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Preliminary communication

SYNTHESIS AMD CHARACTERIZATION OF $[Et_4N]_2[Mo(CO)_4(SR)_2]$ (R = Ph, Bz): NEW, POTENTIALLY CHELATING BIS-THIOLATE SPECIES

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Summary

The new complexes $[Et_4N]_2[Mo(CO)_4(SR)_2]$ (R = Ph, Bz) have been prepared by reaction of $[Et_4N][SR]$ with (norbornadiene)$Mo(CO)_4$ at low temperature. The IR spectra and electrochemical behavior of these two species are different, perhaps implicating different conformational isomers with respect to the thiolate ligands. These complexes may prove to be valuable reagents for the synthesis of new heterometallic compounds, by virtue of their *cis*-monodentate thiolate ligands.

Recent reports [1,2] from this research group have extended our interest in molybdenum-sulfur chemistry in the direction of low-valent species. While most efforts to model the Fe—Mo—S site of nitrogenase [3] have involved studies of higher oxidation states of molybdenum, relatively little work has been done on the chemistry of molybdenum thiolates in oxidation states below +3, to which organometallic systems provide the most accessible route. We recently reported [2] that the compound *cis*-$Mo(t\text{-}BuNC)_4(t\text{-}BuS)_2$, prepared by Otsuka and coworkers [4], forms simple adducts with ferrous halides and we described the spectral and electrochemical properties of these new dinuclear species. In an attempt to broaden our knowledge of these thiolate-bridged, mixed-metal systems, we have prepared monomeric molybdenum carbonyl species containing *cis*-thiolate ligands and herein describe their synthesis and characterization.

Reaction of $Mo(CO)_6$ with tetralkylammonium thiolates at 45°C in MeCN has been shown [1] to yield thiolate-bridged dinuclear species of the type $[Mo_2(CO)_8(SR)_2]^{2-}$. Our approach to the preparation of monomeric thiolate complexes therefore was to react the well-known precursor, (norbornadiene)-

$Mo(CO)_4$, with tetraethylammonium thiolates in a 1/2 mole ratio under milder conditions (eq. 1) to prevent the formation of the stable bridged systems.

$$Mo(CO)_4(C_7H_8) + 2[Et_4N][SR] \xrightarrow[-23^\circ C]{MeCN} [Et_4N]_2[Mo(CO)_4(SR)_2] + C_7H_8 \qquad (1)$$

Compounds of the form $[Et_4N]_2[Mo(CO)_4(SR)_2]$ (R = Ph, Bz) can in fact be synthesized at low temperatures and isolated at room temperature. Pure samples of $[Et_4N]_2[Mo(CO)_4(SPh)_2]$ appear to be stable under argon at room temperature for weeks to months; samples of $[Et_4N]_2[Mo(CO)_4(SBz)_2]$ under the same conditions are stable over a period of days. They are both quite sensitive to air, but the benzylthiolate derivative especially so.

Elemental analytical and CO evolution data for these products confirm the proposed formulation [7]. The infrared spectra of these compounds are also consistent with this formulation, containing four bands in the carbonyl region which are lower in energy than those of $[Mo_2(CO)_8(SR)_2]^{2-}$, in keeping with the higher concentration of negative charge in the monomeric species. The infrared spectrum of the Bz derivative is very similar in appearance and band positions to that reported for the closely related complex $[Et_4N]_2[Mo(CO)_4$-$(C_6H_4S_2)]$ [8]. The pattern of the bands in the Bz and Ph derivatives is, however, significantly different (see Fig. 1). We have no conclusive explanation for this phenomenon, but speculate that it may be a result of the two thiolates favoring differing conformational isomers [9]. Further support of the proposed formulation was obtained by allowing a sample of $[Et_4N]_2[Mo(CO)_4(SPh)_2]$ to stir in MeCN solution at room temperature for 2 h and then precipitating the product with i-PrOH. $[Et_4N]_2[Mo_2(CO)_8(SPh)_2]$ (identified by its infrared spectrum) was recovered in 60% yield according to eq. 2, illustrating the tendency for terminal thiolate groups to convert to bridging, even under mild

