IR (Nujol mull) 2062 (vs), 1982 (vs) cm^{-1} [ν(CO)].

X-ray Structure Determinations. 1. Needles of the bis(acetonitrile) solvate were dried by passing dry nitrogen over them (drying in vacuo resulted in loss of MeCN). A single crystal, suitable for X-ray diffraction, was mounted in a thin-walled glass capillary under nitrogen and held in place by an epoxy glue. All measurements were made on a Nicolet P3m diffractometer at room temperature, using graphite-monochromated Mo Kα X-radiation (λ = 0.710 69 Å). Two check reflections, remeasured after every 100 ordinary data, showed 18% decay over the period of data collection, and an appropriate correction was therefore applied, as were Lorentz and polarization corrections. The intensity data were corrected for absorption effects by calculation of transmission coefficients based on a six-parameter fit to 400 azimuthal scan data. The structure was solved by conventional heavy-atom (Patterson and Fourier) methods. All non-hydrogen atoms were assigned ansitropic thermal parameters and refined without positional constraints. All hydrogens were constrained to idealized geometries (C–H = 0.96 Å; ∠H–C–H = 109.5° for aliphatic hydrogens) and assigned common isotropic temperature parameters by type (i.e., phenyl and pyridyl, methylene and methyl). The structure was refined by full-matrix blocked-cascade least-squares analysis. All calculations were carried out on a Nicolet R3m/V structure determination system using programs of the SHELXTL-PLUS package.[7] Neutral-atom scattering factors were taken from ref 8. Details of the data collection and structure determination are gathered in Table III, positional and equivalent isotropic thermal parameters are given in Table IV, and selected bond distances and angles are collected in Table V.

2. Suitable crystals were obtained by crystallization from hot benzonitrile. The structure determination was carried out as described above, with the following differences. The absorption correction was carried out numerically: crystal faces [distances from origin in mm] (101) [0.35], (010) [0.092], (0,–1,0) [0.092], (–3,–2,4) [0.075], (1,0,–1) [0.075], (–1,–1,0) [0.15], (–1,1,0) [0.13]. Three check reflections remeasured after every 50 ordinary data showed no significant variation during data collection. Nonhydrogen atoms were refined anistropically; hydrogens were constrained to idealized geometries and assigned fixed isotropic displacement parameters ca. 1.2 times U_{iso} of their attached carbon atom. Positional and equivalent isotropic thermal parameters are given in Table VI, and selected bond distances and angles are collected in Table VII.

Supplementary Material Available: Tables of positional and thermal parameters and bond lengths and angles for 1 and 2 (6 pages); tables of observed and calculated structure factors for compounds 1 and 2 (56 pages). Ordering information is given on any current masthead page.

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Synthesis of Dipositive Molybdenum(II) and Tungsten(II) Carbonyl Cations by Electrochemically Generated Internal Addition Reactions

Alan M. Bond,*[,1] Ray Colton,*[,2] and Katherine McGregor[2]

Department of Chemical and Analytical Sciences, Deakin University, Geelong, Victoria 3217, Australia, and Department of Inorganic Chemistry, University of Melbourne, Parkville, Victoria 3052, Australia

