,a} \simeq 1$ for sweep rates (v) between 50 and 500 mV/s, and the ratio $i_p/v^{1/2}$ was constant for this same sweep rate range, in accord with diffusion control. Because of the low solubility of III in dichloromethane and, as a consequence, the attendant low peak currents, measurements were carried out at only one sweep rate (200 mV/s).[16]

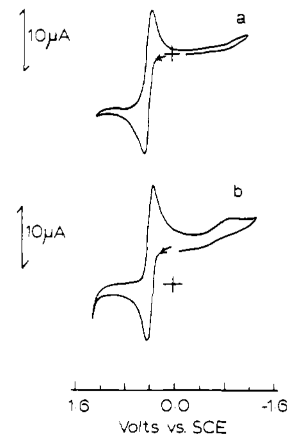

Figure 1. Cyclic voltammograms in 0.2 M TBAH–dichloromethane of $Mo_2Cl_4(P\text{-}n\text{-}Pr_3)_4$: (a) before and (b) after exhaustive electrolysis at +0.5 V. The cyclic voltammogram in (a) was recorded at room temperature; that in (b) at 0 °C.

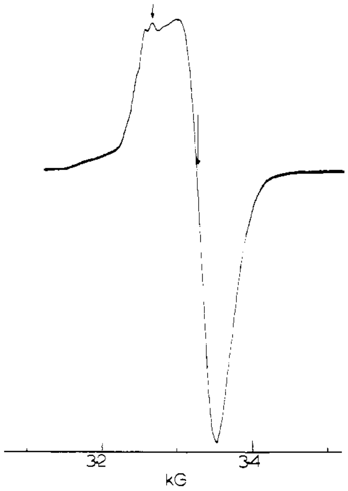

Figure 2. X-Band ESR spectrum of a CH_2Cl_2 glass (−180 °C) containing electrochemically generated $[Mo_2Cl_4(P\text{-}n\text{-}Pr_3)_4]^+$.

The potential separation, ΔE_p, between the anodic and cathodic peaks was in all cases greater than 60 mV and varied with sweep rate. For example, ΔE_p for II varied from 110 to 140 mV for v between 100 and 500 mV/s and between 95 and 160mV for these same scan rates in the case of IV. Although these electrochemical properties can be viewed as being in accord with quasi-reversible electron-transfer processes,[20,21]

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(16) The similarity of the $E_{1/2}$ values for I and II is expected because of their close structural similarity.[14,17] Both complexes possess an eclipsed rotational configuration of D_{2d} symmetry with *trans*-$MoCl_2(PR_3)_2$ units. While $Mo_2Cl_4(dppe)_2$ also has an eclipsed configuration, the electrochemical data we report is for the α isomer, wherein the individual $MoCl_2P_2$ units have a cis geometry.[18] These complexes are in turn different from $Mo_2Br_4(dppe)_2$, which has a partially staggered configuration (α close to 30°), bridging dppe ligands and a trans arrangement within the $MoBr_2P_2$ units.[18,19] Accordingly, these complexes all possess a $(\sigma)^2(\pi)^4(\delta)^2$ electronic configuration, but structural differences preclude any simple explanation of the trend in $E_{1/2}$ values.
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we believe that they are best considered in a qualitative sense as reversible. Measurements of the known reversible couples $(C_5H_5)_2Fe/(C_5H_5)_2Fe^+$ and $Ru(bpy)_3^{2+}/Ru(bpy)_3^{3+}$ under these same experimental conditions[22] gave $E_{1/2}$ values of +0.43 and +1.42 V, respectively, and ΔE_p values of 90 and 85 mV at v = 100 mV/s. Since ΔE_p increased with increase in v, being ca. 120 mV at 400 mV/s, the behavior of these systems parallels closely that which we observe for the molybdenum complexes.

