dppb is $(C_6H_5)_2PCH_2CH_2CH_2CH_2P(C_6H_5)_2$, and dab is *cis*-$(CH_3)_2AsC(CF_3){=}C(CF_3)As(CH_3)_2$.
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Oxidation of Chromium, Molybdenum, and Tungsten Dicarbonylbis(diphenylphosphino)methane Complexes

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Chemical oxidation of the series of complexes *cis*-$M(CO)_2(DPM)_2$ (M = Cr, Mo, W; DPM = bis(diphenylphosphino)methane) has been investigated. Products have been characterized by ir, NMR, ESR, electrochemistry, and conductivity. In agreement with electrochemical data, these complexes are easier to oxidize than the analogous DPE complexes (DPE = 1,2-bis(diphenylphosphino)ethane) and both oxidation state I and oxidation state II compounds can be obtained. In oxidation state I complexes containing the low-spin paramagnetic *trans*-$[M(CO)_2(DPM)_2]^+$ cation are formed. ESR studies of the complexes reveal that the electron density on the phosphorus atoms is considerable. Electrochemical reduction of the trans$^+$ cation yields *trans*-$M(CO)_2(DPM)_2$ while oxidation occurs via the pathway

$$trans\text{-}[M(CO)_2(DPM)_2]^+ \rightarrow trans\text{-}[M(CO)_2(DPM)_2]^{2+} + e \rightarrow \text{products}$$

In oxidation state II, six-coordinate dipositive cations are unstable and these species are not isolated. Using $O_2/HClO_4$ as the oxidant, the hydride complexes *trans*-$[MH(CO)_2(DPM)_2]ClO_4$ are formed. With chromium this represents one of the few examples of oxidation state II carbonyl complexes. The hydrides are believed to be seven-coordinate capped octahedra, although a pentagonal-bipyramidal structure cannot be excluded. Products obtained with a range of other oxidants are also discussed.

Introduction

Electrochemical studies on the oxidation of a series of *cis*-$M(CO)_2(DPE)_2$ and *cis*-$M(CO)_2(DPM)_2$ complexes, where M = Cr, Mo, W, DPE = 1,2-bis(diphenylphosphino)ethane, and DPM = bis(diphenylphosphino)methane, have recently been undertaken in these laboratories.[1,2] In both cases a series of complexes $[M(CO)_2(P\text{–}P)_2]^{0,+,2+}$ (where P–P = DPE or DPM) was shown to exist with cis and trans isomeric forms (isomerism refers to carbonyls) being possible in each oxidation state. In oxidation state zero and II, the cis isomers were shown to be thermodynamically favored, while in oxidation state I, the cis form isomerizes rapidly to the trans isomer, even on the short electrochemical time scale. In oxidation state II, the complexes were demonstrated to be generally unstable and the reaction pathway was described as

$$[M(CO)_2(P\text{–}P)_2]^{2+} \rightarrow \text{products} \qquad (1)$$

In terms of $E_{1/2}$ values, the oxidation pathway for the reactions

$$\begin{aligned} cis\text{-}M(CO)_2(P\text{–}P)_2 &\rightleftharpoons cis[M(CO)_2(P\text{–}P)_2]^+ + e \\ &\qquad\downarrow \\ &\quad trans\text{-}[M(CO)_2(P\text{–}P)_2]^+ \end{aligned}$$

was very similar for both ligands.[1,2] However, it was observed that the $E_{1/2}$ value for the *trans*-$M(CO)_2(DPM)_2|$*trans*-$[M(CO)_2(DPM)_2]^+$ couple was considerably more negative than for the corresponding couple of the DPE complex, and in principle the DPM series of complexes could exhibit different chemical oxidation pathways. Further, $E_{1/2}$ values suggested that oxidation state II could be more readily obtained with DPM as the ligand.

The chemical oxidation of the $M(CO)_2(DPE)_2$ series of complexes has been studied extensively.[3-5] Predominantly, only oxidation state I complexes were obtained. However, no reliable data are available for the DPM complexes, the only report being a reaction of *trans*-$Mo(CO)_2(DPM)_2$ with iodine,[6] which was shown to be probably incorrect.[2] However, many Mo^{II}- and W^{II}-, although no Cr^{II}DPM derivatives, have been prepared directly from carbonyl halides.[7] Oxidation state I complexes do not appear to have been reported for any of the metals with DPM.

The purpose of the present work was to investigate the chemical oxidation of the zerovalent DPM complexes in an endeavor to see whether the products are indeed different from the DPE case. Further, it was hoped to establish the possibility of isolating some higher oxidation state compounds, since with Cr, in particular, these are extremely rare.[8] Finally, detailed characterization of the products in different oxidation states was expected to lead to additional knowledge on the oxidation pathways to supplement that already gained from the electrochemical investigations.

