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Electrooxidation of Molybdenum Halide Complexes of the Type $CpMo(CO)_{3-n}(PR_3)_nX$

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The literature contains reports of the reductive electrochemistry of the molybdenum halide complexes $CpMo(CO)_3X$ ($Cp = \eta^5\text{-}C_5H_5$; X = Cl, I) [1–3] and $CpMo(CO)_2(PPh_3)I$ [1], as determined by conventional d.c. and/or a.c. polarography. These complexes are reduced in either two one-electron steps or one two-electron step, resulting in loss of halide and formation of the corresponding anionic molybdenum species. As is so frequently the case with studies limited to mercury electrodes, the oxidative electrochemistry has been neglected. There are reports of electrochemical oxidations of related complexes. The dimer $[CpMo(CO)_3]_2$ is oxidized by two electrons, causing cleavage of the metal–metal bond [4]. A series of dichalcogenocarbamato complexes, $CpMo(CO)_n(XYCNMe_2)$, derived from $CpMo(CO)_3Cl$, have been found to undergo reversible or quasi-reversible oxidations in acetonitrile and dichloromethane [5].

As a part of an investigation of the oxidative electrochemistry of molybdenum alkyl complexes of the type $CpMo(CO)_{3-n}(PR_3)_nR'$, we were surprised to find that an undesired by-product, $CpMo(CO)_2(PPh_3)I$, displayed a reversible oxidation by cyclic voltammetry in dichloromethane. Since the oxidative electrochemistry of this compound and the other members of this family of halide complexes had never been reported, we decided to investigate the effect of phosphine and halide substitution on the potential of the Mo(III/II) redox couple and the stability of the 17-electron cation.

Experimental

Complexes **1** [6], **2**, **3**, **6**, **9** [7], **4**, **7** [8], **5**, **8** [9], **10** and **11** [10] were prepared by literature methods and identified by their IR and ^1H NMR spectra. Solvents were high purity (Burdick and Jackson, distilled in glass or Fisher optima) and were distilled under nitrogen before use: tetrahydrofuran from Na/benzophenone; dichloromethane from calcium hydride; and acetonitrile from phosphorus pentoxide. All other chemicals were reagent grade or better and were used as received.

Cyclic voltammetry was performed with a Bioanalytical Systems BAS 100A electrochemical analyzer equipped with a C-1A cell stand, platinum disc working electrode (1.6 or 0.5 mm diameter) polished with 0.3 micron alumina polishing powder (Buehler), platinum wire counter electrode, and saturated KCl silver–silver chloride (Ag/AgCl) reference electrode. Controlled potential electrolyses were performed with an EG & G Princeton Applied Research Model 273 potentiostat and a three-compartment electrochemical cell with 25 × 25 mm platinum foil working and counter electrodes, and a silver wire quasi-reference electrode. Spectroelectrochemistry was performed with a cell similar to ones described in the literature [11, 12] having calcium fluoride windows and a 100-mesh platinum gauze working electrode. The potential of the working electrode was controlled with a Bioanalytical Systems CV-27 voltammograph and IR spectra were recorded with a Mattson Cygnus 100 FTIR spectrophotometer. The supporting electrolyte in all experiments was tetrabutylammonium hexafluorophosphate (Southwestern Analytical Chemicals, electrometric grade, 0.1 M for cyclic voltammetry and controlled potential electrolysis, 0.5 M for spectroelectrochemistry). Solutions were purged with either nitrogen or argon and measurements were performed under an inert atmosphere. All potentials are expressed relative to the formal potential of the ferrocenium/ferrocene couple (Fc^+/Fc), which we measure as +0.60 V *versus* Ag/AgCl.

Results and Discussion

Table 1 lists the formal potentials obtained by cyclic voltammetry in dichloromethane and acetonitrile for the complexes studied. All three tricarbonyl complexes, **1**–**3**, displayed irreversible oxidations in both solvents at a scan rate of 200 mV/s. This irreversibility was evidenced by the lack of a cathodic peak on the return scan and probably results from rapid decomposition of the cation. However, in dichloromethane the oxidation of the iodo complex **3** displayed reversible behavior (approximately equal anodic and cathodic peak currents) upon increasing the scan rate to 5 V/s. At this scan rate the chemical reaction(s) which produce(s) decomposition of the cation are apparently slow relative to the time scale of the cyclic voltammetric experiment.