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Electrochemical oxidation of $M(CO)_3(\eta^1\text{-L-L})(\eta^2\text{-L-L})$ (M = Mo, W; L-L = various ditertiary phosphines and a mixed phosphine/arsine) in acetone (0.1 M Et_4NClO_4) or in dichloromethane (0.1 M Bu_4NClO_4) solution under carbon monoxide at a platinum electrode yields isolable $[M(CO)_3(\eta^2\text{-L-L})_2]^{2+}$ cations by the electrochemically generated internal addition reaction $M(CO)_3(\eta^1\text{-L-L})(\eta^2\text{-L-L}) \rightarrow [M(CO)_3(\eta^2\text{-L-L})_2]^{2+} + 2e^-$. Electrochemical synthesis therefore provides at present the only route to novel dipositive carbonyl cations in the special case where a pendent phosphorus (or arsenic) atom is available to provide the additional donor ligand required to achieve an 18-electron configuration. Chemical oxidations do not give the same products because of nucleophilic attack by solvent, the anion of the oxidant, or adventitious impurities on the dipositive cation. The $[M(CO)_3(\eta^2\text{-L-L})_2]^{2+}$ cations decompose very slowly under carbon monoxide and much more rapidly under nitrogen to give first the 16-electron *trans*-$[M(CO)_2(\eta^2\text{-L-L})_2]^{2+}$ species (or weakly solvated species), which then undergo nucleophilic attack by the electrochemical supporting electrolyte NBu_4ClO_4 to generate $[M(CO)_2(\eta^2\text{-L-L})_2(ClO_4)]^+$: $[M(CO)_3(\eta^2\text{-L-L})_2]^{2+} \rightarrow$ *trans*-$[M(CO)_2(\eta^2\text{-L-L})_2]^{2+} \rightarrow [M(CO)_2(\eta^2\text{-L-L})_2(ClO_4)]^+$. The product of the oxidation of $Mo(CO)_3(\eta^1\text{-dpm})(\eta^2\text{-dpm})_2$ (dpm = $Ph_2PCH_2PPh_2$) by $AgClO_4$ has been isolated and shown to be $Mo(\eta^2\text{-dpm})_2(ClO_4)_2$, but its structure is not known.

Introduction

Oxidation state II molybdenum and tungsten carbonyl complexes are well-known, and they usually have seven-coordinate geometry.[3,4] They were originally prepared by halogen oxidation of substituted zerovalent carbonyl compounds[3,5] such as in eq 1. In these chemical oxidative

$$Mo(CO)_4(PPh_3)_2 + Br_2 \rightarrow Mo(CO)_3(PPh_3)_2Br_2 + CO \quad (1)$$

reactions, the stable 18-electron configuration is retained in both the zerovalent and divalent complexes.

Electrochemical oxidation studies of zerovalent molybdenum and tungsten compounds have also been carried out. In most cases an overall two-electron oxidation is

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(2) University of Melbourne.

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observed, which occurs via either two one-electron steps or a single two-electron step:[6,7]

$$\mathrm{M(0)} \xrightarrow{e^-} \mathrm{M(I)} \xrightarrow{e^-} \mathrm{M(II)} \qquad (2)$$

$$\mathrm{M(0)} \xrightarrow{2e^-} \mathrm{M(II)} \qquad (3)$$

The product of the electrochemical two-electron oxidation of a neutral zerovalent carbonyl complex is expected to be a 16-electron dipositive cation, which is likely to be highly reactive. This reactivity is consistent with the experimental observations that such two-electron-oxidation processes are usually chemically irreversible on the normal voltammetric time scale[6] due to reactions of the cations with the solvent, the electrolyte, or any other nucleophile that may be present. Thus, attempts at electrochemical syntheses of new oxidation state II dipositive carbonyl complexes have invariably failed due to extremely rapid nucleophilic attack on the dipositive 16-electron cation, which ultimately results in the loss of carbon monoxide to produce non-carbonyl-containing inorganic species as the only isolable products. Consequently, electrochemical synthetic methods have so far failed to contribute to the isolation of highly charged cationic carbonyl species inaccessible by chemical oxidation. However, recent preliminary electrochemical studies[8] on the complexes $M(CO)_3(\eta^1\text{-L-L})(\eta^2\text{-L-L})$ (M = Mo, W; L-L = $Ph_2PCH_2PPh_2$ (dpm), $Ph_2PCH_2CH_2PPh_2$ (dpe)) have produced some evidence in solution for the new class of dipositive carbonyl complexes $[M(CO)_3(\eta^2\text{-L-L})_2]^{2+}$, which are not accessible by chemical oxidation:[9,10]

$$M(CO)_3(\eta^1\text{-L-L})(\eta^2\text{-L-L}) \rightarrow [M(CO)_3(\eta^2\text{-L-L})_2]^{2+} + 2e^- \qquad (4)$$