Experimental Section

Reagents. The complexes *cis*-$M(CO)_2(DPM)_2$ and *cis*-$M(CO)_2(DPE)_2$ were prepared as described in the literature.[1,2]

Instrumentation. Electrochemistry. The instrumentation used was as described elsewhere.[2] A.R. grade acetone (0.1 *M* Et_4NClO_4) was used as the solvent and Ag|AgCl (0.1 *M* LiCl) as the reference electrode. All solutions used were 10^{-3} *M*.

NMR. All NMR spectra were recorded on a Varian HA 100 NMR system. Time averaging was undertaken with a D.E.C. PDP 15 computer. Tetramethylsilane was used as an internal reference.

ESR. A varian 450/15 spectrometer was used to record all ESR spectra.

Magnetism. Magnetic measurements were performed on a magneto balance at 20° using the Gouy method.

Results and Discussion

Table I provides ir and conductivity data for representative examples of the complexes characterized in the present work. ESR, NMR, electrochemical, and other data along with detailed discussion on the interpretation of results are presented below for each of the metals in turn.

Oxidation of *cis*-$Cr(CO)_2(DPM)_2$. (i) Iodine. Addition of an excess of iodine in CH_2Cl_2 to a stirred solution of *cis*-$Cr(CO)_2(DPM)_2$ in the same solvent gave a red-brown solution. On addition of *n*-hexane, the yellow-brown *trans*-

Table I. Infrared and Conductivity Data for Some of the Complexes

	Infrared (carbonyl region)		Conductivity,[a,b] ohm^{-1} cm^2 mol^{-1}
Compd[d]	CH_2Cl_2	KBr disk	
trans-$[Cr(CO)_2(DPM)_2]I_3$	1868	1860	78.6
trans-$[Cr(CO)_2(DPM)_2]PF_6$	1869	1858	
trans-$[Cr(CO)_2(DPM)_2]ClO_4$	1869		
trans-$[CrH(CO)_2(DPM)_2]ClO_4$	1881	1871	85.5
trans-$[Mo(CO)_2(DPM)_2]ClO_4$	1878		
trans-$[MoH(CO)_2(DPM)_2]ClO_4$	1894	1880	77.6[c]
cis-$[MoI(CO)_2(DPM)_2]I_3$	1888, 1949	1859, 1929	81.5
trans-$[MoI(CO)_2(DPM)_2]I_3$	1905		
cis-$[MoBr(CO)_2(DPM)_2]Br_3$	1887, 1948	1875, 1939	
trans-$[MoBr(CO)_2(DPM)_2]Br_3$	1905		
trans-$[WH(CO)_2(DPM)_2]ClO_4$	1878	1862	
Et_4NClO_4			110.2

[a] All concentrations ~10^{-3} *M*. [b] 60/40 acetone/dichloromethane by volume. [c] The compound decomposed slowly during the measurement. [d] Cis and trans refer to relative positions of carbonyls only.

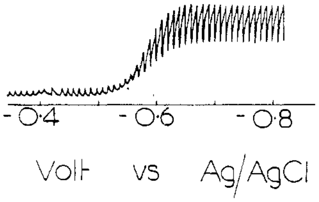

Figure 1. A dc polarogram of *trans*-$[Cr(CO)_2(DPM)_2]^+$ showing a reversible, one-electron reduction wave, with $E_{1/2} = -0.58$ V. The drop time was 0.5 sec and the scan rate was 20 mV/sec.

$[Cr^I(CO)_2(DPM)_2]I_3$ was obtained. Anal. Calcd: C, 49.6; P, 9.9; H, 3.6; I, 30.3. Found: C, 49.3; P, 9.7; H, 3.7; I, 29.4. This was recrystallized from CH_2Cl_2/*n*-hexane. With an equimolar amount of iodine, analytical data indicated that a mixture of *trans*-$[Cr^I(CO)_2(DPM)_2]I$ and *trans*-$[Cr^I(CO)_2(DPM)_2]I_3$ was formed. The complex with I^- as the anion could not be prepared in a pure form and physical measurements were undertaken on the triiodide salt. Conductivity and ir data in Table I are consistent with the formulation of a trans, 1:1 electrolyte.