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TABLE 1. Formal Potentials for the Oxidation of $CpMo(CO)_{3-n}(PR_3)_nX$ in Dichloromethane and Acetonitrile

Compound	PR_3[a]	X	E_f in CH_2Cl_2 (V)[b]	E_f in CH_3CN (V)[b]
1	none	Cl	$+0.63^c$	$+0.71^c$
2	none	Br	$+0.64^c$	$+0.73^c$
3	none	I	$+0.68^d$	$+0.63^c$
4	PPh_3	Cl	$+0.26$	$+0.25^{c,e}$
5	PPh_3	Br	$+0.28$	$+0.29^f$
6	PPh_3	I	$+0.30$	$+0.33^g$
7	PBu_3	Cl	$+0.21$	$+0.19^g$
8	PBu_3	Br	$+0.22$	$+0.20^g$
9	PBu_3	I	$+0.24$	$+0.23^h$
10	dppe	Cl	-0.25	-0.21
11	dppe	I	-0.23	-0.18

[a] Ph = phenyl, Bu = n-butyl, dppe = η^2-bis(diphenylphosphino)ethane ($n = 2$). [b] Average of anodic and cathodic peak potentials measured in indicated solvent at $\nu = 200$ mV/s and referenced to Fc^+/Fc internal standard. All peak potential separations approximately 60–80 mV. [c] Anodic peak potential of irreversible oxidation. [d] $\nu = 5$ V/s. [e] Some reversibility observed at $\nu = 25$ V/s. [f] $\nu = 2.5$ V/s. [g] $\nu = 2$ V/s. [h] $\nu = 1$ V/s.

Substitution of one carbonyl ligand with a triphenylphosphine, producing compounds **4**–**6**, lowered the potential necessary for oxidation by 300 to 500 mV and resulted in substantial stabilization of the Mo(III) cation, that is, a decrease in its rate of chemical decomposition. All of the oxidations were completely reversible in dichloromethane at 200 mV/s. In acetonitrile the chloro complex **4** displayed a small cathodic peak at 25 V/s, while oxidation of the iodo complex **6** was reversible at 2 V/s. Formal potentials were decreased by about another 60 mV in complexes **6**–**9**, which contain the more powerful electron donor tri-n-butylphosphine. The lowest formal potentials for the Mo(III/II) couple, and the most stable cations, were observed with the dppe complexes **10** and **11**. Both showed completely reversible oxidations at 200 mV/s in both dichloromethane and acetonitrile. It should be noted that the bromo dppe complex has not been reported and our attempts to synthesize it have so far proved unsuccessful. In all cases, as the halide was changed the apparent stability of the cation increased in the order Cl < Br < I.

The infrared spectra of the oxidized dppe complexes were obtained in an infrared spectroelectrochemical cell similar to ones described in the literature [11, 12]. For both compounds **10** and **11** oxidation in dichloromethane was accompanied by a smooth decrease in the intensity of the original carbonyl bands at 1846 and 1847 cm^{-1}, respectively, and appearance of new bands at 2011 and 2003 cm^{-1}, respectively, for the cations $\mathbf{10}^+$ and $\mathbf{11}^+$. This increase in frequency was expected since the cations are less electron-rich and thus backbond less to the carbonyl ligands. The lower carbonyl stretching frequency of the iodo complex, probably reflecting a higher electron density at the metal center, may provide a clue to the greater stability of the oxidized iodo complexes relative to the bromo and chloro species.

Controlled potential electrolysis of **11** in dichloromethane at −44 °C (acetonitrile slush) consumed 1.0 Faraday per mole of complex and resulted in a color change from orange to purple. Cyclic voltammetry indicated formation of a stable solution of the 17-electron cation. While the purple solution of the cation was stable at −44 °C, on warming to room temperature the color quickly returned to the orange of the neutral complex. An IR spectrum obtained immediately after electrolysis showed a carbonyl band with the same stretching frequency as was seen in the spectroelectrochemical cell.

Cyclic voltammetry in acetonitrile demonstrated that the cations were less stable in that solvent. This instability was also observed in dichloromethane on addition of nucleophiles. The addition of acetonitrile, pyridine, or trimethylphosphite led to a decrease in the cathodic peak currents of the oxidations. We are currently investigating the kinetics and mechanism of the reaction between nucleophiles and the cationic 17-electron molybdenum halide complexes which leads to this loss of cyclic voltammetric reversibility.

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