Our attempts to generate the monocations of the halide complexes (I–IV) were restricted to $Mo_2Cl_4(P\text{-}n\text{-}Pr_3)_4$ and $Mo_2Br_4(dppe)_2$. In the case of IV, the room-temperature controlled-potential electrolysis at +0.8 V led to the decomposition of a major portion of the complex. Decomposition, albeit less rapid, also occurred upon electrolyzing a dichloromethane solution of $Mo_2Cl_4(P\text{-}n\text{-}Pr_3)_4$ at room temperature, and an attempt to chemically oxidize $Mo_2Cl_4(P\text{-}n\text{-}Pr_3)_4$ with use of an acetonitrile solution of $NOPF_6$[23] led to the same result. However, when the electrolysis of $Mo_2Cl_4(P\text{-}n\text{-}Pr_3)_4$ was carried out at 0 °C, the blue solution turned dark green and the oxidation (n = 0.98 by coulometry) was found to proceed smoothly to afford stable solutions of the monocation. The cyclic voltammogram of the resulting solution (Figure 1b) indicated that the structure was intact, and coulometry revealed that the single reversible wave now corresponded to a reduction. When this solution was warmed to room temperature, the cation decomposed fairly slowly to afford unidentified products.[24] The X-band ESR spectrum of a dichloromethane glass of $[Mo_2Cl_4(P\text{-}n\text{-}Pr_3)_4]^+$ which had been generated electrochemically is shown in Figure 2. Two g values were observed at 1.95 and 1.99, the latter exhibiting some poorly resolved hyperfine structure. The origin of the broad reproducible feature at 3200 G is unknown. The spectrum of $[MoCl_4(P\text{-}n\text{-}Pr_3)_4]^+$ has the appearance of an axially symmetric system (i.e., $g_{\parallel} = 1.99$ and $g_{\perp} = 1.95$). The lower symmetry of this cation (D_{2d}) relative to that of the formally isoelectronic $[Mo_2(O_2CC_3H_7)_4]^+$ and $[Mo_2(SO_4)_4]^{3-}$ ions,[5,6] for which $g_{\parallel} = g_{\perp} = 1.941$[5] and $g_{\parallel} = 1.891$ and $g_{\perp} = 1.909$,[6] respectively, should be reflected in ESR spectral differences. Of particular note is the decrease in the orbital contribution in $[Mo_2Cl_4(P\text{-}n\text{-}Pr_3)_4]^+$ compared to that in the propionate and sulfate-bridged dimers, the g values of the phosphine cation being closer to 2.0.

The oxidations of the isothiocyanate complexes VI and VII (dppe = 1,2-bis(diphenylphosphino)ethane and dppm = bis(diphenylphosphino)methane) were irreversible, the $i_{p,c}/i_{p,a}$ ratios having values much less than 1 in both cases. For $Mo_2(NCS)_4(PEt_3)_4$ this ratio was close to 1 for sweep rates of 100 mV/s or more, but became less than 1 at low sweep rates. Upon controlled-potential electrolysis at +0.92 V, the blue solution V turned black ($n > 1$) and the cyclic voltammogram of the resultant solution confirmed that the complex has decomposed. In contrast to the halide dimers, these isothiocyanate complexes also exhibited one or two reductions (Table I). For V, the reduction at $E_{1/2} = -1.17$ V was reversible, the blue solution turning green upon electrolysis at −1.32 V (n = 0.92 by coulometry). This anion reverts slowly to the blue unreduced $Mo_2(NCS)_4(PEt_3)_4$ upon standing. A similar reduction ($E_{1/2} = -1.07$ V) was observed for acetonitrile solutions of V. While neither of the reductions of $Mo_2(NCS)_4(dppm)_2$ is reversible, the orange monoanion of $Mo_2(NCS)_4(dppe)_2$ may be generated (n = 1.04 by coulometry) upon electrolysis at −1.3 V.[25]

The absence of reductions in the electrochemistry of the halide dimers of Mo_2^{4+} suggests that those which are exhibited by the isothiocyanate complexes in the potential range −0.80 to −1.60 V do not involve processes which utilize the metal-based σ, π, and δ orbital sets. On the other hand, the existence of readily accessible one-electron oxidations with the halide and isothiocyanate dimers I–VII is certainly in accord with the ease of oxidizing $Mo_2(O_2CC_3H_7)_4$ to its monocation and $[Mo_2(SO_4)_4]^{4-}$ to $[Mo_2(SO_4)_4]^{3-}$. These oxidations involve the configuration change $(\sigma)^2(\pi)^4(\delta)^2$ to $(\sigma)^2(\pi)^4(\delta)^1$ and demonstrate the close electronic relationship and similarity in redox behavior between $Mo_2Cl_4(PR_3)_4$, $Mo_2X_4(dppe)_2$, $Mo_2(O_2CR)_4$, and $[Mo_2(SO_4)_4]^{4-}$.