Figure 1 shows a dc polarogram of this complex. In acetone, a reversible one-electron reduction step was found, with $E_{1/2} = -0.58$ V vs. Ag|AgCl. This is as predicted from previous data,[2] and the electrode process is *trans*-$[Cr(CO)_2(DPM)_2]^+ + e \rightleftarrows$ *trans*-$[Cr(CO)_2(DPM)_2]$. On the electrochemical time scale no isomerism of *trans*-$Cr(CO)_2(DPM)_2$ was indicated, in contrast to the very rapid isomerism of *cis*-$[Cr(CO)_2(DPM)_2]^+$ reported previously.[2] The limiting currents per unit concentration for oxidation of *cis*-$Cr(CO)_2(DPM)_2$ and reduction of *trans*-$[Cr(CO)_2(DPM)]^+$ were almost identical, as expected (cf. hydride perchlorate salt; see section iv below).

Figure 2 shows the ESR spectrum of *trans*-$[Cr(CO)_2(DPM)_2]^+$ in acetone at room temperature. The classic five-line spectrum with relative itensities 1:4:6:4:1 and the hyperfine splitting (A = 27.4 G) is due to coupling of the unpaired electron with four equivalent phosphorus atoms. These data demonstrate that the electron density on the phosphorus atoms is considerable. The *g* value is 2.00. Bulk susceptibility measurements gave an effective magnetic moment of 1.82 BM at 20°.

(ii) Nitrosyl Hexafluorophosphate. The reaction of equimolar amounts of $NO^+PF_6^-$ and *cis*-$Cr(CO)_2(DPM)_2$ in CH_2Cl_2 produced yellow *trans*-$[Cr(CO)_2(DPM)_2]PF_6$ on the addition of *n*-hexane. The addition of excess $NO^+PF_6^-$ oxidized the compound further, although this subsequent reaction has not yet been characterized. ESR, conductivity, and other properties of the Cr(I) salt were identical with those of the triiodide, as expected. The reason for isolating the PF_6^- salt was to enable the electrochemical oxidation to be studied, iodide salts being unsuitable for this purpose. Anal. Calcd: C, 61.1; H, 4.31; P, 15.2; F, 11.2. Found: C, 59.3; H, 4.39; P, 14.7; F, 11.5.

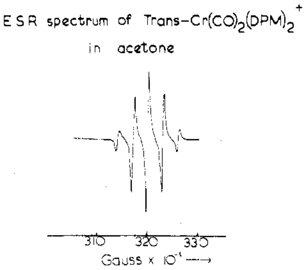

Figure 2. The ESR spectrum of *trans*-$[Cr(CO)_2(DPM)_2]^+$ cation (in acetone). The spectrum exhibits five lines with relative intensities 1:4:6:4:1. The *g* value is 2.00 and the hyperfine splitting A = 27.4 G. (Spectrum for DPE cation is similar.)

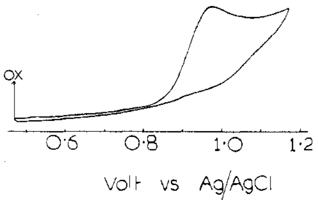

Figure 3. A cyclic voltammogram at a Pt electrode for the oxidation of *trans*-$[Cr(CO)_2(DPM)_2]^+$. The oxidation wave has a peak potential of 0.98 V. The scan rate was 200 mV/sec.

Figure 3 shows a cyclic voltammogram for the oxidation of *trans*-$[Cr(CO)_2(DPM)_2]^+$ at −75°. At low temperature and all conditions the electrode process was

$$trans\text{-}[Cr(CO)_2(DPM)_2]^+ \rightarrow trans\text{-}[Cr(CO)_2(DPM)_2]^{2+} \\ \downarrow \\ \text{products}$$

The six-coordinate oxidation state II $trans^{2+}$ cation appears to have no inherent stability and rapidly reacts with solvent or decomposes.

(iii) Silver and Mercury Salts. Each of $AgClO_4$ and Hg_2X_2 or HgX_2 (X = F, Cl, Br, I) oxidized *cis*-$Cr(CO)_2(DPM)_2$ to the $trans^+$ cation in CH_2Cl_2 or acetone.

(iv) Preparation and Characterization of an Oxidation State II Hydride Complex. With DPE as a ligand, oxidation of $Cr(CO)_2(DPE)_2$ with $O_2/HClO_4$ leads to the formation of the $trans^+$ cation.[4] When concentrated perchloric acid was added to a solution of *cis*-$[Cr(CO)_2(dpm)_2]$ in acetone, the solution decolorized rapidly. On immediate addition of water, a pale yellow precipate was obtained. This was recrystallized from CH_2Cl_2/*n*-hexane. This complex gave an intense ir carbonyl frequency at 1881 cm^{-1} in CH_2Cl_2 which, as can be seen from Table I, is 12 cm^{-1} higher than that observed for the previously characterized $trans^+$ cation. Conductivity data indicated the species to be a 1:1 electrolyte. However, an electrochemical investigation in acetone revealed only a very small wave attributed to the $trans^+$ cation and in the solid state the complex was diamagnetic. The absence of an ESR signal also confirmed the diamagnetism, although, on standing in acetone the growth of the $trans^+$ cation signal was observed. The product of the $O_2/HClO_4$ reaction was clearly different from the DPE case.