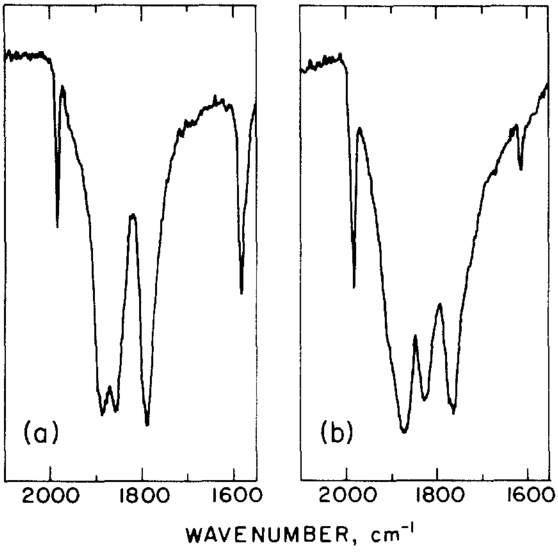

Fig. 1. Infrared spectra of $[Et_4N]_2[Mo(CO)_4(SPh)_2]$ (a) and $[Et_4N]_2[Mo(CO)_4(SBz)_2]$ (b) as KBr pellets.

$$2[Et_4N]_2[Mo(CO)_4(SR)_2] \rightarrow [Et_4N]_2[Mo_2(CO)_8(SR)_2] + 2[Et_4N][SR] \quad (2)$$

conditions, and the relative stability of the binuclear complex.

The existence of the relatively-stable 18-electron Mo^0 dianions $[Mo(CO)_4(SR)_2]^{2-}$ stands in contrast to that of structurally-related, but 16-electron, Mo^{II} species $Mo(R'NC)_4(SR)_2$ [4]. These latter compounds are apparently stabilized in the higher oxidation state by the more electron-donating isocyanide ligands and, consistent with the observation, cyclic voltammetry studies [2 and unpublished data] show no reversible reductive processes for these neutral species. These data confirm the instability of the hypothetical 18-electron Mo^0 complex $[Mo(R'NC)_4(SR)_2]^{2-}$ and demonstrate that the oxidation state of the most stable form of the $[MoL_4(SR)_2]$ structural unit is directed by the nature of L.

Although the thermal instability of the Mo^0 compounds prevented an investigation of their electrochemistry at ambient temperature, at —40° C in PrCN it was possible to obtain cyclic voltammetric [11] data for these species (Fig. 2). The CV of $[Mo(CO)_4(SPh)_2]^{2-}$ contains three well-defined oxidation waves of approximately equal current intensity [12]. As shown in the inset of Fig. 2a, the most negative of these waves is pseudo-reversible (ΔE 100 mV; $i_{pa}/i_{pc} = \sim 1.6$) when the scan is reversed prior to the more positive redox events. By contrast, the CV of the SBz analog is characterized by only two oxidation waves, with the more positive of these being very broad. The isolated more-negative redox event for $[Mo(CO)_4(SBz)_2]^{2-}$ is also much less reversible ($i_{pa}/i_{pc} = \sim 5.5$) than its phenyl analog. Although no definitive assignment of the redox events for these complexes can be made at present, we speculate that the three-wave pattern in the CV of $[Mo(CO)_4(SPh)_2]^{2-}$

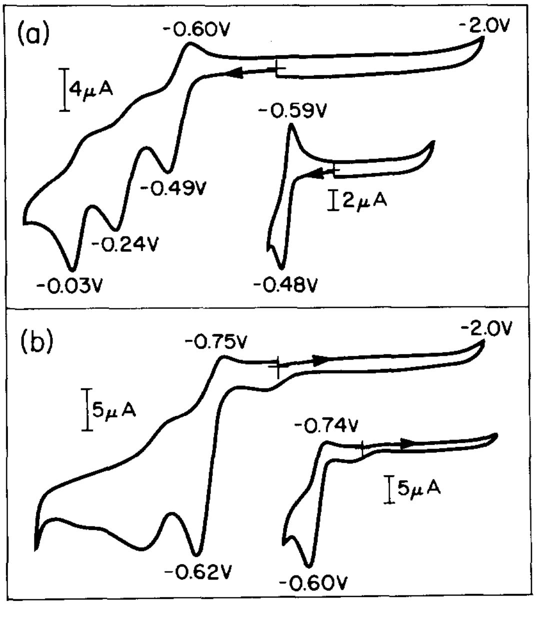

Fig. 2. Cyclic voltammograms of $[Mo(CO)_4(SPh)_2]^{2-}$ (a) and $[Mo(CO)_4(SBz)_2]^{2-}$ (b) in PrCN at —50 and —45° C, respectively. The scan rate was 50 mV/s.

could be due to sequential, metal-centered [14] oxidations corresponding to Mo^0/Mo^I, Mo^I/Mo^{II}, and Mo^{II}/Mo^{III} couples. The potentials of the primary oxidative process for the SBz and SPh compounds vary as expected with the SBz being the easier to oxidize. The remaining differences in the electrochemical behavior of the two species are not fully understood.