Experimental Section

The complexes $Mo_2Cl_4(PR_3)_4$ (R = Et or n-Pr), $Mo_2Cl_4(dppe)_2$, $Mo_2Br_4(dppe)_2$, $Mo_2(NCS)_4(PEt_3)_4$, $Mo_2(NCS)_4(dppe)_2$, and $Mo_2(NCS)_4(dppm)_2$ were available from previous investigations.[14,18,26] Tetra-n-butylammonium hexafluorophosphate (TBAH) was obtained by reacting tetra-n-butylammonium iodide with KPF_6 in hot water. The product was recrystallized from aqueous ethanol and dried in vacuo.

Solvents used for electrochemical experiments were of the highest purity commercially available (Fisher Scientific Co.) and were used without further purification. The CH_2Cl_2 used in obtaining the ESR glass spectra was freshly distilled and stored under N_2 in the dark prior to use.

X-Band ESR spectra of CH_2Cl_2 glasses were recorded at −180 °C with a Varian E-109 spectrometer. Electrochemical measurements were made on dichloromethane solutions containing 0.2 M tetra-n-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. $E_{1/2}$ values (taken as $(E_{p,a} + E_{p,c})/2$) are referenced to the saturated potassium chloride calomel electrode (SCE) at 22 ± 2 °C and are uncorrected for junction potentials. Cyclic voltammetry experiments were performed with use of a BioAnalytical Systems Inc. Model CV-1A instrument in conjunction with a Hewlett-Packard Model 7035B X-Y recorder. Potential control for coulometric experiments was maintained with a potentiostat purchased from BioAnalytical Systems Inc. Values of n, where n is the total number of equivalents of electrons transferred in exhaustive electrolyses at constant potentials, were calculated after measuring the total area under current vs. time curves for the complete reactions. The reactions were judged to be complete when the current had fallen below 1% of the initial value. All voltammetric measurements were made at a platinum-bead electrode in solutions deaerated with a stream of dry nitrogen. The platinum electrode was cleaned with the chromic acid and aqua regia procedures described by Adams.[27]

Acknowledgment. The work was supported by the National Science Foundation through Grant No. CHE79-09233. The Varian E-139 ESR spectrometer was purchased with a grant from the National Science Foundation (Grant No. BMS 75-19127). We thank Professor R. R. Schrock for providing us with the information described in ref 24 and Professor D. R. McMillin for discussions concerning the interpretation of the ESR spectral data.

Registry No. I, 38832-71-2; II, 39043-51-1; III, 64490-77-3; IV, 64508-29-8; V, 64784-48-1; VI, 64784-51-6; VII, 64784-41-4.

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(23) This reagent has been used by us previously[13] to oxidize $Re_2Cl_4(PR_3)_4$ (R = Et or Pr) to $[Re_2Cl_4(PR_3)_4]^+$.

(24) We have been informed by Professor R. R. Schrock, Massachusetts Institute of Technology, that he has successfully generated solutions of $[Mo_2Cl_4(PR_3)_4]^+$ by the low-temperature chemical oxidation of $Mo_2Cl_4(PR_3)_4$ in acetonitrile. Accordingly, we abandoned any further attempts to isolate this cation.

(25) The cyclic voltammograms of dichloromethane solutions of $(Bu_4N)_2Mo_2(NCS)_6(PEt_3)_2$ were also recorded. A quasi-reversible reduction occurs at $E_{1/2} = -1.61$ V (−1.54 V in acetonitrile), but controlled-potential electrolysis at −1.78 V led to decomposition. An irreversible oxidation at $E_{p,a} = +0.24$ V (+0.23 V in acetonitrile) exhibited no cathodic component on the reverse sweep using a switching potential of +0.5 V.

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