The ^1H NMR spectrum of the complex in CD_2Cl_2 showed a broad phenyl region centered at τ 2.60 (relative to TMS = 10), a broad methylene region centered at τ 5.18, and a very weak signal at approximatley τ 17. The integrated ratio of the phenyl to methylene signals was 10:1, consistent with both

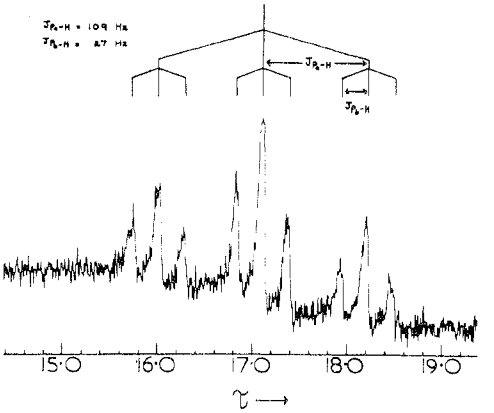

Figure 4. The time averaged (210 scans) NMR spectrum of the hydride for *trans*-$[CrH(CO)_2(DPM)_2]^+$. The triplet of triplets is centered at τ 17.10 with J_{P_A-H} = 109 Hz and J_{P_B-H} = 27 Hz.

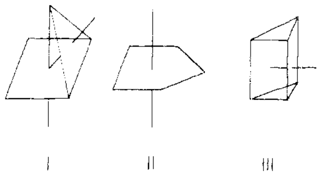

Figure 5. The three possible structures for a seven-coordinate cation. Structure I is a capped octahedron, structure II is a pentagonal bipyramid, and structure III is a trigonal prism.

DPM ligands being bidentate. With time averaging (210 scans) around τ 17, a well-defined triplet of triplets centered at τ 17.10 was found (see Figure 4). This signal can only be attributed to the presence of a hydride. The observed pattern strongly suggests the hydride is coupled to two inequivalent pairs of phosphorus atoms with J_{P_A-H} = 109 Hz and J_{P_B-H} = 27 Hz. Integration of the three signals gave relative intensities of 40:4:1. Recently, Connor et al.[9] have reported the formation of *trans*-$[MoH(CO)_2(DMPE)_2]HCl_2$ (DMPE = $Me_2PCH_2CH_2PMe_2$) by reaction of HCl with *cis*-$Mo(CO)_2(DMPE)_2$ and the NMR of the hydride in this case was also a triplet of triplets.

The analytical, infrared, NMR, and conductivity data all indicate the formation of a seven-coordinate monomeric hydride complex of Cr(II) $[CrH(CO)_2(DPM)_2]^+$ which obeys the E.A.N. rule. Anal. Calcd: C, 63.9; P, 12.7; H, 4.6; Cl, 3.6. Found: C, 63.0; P, 12.5; H, 4.7; Cl, 3.8.

Three structural types can be envisaged for seven-coordination as shown in Figure 5. Although structure III has been proven by X-ray diffraction to exist for at least two compounds of Mo(II),[10,11] it can be eliminated for the chromium hydride because there is no way in which the carbonyl groups can become trans and give rise to only one observable stretching frequency in the infrared spectrum in the carbonyl region. Structure II is very attractive, as one carbonyl stretch is reasonable and the phosphorus atoms could be regarded as forming two nonequivalent pairs with respect to the hydride. However, it would be anticipated that nonequivalence of the phosphorus atoms in each DPM ligand should give observable effects in the methylene region of the NMR spectrum (see below). The absence of definitive evidence to support this structure and the fact that no example of this stereochemistry is found in group 6 carbonyl compounds must weigh against it.