To date, the new class of dipositive cationic products have not been isolated or characterized by spectroscopic techniques. In this paper we describe the preparation, isolation, spectroscopic and analytical characterization, and decomposition of several electrochemically generated $[M(CO)_3(\eta^2\text{-L-L})_2]^{2+}$ cations for L-L = dpm, dpe, $Ph_2AsCH_2CH_2PPh_2$ (ape), and $Ph_2PCH_2CH_2CH_2PPh_2$ (dpp). We believe this new synthetic route, which we call electrochemically generated internal addition, may be generally applicable to the preparation of positively charged species from carbonyl systems that include a pendent donor group which inhibits the usual rapid nucleophilic attack by solvent, electrolyte, etc.

Experimental Section

Materials. All solvents and reagents were of AR grade or better. The electrochemical supporting electrolytes were obtained from Southwestern Analytical and were dried under vacuum before use. The ligands dpm, dpe, ape, and dpp (Strem) were used as received.

Preparations. (a) $M(CO)_3(\eta^1\text{-L-L})(\eta^2\text{-L-L})$. The new complexes with L-L = ape and dpp were prepared in the same manner as the previously reported dpm and dpe complexes.[8]

(b) $[M(CO)_3(\eta^2\text{-L-L})_2](ClO_4)_2$. *Caution!* Although we have experienced no difficulties with these compounds, all perchlorates should be handled carefully and not subjected to heat or shock. The complexes $[M(CO)_3(\eta^2\text{-L-L})_2](ClO_4)_2$ were prepared by oxidative controlled-potential electrolysis at a platinum-gauze electrode of 1 × 10^{-3} M *fac*-$M(CO)_3(\eta^1\text{-L-L})(\eta^2\text{-L-L})$ in either acetone (0.1 M Et_4NClO_4) or dichloromethane (0.1 M Bu_4NClO_4) at 0.3 V vs Fc^+/Fc (Fc = ferrocene) under carbon monoxide at room temperature. To isolate the solids, the acetone solution was used, and after electrolysis water (25 cm^3) was added and the solution chilled to 0 °C for several hours. The small amount of precipitate was filtered off (the supporting electrolyte stays in solution) and dried. Anal. (Australian Microanalytical Service (AMDEL)) Calcd for $[W(CO)_3(\eta^2\text{-dpm})_2](ClO_4)_2$: C, 51.5; H, 3.6. Found: C, 51.3; H, 4.0. The other complexes were characterized by their similar infrared and ^{31}P NMR spectra.

Table I. Infrared and Phosphorus-31 NMR Data of New Zerovalent Complexes in Dichloromethane Solution at 20 °C

compd	ν_{CO}, cm^{-1}	$\delta(^{31}P)$,[a] ppm	$J_{P,P}$, Hz
fac-$Mo(CO)_3(\eta^1\text{-ape})(\eta^2\text{-ape})$			
η^1-P-bonded	1950, 1850	28.5 d, 51.5 d	22
η^1-As-bonded		−12.5 s, 52.8 s	
fac-$W(CO)_3(\eta^1\text{-ape})(\eta^2\text{-ape})$			
η^1-P-bonded	1945, 1850	11.6 d, 39.4 d	22
η^1-As-bonded		−12.8 s, 41.1 s	
fac-$Mo(CO)_3(\eta^1\text{-dpp})(\eta^2\text{-dpp})$	1938, 1838	−18.4 s, 13.0 d, 22.9 t	24
fac-$W(CO)_3(\eta^1\text{-dpp})(\eta^2\text{-dpp})$	1930, 1830	−18.5 s, −5.5 d, 5.6 t	20

[a] Legend: s = singlet; d = doublet; t = triplet.