We anticipate that these new Mo^0 complexes will be useful reagents for the synthesis of new heteronuclear, thiolate-bridged species, since the sulfur atoms should be quite basic. In this regard, we note that the number of mononuclear species containing two or more monodentate thiolate groups is relatively limited. Examples include $(Cp)_2Mo(SR)_2$ [15] and $Mo(RNC)_4(SR)_2$ [4], both of which have been shown to chelate metal halides [2,10,16] and $Mo(CO)_2[SC_6H_2(i\text{-}Pr)_3]_3^-$ [17], which contains sterically hindered thiolate ligands that may prevent further complexation. Indeed, preliminary results suggest that $[Mo(CO)_4(SR)_2]^{2-}$ does react with ferrous and cobaltous halides, and work is in progress to characterize these new heterometallic species.

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5 Typical procedure: 0.50 g (1.67 mmol) $C_7H_8Mo(CO)_4$ [6] in 10 ml CH_3CN (distilled from CaH_2) was added dropwise over 15 min to a solution of $[Et_4N]SPh$ in 30 ml CH_3CN at −23° C. The reaction mixture was stirred for an additional 3 h, after which 25 ml ether was added, causing the precipitation of yellow crystals. The product was then isolated at room temperature in 27% yield. Attempts to obtain greater yields by addition of a larger volume of ether caused an apparent by-product to precipitate.

The procedure for the benzyl derivatives was similar, but the solution was only stirred for 15 min after addition of the $C_7H_8Mo(CO)_4$. Addition of ether usually resulted in an oil which solidified to a yellow powder after 1—2 h of stirring at low temperature. Yields were about 60%.

6 R.B. King, Organometallic Synthesis, Academic Press, New York, 1965, Vol. 1, p. 124.

7 $[Et_4N]_2[Mo(CO)_4(SPh)_2]$. Found: C, 55.08; H, 7.69; N, 4.09. $C_{20}H_{50}N_2O_4S_2Mo$ calcd. C, 55.94; H, 7.35; N, 4.07%. Percent CO was determined by decomposition of a weighed sample with Br_2 in CH_2Cl_2 and evolved gas was quantitated using a Toepler pump: 97% of predicted for proposed formula.

The benzyl complex was judged to be too unstable for accurate elemental analysis, but a carefully done decomposition experiment on a freshly-prepared samples gave 95 and 100% of the expected CO.

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9 We note that the compound $Mo(t\text{-}BuNC)_4(t\text{-}BuS)_2CuBr$ [10] (admittedly more rigid than the mononuclear compounds reported here) exists in two conformational structures whose infrared spectra differ considerably in the C≡N region. The thermochromic behavior of $(RNC)_4Mo(SR)_2\text{-}FeX_2$ was also attributed [2] to the presence of conformational isomers.

10 N.C. Payne, N. Okura and S. Otsuka, J. Am. Chem. Soc., 105 (1983) 245.

11 Cyclic voltammetry was carried out in a three-electrode cell using 0.1 *M* Bu_4NBF_4 as the supporting electrolyte. The working electrode was a glassy carbon disk and the reference electrode was an aqueous SCE separated from the sample solution by a salt bridge. The cell was immersed in an acetone bath whose temperature could be adjusted by addition of dry ice. A Bioanalytical Systems CV-1 A potentiostat was used.

12 Oxidation wave current parameters $i/ACv^{1/2}$ at 50 mV/s were 219 for the Ph derivative at −50° C and 212 $A\ cm\ s^{1/2}\ V^{-1/2}\ mol^{-1}$ for the Bz derivative at −45° C. These values can be compared with a value of 320 $A\ s^{1/2}\ V^{-1/2}\ mol^{-1}$ for the known [13] one-electron oxidation of $Mo[S_2C_2(CN)_2]^{3-}$ in PrCN.

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