Almost all carbonyl complexes of Mo and W in oxidation state II adopt the capped octahedral stereochemistry.[12] Connor and coworkers,[9] on the basis of extensive proton and phosphorus NMR studies on their hydride complex, *trans*-$[MoH(CO)_2(DMPE)_2]^+$, concluded that this cation adopted this configuration with the hydride in the capping position of the

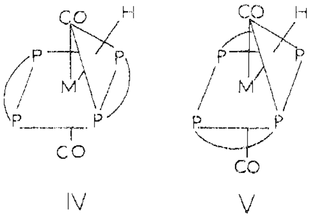

Figure 6. The two possible isomers of structure I.

trans-$Mo(CO)_2P_4$ octahedron. Our similar ^1H NMR data are also consistent with this basic structure, but two isomers are possible as shown in Figure 6.

In each case the hydride would couple with two sets of nonequivalent phosphorus atoms. In structure V, the methylene protons would have the same chemical shifts and each would be coupled to two nonequivalent phosphorus atoms but in structure IV the chemical shifts of the methylene protons, in principle, should not be the same, and each would be coupled to two equivalent phosphorus atoms to give a triplet. In *trans*-$[MoH(CO)_2(DPM)_2]^+$ (see below) the methylene protons do exhibit a sharp triplet (J_{P-H} = 10 Hz) but in the case of the chromium complex *trans*-$[CrH(CO)_2(DPM)_2]^+$ the methylene signal is broad and not well resolved, but could possibly be interpreted as two overlapping triplets. In view of this evidence, structure IV is favored. However, the pentagonal-bipyramidal structure cannot be excluded and the possibility that the chromium hydride is not isostructural with the Mo and W analogs exists.

The isolation and characterization of a Cr(II) carbonyl in this work suggests equivalent complexes may well exist with other substituents as is the case with Mo and W where oxidation state II compounds are common. However, it would appear that even for Cr, six-coordinate oxidation state II complexes are extremely reactive and the preference for a higher coordination number provides the driving force for the isolation of a hydride. Thus the inability to observe a chemically reversible oxidation wave for the M(I)–M(II) process can now be explained in terms of hydride formation. Controlled potential electrolysis (+1.1 V vs. Ag|AgCl) in acetone at a platinum gauze electrode produced *trans*-$[CrH(CO)_2(DPM)_2]^+$ (identified by infrared) and confirmed this suggestion.

On dissolution of the hydride in DMSO, *cis*-$Cr(CO)_2(DPM)_2$ was found to form rapidly. Similarly, addition of base (tetra-*n*-butylammonium hydroxide) to CH_2Cl_2 or acetone solutions produced considerable concentrations of *cis*-$Cr(CO)_2(DPM)_2$. On leaving the hydride standing in acetone or CH_2Cl_2, *trans*-$[Cr(CO)_2(DPM)_2]^+$ was formed and this complex was shown to be an intermediate in the synthesis by ESR studies. In the absence of oxygen, the hydride was found to be stable in basic solution. Thus the equilibria

$$\begin{array}{ccc} \textit{cis}\text{-}[Cr(CO)_2(DPM)_2] & \underset{O_2/OH^-}{\overset{O_2/H^+}{\rightleftharpoons}} & \textit{trans}\text{-}[Cr(CO)_2(DPM)_2]^+ \\ & & O_2/OH^- \uparrow\downarrow O_2/H^+ \\ & & \textit{trans}\text{-}[CrH(CO)_2(DPM)_2]^+ \end{array}$$

can be used to describe the reaction scheme.[4] Isomerism of the $trans^0$ and cis^+ species also needs to be invoked as demonstrated previously.[2] The hydrogen ion dependence of the reactions is clearly demonstrated by using hydrofluoric acid instead of perchloric acid. Hydrofluoric acid is a weak acid and the product isolated is the Cr(I) $trans^+$ cation instead of the hydride.

Oxidation of *cis*-$Mo(CO)_2(DPM)_2$. (i) Silver Perchlorate. Oxidation of *cis*-$Mo(CO)_2(DPM)_2$ with an equimolar amount of $AgClO_4$ in acetone or dichloromethane under argon produced *trans*-$[Mo(CO)_2(DPM)_2]^+$. This could not be isolated analytically pure. Thus evidence for its existence is based

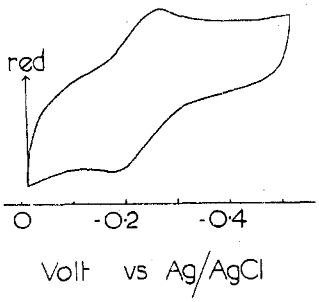

Figure 7. A cyclic voltammogram at a Pt electrode of *trans*-$[Mo(CO)_2(DPM)_2]^+$ in acetone with $E_{1/2} = -0.24$ V. The scan rate was 200 mV/sec.