(c) $M(\eta^2\text{-dpm})_2(ClO_4)_2$. *fac*-$M(CO)_3(\eta^1\text{-dpm})(\eta^2\text{-dpm})$ (M = Mo, W; 1.0 mmol) and $AgClO_4$ (2 mmol) were stirred in dichloromethane (20 cm^3) at room temperature under nitrogen. After 15 min no carbonyl compounds remained (IR spectroscopy). After filtration to remove elemental silver, *n*-hexane was added to give a pale gray precipitate. The compounds have limited solubility in organic solvents and are sensitive to heat and light when in solution. Anal. Calcd for $Mo(\eta^2\text{-dpm})_2(ClO_4)_2$: C, 51.3; H, 3.8; O, 10.9; P, 10.6; Cl, 6.1. Found: C, 51.0; H, 4.1; O, 10.6; P, 10.6; Cl, 6.3.

Controlled-Potential Electrolyses. Controlled-potential electrolyses were performed at a platinum-gauze working electrode with use of a Princeton Applied Research Corp. (PAR, Princeton, NJ) Model 173 potentiostat/galvanostat in conjunction with a PAR Model 179 digital coulometer. The platinum-gauze auxiliary electrode was separated from the test solution via a salt bridge. The reference electrode was Ag/AgCl, whose potential relative to the reversible Fc^+/Fc redox couple was known. Potentials are quoted against the Fc^+/Fc couple.

Spectroscopic Measurements. Phosphorus-31 NMR spectra were recorded in dichloromethane solution with use of a JEOL FX 100 spectrometer operating at 40.32 MHz. External 85% H_3PO_4 was used as the reference, and the high frequency positive convention is used for chemical shifts. Infrared spectra were recorded in dichloromethane solution with the use of a Jasco A-320 spectrophotometer.

Results and Discussion

Characterization of New Zerovalent Complexes. The complexes $M(CO)_3(\eta^1\text{-ape})(\eta^2\text{-ape})$ (M = Mo, W) may exist in two facial and four meridional isomeric forms. Infrared data (Table I) suggest that facial isomers are formed, since only two strong absorptions are observed in the carbonyl region. The phosphorus-31 NMR spectrum of $Mo(CO)_3(\eta^1\text{-ape})(\eta^2\text{-ape})$ in dichloromethane solution consists of two doublets of equal intensity and two equal-intensity singlets. Facial and meridional stereochemistry for these complexes cannot be unambiguously distinguished on the basis of phosphorus-31 NMR spectroscopy alone, but together with the infrared evidence the phosphorus-31 NMR spectrum indicates that this complex

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Table II. Cyclic Voltammetric Data for the Oxidation of *fac*-$M(CO)_3(\eta^1\text{-L-L})(\eta^2\text{-L-L})$ (L-L = ape, dpp) in Acetone (0.1 M Et_4NClO_4) and Dichloromethane (0.1 M Bu_4NClO_4) at a Platinum Electrode at 20 °C[a]

compd	solvent	process[b]				
		1	2		3	4
		E_p^{ox}, V	E_p^{ox}, V	E_p^{red}, V	E_p^{ox}, V	E_p^{red}, V
$Mo(CO)_3(\eta^1\text{-ape})(\eta^2\text{-ape})$	acetone	0.17	0.03	−0.05	0.49	−0.77
	CH_2Cl_2	0.07	0.03	−0.12	0.57	−0.94
$W(CO)_3(\eta^1\text{-ape})(\eta^2\text{-ape})$	acetone	0.14	0.01	−0.05	0.49	−0.74
	CH_2Cl_2	0.05	0.01	−0.11	0.56	−1.09
$Mo(CO)_3(\eta^1\text{-dpp})(\eta^2\text{-dpp})$	acetone	0.08	−0.09	−0.15	0.49	−1.11
	CH_2Cl_2	0.04	−0.14	−0.21	0.65	−1.14
$W(CO)_3(\eta^1\text{-dpp})(\eta^2\text{-dpp})$[c]	CH_2Cl_2	0.02	−0.15	−0.23	0.58	*d*