purely on electrochemical, infrared, and ESR studies. Figure 7 shows a cyclic voltammogram of the reduction of this complex. On the electrochemical time scale the process

$$trans\text{-}[Mo(CO)_2(DPM)_2]^+ + e \rightleftharpoons trans\text{-}[Mo(CO)_2(DPM)_2]$$

is reversible as expected from previous data.[2] The ESR spectrum of the trans$^+$ cation is shown in Figure 8a and is compared with that of the equivalent DPE species (Figure 8b). The spectra are quite different from that of *trans*-$[Cr(CO)_2(DPM)_2]^+$ and are quite complex. The DPM complex has a g value of 1.93 with $A = 24$ G, and the DPE complex has a g value of 2.05 with $A = 29$ G. The interpretation of these spectra requires further study. The trans$^+$ complex unlike its Cr counterpart was not particularly stable in solution. In contrast, *trans*-$[Mo(CO)_2(DPE)_2]^+$ is perfectly stable.

(ii) Iodine. The oxidation of the DPE complex gave the paramagnetic *trans*-$[Mo(CO)_2(DPE)_2]^+$ cation.[3] However, in CH_2Cl_2, oxidation of the DPM complex with iodine gave *cis*-$[Mo(CO)_2(DPM)_2I]I_3$. Anal. Calcd: C, 43.7; P, 8.7; H, 3.1; I, 35.6. Found: C, 43.7; P, 8.7; H, 2.9; I, 35.5. An excess of iodine was required to give the pure, pale brown complex. With an equimolar amount of I_2, a mixture of the I^- and I_3^- species was obtained.

No NMR spectrum could be obtained for this complex due to solubility problems in both $CDCl_2$ and DMSO. Hence no structural information about the complex was obtained. A complex *cis*-$[Mo(CO)_2(DPM)_2I]I$ has been reported previously, prepared via a different synthetic route,[6] but whether the cation is isostructural to the complex isolated in this work is not known at present. The different redox properties of the DPM and DPE series of complexes are illustrated by the iodine reaction.

In acetone, a mixture of two species, assumed to be cis and trans isomers from infrared evidence, was obtained. Also, on dissolution of the pure cis complex in acetone, the yellow solution gradually turned orange to give an equilibrium mixture of the same two species. A range of isomers for complexes with the same stoichiometry as the characterized $[Mo(CO)_2(DPM)_2I]^+$ species has been reported.[6]

(iii) Bromine. Oxidation with bromine in CH_2Cl_2 gave a mixture of *cis*- and *trans*-$[Mo(CO)_2(DPM)_2Br]Br_3$. Anal. Calcd: C, 50.3; P, 10.0; H, 3.8; Br, 25.8. Found: C, 49.4; P, 9.8; H, 3.6; Br, 24.0. Ir data in CH_2Cl_2 (Table I) suggested that these complexes are isostructural with the iodo complexes, but again owing to solubility problems, no NMR data were obtained.

(iv) $O_2/HClO_4$. The reaction of *cis*-$Mo(CO)_2(DPM)_2$ with $O_2/HClO_4$ in acetone was analogous to the Cr case with the pale green diamagnetic *trans*-$[MoH(CO)_2(dpm)_2]ClO_4$ complex being isolated on the addition of water to the reaction mixture. Anal. Calcd: C, 61.1; P, 12.2; H, 4.4; Cl, 3.5. Found: C, 60.4; P, 12.0; H, 4.5; Cl, 3.4. The NMR spectrum again consisted of three regions: a phenyl region centered at τ 2.56, a methylene region at τ 5.26 (see above) and a triplet of triplets centered at τ 11.99 with $J_{P_A-H} = 66$ Hz, $J_{P_B-H} = 14$ Hz (420 scans).

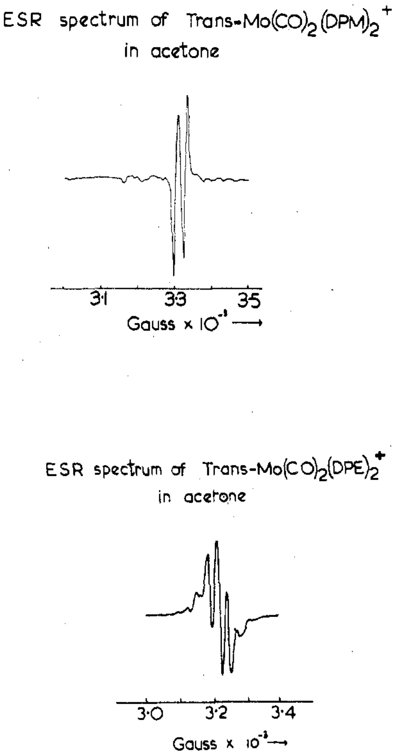

Figure 8. (a) (Top) ESR spectrum of *trans*-$[Mo(CO)_2(DPM)_2]^+$ in acetone (cf. *trans*-$[Cr(CO)_2(DPM)_2]^+$. (b) (Bottom) ESR spectrum of *trans*-$[Mo(CO)_2(DPE)_2]^+$ in acetone (cf. *trans*-$[Mo(CO)_2(DPM)_2]^+$).