[a] The scan rate is 200 mV s^{-1}. E_p^{ox} = oxidation peak potential observed on forward oxidation scan; E_p^{red} = reduction peak potential observed on reverse reduction scan. All potentials are in V vs the Fc^+/Fc redox couple. [b] Process 1 is observed on the first oxidation scan and corresponds approximately to the reaction $fac^0 \rightarrow fac^+ (\rightarrow mer^+) + e^-$. Process 2 is observed on the second and subsequent scans and corresponds to the reaction $mer^0 \rightleftharpoons mer^+ + e^-$. Process 3 is observed on the first oxidation scan and corresponds to the reaction $fac^+/mer^+ \rightarrow [M(CO)_3(\eta^2\text{-L-L})_2]^{2+} + e^-$. Process 4 is observed on the first reduction scan and corresponds to the reaction $[M(CO)_3(\eta^2\text{-L-L})_2]^{2+} + 2e^- \rightarrow$ *mer*-$M(CO)_3(\eta^1\text{-L-L})(\eta^2\text{-L-L})$. See ref 8 for further details. [c] Insoluble in acetone. [d] Not observed.

Table III. Infrared and Phosphorus-31 NMR Data for Divalent Compounds in Dichloromethane Solution at 20 °C

compd	ν_{CO}, cm^{-1}	$\delta(^{31}P)$,[a] ppm	$J_{P,P}$, Hz
$[Mo(CO)_3(dpm)_2]^{2+}$	2000, 1975	−4.9 d, −23.6 d	41
$[Mo(CO)_3(dpe)_2]^{2+}$	2000, 1965	56.0 (AB quartet)	
$[Mo(CO)_3(ape)_2]^{2+}$	1995, 1975	75.0 s	
$[W(CO)_3(dpm)_2]^{2+}$	1990, 1960	−29.4 d, −41.1 d	37
$[W(CO)_3(ape)_2]^{2+}$	1990, 1965	56.8 s	
$[Mo(CO)_2(dpe)_2Cl]^{+}$[b]	1942, 1878	53.4 s	
$[Mo(CO)_2(dpe)_2(ClO_4)]^{+}$	1945, 1880	54.0 s	
$[Mo(CO)_2(dpm)_2(ClO_4)]^{+}$	1950, 1890	37.0 s	
$[Mo(CO)_2(ape)_2(ClO_4)]^{+}$	1950, 1880	78 s	
trans-$[Mo(CO)_2(dpm)_2]^{2+}$	2040	−2.0	
trans-$[Mo(CO)_2(dpe)_2]^{2+}$	2025	32	
trans-$[Mo(CO)_2(ape)_2]^{2+}$	2050	75	

[a] Legend: s = singlet; d = doublet. [b] Data from ref 12.

exists in solution as a mixture of the η^1-ape As-bonded and η^1-ape P-bonded facial isomers. A singlet at δ −12.5 coincides with that for free ape and is therefore assigned to the pendent phosphorus atom of the η^1-ape As-bonded isomer, and the other singlet is assigned to the coordinated phosphorus of this isomer. The two doublets are assigned to the η^1-P-bonded isomer. The relative intensities of the signals indicate a mixture of 60% η^1-ape P-bonded and 40% η^1-ape As-bonded isomers. *fac*-$W(CO)_3(\eta^1\text{-ape})(\eta^2\text{-ape})$ is isolated as a 50:50 mixture of η^1-ape P-bonded and η^1-ape As-bonded isomers. As for the analogous dpe complexes,[8] meridional isomers of $M(CO)_3(\eta^1\text{-ape})(\eta^2\text{-ape})$ (M = Mo, W) could not be prepared. NMR data for all compounds are given in Table I.

The phosphorus-31 NMR spectra of *fac*-$M(CO)_3(\eta^1\text{-dpp})(\eta^2\text{-dpp})$ (M = Mo, W) are similar to those observed for the analogous dpm and dpe complexes[8] and consist of a triplet, a doublet, and a singlet (1:2:1), which is consistent only with facial geometry; the meridional isomers could not be prepared.

Voltammetric Oxidation at Platinum Electrodes of New Zerovalent Complexes. We have previously shown[8] for $M(CO)_3(\eta^1\text{-L-L})(\eta^2\text{-L-L})$ (L-L = dpm, dpe) that both the *fac* and *mer* isomers are oxidized to $[M(CO)_3(\eta^2\text{-L-L})_2]^{2+}$, sometimes via an observable *mer*-$[M(CO)_3(\eta^1\text{-L-L})(\eta^2\text{-L-L})]^+$ intermediate. The $[M(CO)_3(\eta^2\text{-L-L})_2]^{2+}$ cations may be reduced electrochemically back to *mer*-$M(CO)_3(\eta^1\text{-L-L})(\eta^2\text{-L-L})$:

$$fac/mer\text{-}M(CO)_3(\eta^1\text{-L-L})(\eta^2\text{-L-L}) \rightarrow [M(CO)_3(\eta^2\text{-L-L})_2]^{2+} + 2e^- \quad (5)$$

$$[M(CO)_3(\eta^2\text{-L-L})_2]^{2+} + 2e^- \rightarrow mer\text{-}M(CO)_3(\eta^1\text{-L-L})(\eta^2\text{-L-L}) \quad (6)$$

However, although these reactions are chemically reversible at an electrode surface, they are not electrochemically reversible in the Nernstian sense since there are large separations in the oxidation and reduction potentials. The new ape and dpp complexes show generally similar behavior, and all data in acetone (0.1 M Et_4NClO_4) are given in Table II (see ref 8 for details of assignments of the processes). Qualitatively similar data are obtained in dichloromethane (0.1 M Bu_4NClO_4) solution.

Characterization of the Divalent Cationic Species. Voltammetric studies[8] have implied that, in both acetone and dichloromethane solutions, oxidation of *fac*- or *mer*-$M(CO)_3(\eta^1\text{-dpm})(\eta^2\text{-dpm})$ occurs by a two-electron process to give $[M(CO)_3(\eta^2\text{-dpm})_2]^{2+}$ (eq 5), but the oxidation products were not isolated or characterized spectroscopically at that time. We now report that oxidative controlled-potential electrolysis of a 1×10^{-3} M solution of *fac*-$M(CO)_3(\eta^1\text{-dpm})(\eta^2\text{-dpm})$ (M = Mo, W), at 0.3 V vs Fc^+/Fc, under a carbon monoxide atmosphere in acetone (0.1 M Et_4NClO_4) leads to the quantitative preparation in solution and subsequent isolation of $[M(CO)_3(\eta^2\text{-dpm})_2](ClO_4)_2$ and that in the case of the molybdenum complex analytical data have been obtained that support this formulation. In the absence of the carbon monoxide atmosphere, considerable decomposition occurs in solution even on the time scale of controlled-potential electrolysis experiments.

The infrared spectrum of $[Mo(CO)_3(\eta^2\text{-dpm})_2]^{2+}$ obtained by oxidation of $Mo(CO)_3(\eta^1\text{-dpm})(\eta^2\text{-dpm})$ in dichloromethane solution shows two strong bands at 2010 and 1975 cm^{-1}, compared with bands at 1942 and 1845 cm^{-1} for the starting material. The phosphorus-31 NMR spectrum at 20 °C obtained immediately after electrolysis consists of two doublets of equal intensity that display a small amount of AB character ($J_{P,P}$ = 42 Hz, $\Delta\nu_0$ = 758 Hz), and a similar spectrum is obtained at low temperature. This spectrum is simpler than expected for the seven-coordinate $[Mo(CO)_3(\eta^2\text{-dpm})_2]^{2+}$ species, but the phosphorus-31 NMR spectrum of the related complex[11] $[Mo(H)(CO)_2(\eta^2\text{-dpm})_2]^+$ is also deceptively simple, consisting of two doublets of equal intensity. Similar spectroscopic data were obtained for the corresponding dpe, ape, and dpp complexes, except that the two doublets appear as an AB quartet for the dpe complex, and these data are given in Table III.