The NMR data for the Mo hydride are consistent with those observed for the Cr hydride. Hence a capped octahedral structure is again proposed. This is the same structure postulated for the known hydride of Mo[9] and the isoelectronic $TaH(CO)_2(DMPE)_2$ complex.[13]

Replacement of perchloric acid with hydrofluoric acid also leads to the generation of the oxidation state II hydride. This can be compared with the Cr case where the oxidation state I complex is isolated using hydrofluoric acid. This is indicative of the kinetic inertness of Cr(I) compared with the instability of Mo in the same oxidation state.

Recently, the complex $MoH(acac)(DPE)_2$ has been isolated.[14] In this case, the NMR signal of the hydride is a multiplet centered at τ 14.1. No structure was postulated but obviously a capped octahedron which must be in the cis isomeric form is a distinct possibility. For this structure, none of the phosphorus atoms are equivalent and a complex NMR signal is predicted for the hydride.

In contrast to *trans*-$[CrH(CO)_2(DPM)_2]ClO_4$, the MoDPM hydride was somewhat unstable, decomposing on standing in acetone. In DMSO the hydride complex reverts to *cis*-$Mo(CO)_2(DPM)_2$. ESR monitoring of the $O_2/HClO_4$ reaction demonstrated that the trans$^+$ species is an intermediate in the reaction.

On reaction of *trans*-$[MoH(CO)_2(DPM)_2]^+$ with I_2 or Br_2 in CH_2Cl_2, the ir peak at 1894 cm^{-1} disappeared and was replaced by one at 1905 cm^{-1} which is assigned to *trans*-$[Mo(CO)_2(DPM)_2X]^+$ where X = I and Br. Subsequently the cis isomer began to form

$$\begin{array}{l} trans\text{-}[MoH(CO)_2(DPM)_2]ClO_4 + X_2 \rightleftharpoons \\ \quad trans\text{-}[Mo(CO)_2(DPM)_2X]^+ + HX \\ \qquad\qquad \downarrow \text{slow} \\ \quad cis\text{-}[Mo(CO)_2(DPM)_2X]^+ \end{array}$$

Oxidation of *cis*-$W(CO)_2(DPM)_2$. Since the Mo and W complexes are usually very similar in their reactions, only the $O_2/HClO_4$ oxidation was carried out. In this case pale yellow, diamagnetic *trans*-$[WH(CO)_2(DPM)_2]ClO_4$ was isolated. Anal. Calcd: C, 53.6; P, 11.2; H, 4.1; Cl, 3.2. Found: C, 55.2; P, 10.9; H, 4.3; Cl, 3.4.

The NMR spectrum for the tungsten hydride was similar to that for the molybdenum hydride. It consisted of a phenyl region centered at τ 2.59, a triplet in the methylene region at τ 5.08 with $J_{P-H} = 8$ Hz, and a triplet of triplets centered at τ 11.54 with $J_{P-H} = 66$ Hz and $J_{P-H} = 14$ Hz (536 scans).

trans-$[W(CO)_2(DPM)_2]^+$ was identified as an intermediate in the reaction by ESR monitoring. The ESR spectrum of this complex is not well defined as is the case with the DPE complex. The respective g values are 1.92 (DPM) and 2.08 (DPE).

The same hydride was isolated using hydrofluoric acid instead of perchloric acid.

Conclusions

The reactions of the DPM complexes demonstrated electrochemical predictions, based on $E°$ values, that the DPM complexes would be easier to oxidize than the DPE complexes. In oxidation state II, six-coordinate species such as $[M(CO)_2(DPM)_2]^{2+}$ are unstable and the oxidation state II complexes isolated are seven-coordinate hydrides. In oxidation state I, six-coordinate species such as $[M(CO)_2(DPM)_2]^+$ do exist with cis complexes rapidly isomerizing to the trans form in good agreement with electrochemical data.