Decomposition of $[M(CO)_3(\eta^2\text{-L-L})_2]^{2+}$ Cations. A solution of $[Mo(CO)_3(\eta^2\text{-dpm})_2]^{2+}$ produced by oxidative controlled-potential electrolysis under a carbon monoxide atmosphere is stable for 7–10 days, but if the electrolysis is performed under a nitrogen atmosphere, decomposition begins during the course of the electrolysis. The phosphorus-31 NMR spectrum of such a solution consists of two doublets due to $[Mo(CO)_3(\eta^2\text{-dpm})_2]^{2+}$ and a singlet at near δ −2 ppm. The infrared spectrum shows two ab-

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(11) Bond, A. M.; Colton, R.; Jackowski, J. J. *Inorg. Chem.* **1975**, *14*, 2526.

sorptions due to $[Mo(CO)_3(\eta^2\text{-dpm})_2]^{2+}$ and a new peak growing at ~2040 cm^{-1}. Over a long period of time the phosphorus-31 NMR spectrum shows two new singlets near δ 25 and 37 ppm, but their relative intensities vary from solution to solution, suggesting that they are produced by different species. The resonance at δ 25 is assigned to $dpmO_2$. Two new bands slowly grow in the infrared spectrum at 1950 and 1890 cm^{-1} and appear to be due to the species giving the singlet resonance at δ 37 in the phosphorus-31 NMR spectrum. Similar results are obtained for the decomposition of $[Mo(CO)_3(\eta^1\text{-dpe})(\eta^2\text{-dpe})]^{2+}$ except that the decomposition is much more rapid. However, in this case the second product of the decomposition sequence can be related to known compounds. The infrared and phosphorus-31 NMR spectra of $[Mo(CO)_2(\eta^2\text{-dpe})_2X]^+$ (X = F, Cl, Br, I)[12] are very similar to those described here and are consistent with a fluxional capped-trigonal-prismatic arrangement. On the basis of this evidence it appears that $[Mo(CO)_3(\eta^2\text{-L-L})_2]^{2+}$ (L-L = dpm, dpe) loses one molecule of carbon monoxide to form *trans*-$[Mo(CO)_2(\eta^2\text{-L-L})_2]^{2+}$. It is likely that solvent attack by acetone or dichloromethane initially replaces CO to generate $[M(CO)_2(\eta^2\text{-L-L})_2(\text{solvent})]^{2+}$ as an intermediate. It appears that the perchlorate anion, present in the supporting electrolyte as NBu_4ClO_4 or NEt_4ClO_4, coordinates to these species to form the seven-coordinate 18-electron species $[Mo(CO)_2(\eta^2\text{-L-L})_2(ClO_4)]^+$. Although the perchlorate anion is a poor coordinating ligand, there are examples known of its coordination to metal centers, particularly in nonaqueous solvents,[13,14] and examples are known of the even weaker ligands $[BF_4]^-$ and $[PF_6]^-$ coordinating to 16-electron molybdenum carbonyl compounds.[13] For example, Beck and Schloter[15] have shown that $(\eta^5\text{-}C_5H_5)Mo(CO)_3(PF_6)$ yields $[(\eta^5\text{-}C_5H_5)Mo(CO)_3(CH_2Cl_2)]PF_6$ in dichloromethane. Also Leoni and coworkers[16,17] have studied the reactivity of the unipositive Mo(II) compound $[(\eta^5\text{-}C_5Me_5)Mo(CO)_3]BF_4$ and shown that it is very prone to nucleophilic attack. A dipositively charged cation, such as those described here, would be expected to be even more reactive with respect to nucleophilic attack.

A similar decomposition pathway is observed for all the other $[M(CO)_3(\eta^2\text{-L-L})_2]^{2+}$ species.

Chemical Oxidation of $M(CO)_3(\eta^1\text{-L-L})(\eta^2\text{-L-L})$. In many cases chemical oxidants such as $AgClO_4$ and $NOPF_6$ react with metal carbonyl complexes to give the same products as electrochemical oxidation,[18,19] but that is not the case for the present systems.

Oxidation of *fac*- or *mer*-$Mo(CO)_3(\eta^1\text{-dpm})(\eta^2\text{-dpm})$ in dichloromethane with 2 mol of $AgClO_4$ gives elemental silver and results in the isolation of a pale gray powder that shows no absorbances in the carbonyl region of the infrared spectrum. The phosphorus-31 NMR spectrum at 20 °C of a dichloromethane solution of this complex consists of two complex resonances near δ 18 and 4 ppm of equal intensity that are mirror images of each other. This is the type of pattern expected for an AA′BB′ arrangement of phosphorus atoms and indicates that both dpm ligands are chelated. Microanalytical data for the compound indicate the surprising formulation $Mo(\eta^2\text{-dpm})_2(ClO_4)_2$. The proton NMR spectrum discounts the possibility of hydride formation. $Mo(\eta^2\text{-dpm})_2(ClO_4)_2$ is stable under refrigeration and in the absence of light, but at room temperature its solutions decompose within 15 min.

The infrared spectrum in the Cl–O region shows no bands due to ionic perchlorate (~1095 cm^{-1} in solution[20]), but it is difficult to observe bands due to coordinated perchlorate, because of overlap with bands due to the dpm ligands. No signals were observed in the chlorine-35 NMR spectrum of a solution of $Mo(dpm)_2(ClO_4)_2$, but an equimolar solution (with respect to perchlorate) of Bu_4NClO_4 gives a sharp strong signal for the same number of scans. Chlorine-35 is a quadrupolar nucleus (spin $^3/_2$, abundance 75.53%, quadrupolar magnetic moment -7.89×10^{-2}). Chloride and perchlorate anions, due to their very high symmetry, do produce sharp chlorine-35 NMR signals, but coordination lowers the local symmetry and the high electric quadrupole moment broadens the lines so much that signals are not observed. Thus, the lack of an NMR signal supports the proposal of coordinated perchlorate groups, but we have no further information on the structure of the compounds.

Oxidation of $M(CO)_3(\eta^1\text{-L-L})(\eta^2\text{-L-L})$ compounds with $NOPF_6$ produces solutions containing only the decomposition products of $[M(CO)_3(\eta^2\text{-L-L})_2]^{2+}$.

Conclusions

In the special case where a pendent donor is available, in these cases a phosphorus or arsenic atom, electrochemically generated internal addition provides a synthetic pathway to dipositive carbonyl complexes of the kind $[M(CO)_3(\eta^2\text{-L-L})_2]^{2+}$. The availability of the pendent ligand in close proximity to the metal center provides an alternative, and kinetically rapid, pathway to the commonly observed nucleophilic attack by solvent, anionic ligands, or adventitious impurities such as water. However, these complexes are still reactive with respect to loss of carbon monoxide and are prone to nucleophilic attack on the longer time scale even by weak ligands such as perchlorate.

In contrast, chemical oxidants such as $AgClO_4$ and $NOPF_6$ are likely to contain nucleophiles that modify the reaction pathway (e.g. NO coordination or Ag^+ interaction with the pendent phosphorus). In these cases, the chemical oxidants are noninnocent[21] in these reactions, unlike the electrode, which simply acts as a sink for electron transfer. In addition, Snow and Wimmer[12] have shown that the usually innocent PF_6^- anion acts as a source of fluoride to give $[Mo(CO)_2(dpe)_2F]^+$ in chemically similar systems. Thus, the electrochemical method of oxidation in the presence of perchlorate is therefore an interesting example where electrochemical synthesis may yield compounds that are difficult to synthesize chemically.

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