One distinct difference between the Cr and the other two metals is the stability of its oxidation state I complexes. This presumably reflects kinetic differences noted previously.[2]

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Registry No. *cis*-$Cr(CO)_2(DPM)_2$, 53092-55-0; *cis*-$Mo(CO)_2(DPM)_2$, 53152-36-6; *cis*-$W(CO)_2(DPM)_2$, 53092-56-1; *trans*-$[Cr(CO)_2(DPM)_2]I_3$, 56210-39-0; *trans*-$[Cr(CO)_2(DPM)_2]PF_6$, 56210-40-3; *trans*-$[Cr(CO)_2(DPM)_2]ClO_4$, 56210-41-4; *trans*-$[CrH(CO)_2(DPM)_2]ClO_4$, 56210-43-6; *trans*-$[Mo(CO)_2(DPM)_2]ClO_4$, 56210-44-7; *cis*-$[MoI(CO)_2(DPM)_2]I_3$, 56210-46-9; *trans*-$[MoI(CO)_2(DPM)_2]I_3$, 56210-48-1; *cis*-$[MoBr(CO)_2(DPM)_2]Br_3$, 56271-06-8; *trans*-$[MoBr(CO)_2(DPM)_2]Br_3$, 56271-08-0; *trans*-$[MoH(CO)_2(DPM)_2]ClO_4$, 56210-50-5; *trans*-$[WH(CO)_2(DPM)_2]ClO_4$, 56210-52-7.

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Preparation and Properties of Dinitrogen–Molybdenum Complexes.
II.[1] Dinitrogen(organonitrile) Complexes of Molybdenum

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Various para-substituted benzonitriles have been shown to react with the bis(dinitrogen) complex *trans*-$Mo(N_2)_2(DPE)_2$ [DPE = 1,2-bis(diphenylphosphino)ethane] to form a new series of mono(dinitrogen)molybdenum complexes *trans*-$Mo(N_2)(4\text{-}XC_6H_4CN)(DPE)_2$, where X = NH_2, CH_3O, CH_3, H, Cl, and $COCH_3$. A good correlation is observed between the N_2 stretching vibration in the ir spectra of these complexes and the Hammett substitution parameter, σ_p. Analogous mono(dinitrogen) complexes of organonitiles are obtained by the reaction of the bis(dinitrogen) complex with 2-methylbenzonitrile, acetonitrile, and propionitrile. In all the complexes the CN stretching frequency of a coordinated organonitrile shows a decrease from the free ligand value. These mono(dinitrogen) complexes of para-substituted benzonitriles are assigned trans configuration on the basis of the ir and ^{31}P NMR spectra. The benzoylazo complex $MoCl(N_2COPh)(DPE)_2$ is prepared by the reaction of the bis(dinitrogen) and mono(dinitrogen) complexes with benzoyl chloride. These reactions are shown to be remarkably affected by the coordinated organonitriles. Reaction of the benzoylazo complex with hydrochloric acid yields $MoCl_2(N_2HCOPh)(DPE)_2$, and the reaction is reversed by addition of triethylamine.

Introduction

Acetylene, organonitriles, organoisonitriles, dinitrogen oxide, and azide ion, as well as dinitrogen, are reducable by nitrogenase. The correlation between the relative affinity of these various ligands, including carbon monoxide, which is an inhibitor to nitrogenase, for nitrogenase and for ruthenium,[2] osmium,[3] and cobalt[4] complexes that bind dinitrogen indicates that these dinitrogen complexes may be valid models for biological nitrogen fixation. In view of the key role of molybdenum in biological nitrogen fixation, we have previously reported the preparation and properties of the first molybdenum–dinitrogen complexes.[1] In order to gain further knowledge of the character of this dinitrogen binding site, we have now studied the reaction of organonitriles with *trans*-$Mo(N_2)_2(DPE)_2$ [DPE = 1,2-bis(diphenylphosphino)ethane] and prepared a new series of mono(dinitrogen) complexes of the type $Mo(N_2)(RCN)(DPE)_2$, where R is a substituted aryl or alkyl group. The electronic effect of the organonitrile as the coligand to the ligating dinitrogen was also investigated, since there have been few such systematic studies except those including cobalt,[5] osmium,[6] and rhenium[7] dinitrogen complexes.

Chatt et al. recently obtained complexes of the type $WCl_2(N_2HCOR)(DPE)_2$ and $WCl(N_2COR)(DPE)_2$ from *trans*-$W(N_2)_2(DPE)_2$ and organic acid chlorides and briefly commented that *trans*-$Mo(N_2)_2(DPE)_2$ reacted analogously with organic acid chlorides.[8] We have now found that these mono(dinitrogen)molybdenum complexes obtained react with benzoyl chloride to afford the benzoylazo complex $MoCl(N_2COPh)(DPE)_2$, from which $MoCl_2(N_2HCOPh)(DPE)_2$