$C_5H_5Mo(CO)_2N_3Ph_2$, 53092-57-2; $C_5H_5Co(C_3F_7)N_3Ph_2$, 53092-59-4; $C_5H_5Mo(NO)(N_3Ph_2)I$, 53092-58-3; $Cr(CO)_6$, 13007-92-6; $Mo(CO)_6$, 13939-06-5; $W(CO)_6$, 14040-11-0; $Mn(CO)_5Br$, 14516-54-2; $Mn_2(CO)_{10}$, 10170-69-1; $Re(CO)_5Br$, 14220-21-4; $C_5H_5Mo(CO)_3Cl$, 12128-23-3; $[C_5H_5Mo(CO)_3]_2$, 12091-64-4; $CH_3Mo(CO)_3C_5H_5$, 12082-25-6; $C_5H_5Co(CO)(n\text{-}C_3F_9)I$, 12128-52-8; $[C_5H_5Mo(NO)I_2]_2$, 37368-74-4; sodium 1,3-diphenyltriazenide, 53092-69-6.

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Characterization and Electrochemical Behavior of Group VI Dicarbonylbis(diphenylphosphino)methane Complexes

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The complexes *cis*-$M(CO)_2(DPM)_2$ have been characterized [M = Cr, Mo, W; DPM = bis (diphenylphosphino)methane]. Electrochemical studies show that a series of $[M(CO)_2(DPM)_2]^{0,+,2+}$ complexes exist. However, thermodynamically the equilibria for the reactions

$$\textit{cis}\text{-}M(CO)_2(DPM)_2 + \textit{trans}\text{-}[M(CO)_2(DPM)_2]^+ \overset{K_1}{\rightleftharpoons} \textit{cis}\text{-}[M(CO)_2(DPM)_2]^+ + \textit{trans}\text{-}M(CO)_2(DPM)_2$$

$$\textit{trans}\text{-}[M(CO)_2(DPM)_2]^+ + \textit{cis}\text{-}[M(CO)_2(DPM)_2]^{2+} \overset{K_2}{\rightleftharpoons} \textit{trans}\text{-}[M(CO)_2(DPM)_2]^{2+} + \textit{cis}\text{-}[M(CO)_2(DPM)_2]^+$$

lie to the left and only the cis^0, trans$^+$, and cis^{2+} species are thermodynamically stable, with the cis$^+$, trans^0, and trans^{2+} species readily isomerizing. Electrochemical oxidation pathways are therefore characterized by equations of the kind

$$\textit{cis}\text{-}M(CO)_2(DPM)_2 \underset{+e}{\overset{-e}{\rightleftharpoons}} \textit{cis}\text{-}[M(CO)_2(DPM)_2]^+ \rightarrow \textit{trans}\text{-}[M(CO)_2(DPM)_2]^+$$

$$\textit{trans}\text{-}[M(CO)_2(DPM)_2]^+ \underset{-e}{\overset{+e}{\rightleftharpoons}} \textit{trans}\text{-}M(CO)_2(DPM)_2 \rightarrow \textit{cis}\text{-}M(CO)_2(DPM)_2$$

$$\textit{trans}\text{-}[M(CO)_2(DPM)_2]^+ \underset{+e}{\overset{-e}{\rightleftharpoons}} \textit{trans}\text{-}[M(CO)_2(DPM)_2]^{2+} \rightarrow \textit{cis}\text{-}[M(CO)_2(DPM)_2]^{2+}$$

Low-temperature electrochemistry reveals that at −75° the rate of isomerism is slowed down considerably. Kinetically, Cr complexes are more inert than either Mo or W complexes and rate constants decrease in the order Cr $<$ Mo $<$ W. Oxidation state II complexes possess no inherent stability at room temperature and M(I) to M(II) electrode processes are characterized by the reaction

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

Comparisons with the 1,2-bis(diphenylphosphino)ethane series of complexes reveal interesting thermodynamic and kinetic differences.

Introduction

A series of complexes of the general formula $[Mo(CO)_2(DPE)_2]^{0,+,2+}$ are known,[1] where M = Cr, Mo, W and DPE = 1,2-bis(diphenylphosphino)ethane. These compounds, as well as existing in different oxidation states, also exist in both cis and trans isomeric forms. The electrochemistry of these complexes has been studied.[1] Cyclic voltammetry, in particular, enables characterization of the different complexes with respect to both thermodynamic and kinetic considerations.

However, little is known about the analogous series of DPM complexes where DPM = bis(diphenylphosphino)methane. Only two complexes, namely, *trans*-$Mo(CO)_2(DPM)_2$ (*via* a reflux reaction) and *cis*-$Cr(CO)_2(DPM)_2$ (sealed tube reaction) have been reported.[2,3] The reported existence of the trans isomer rather than the cis isomer of $Mo(CO)_2(DPM)_2$ is interesting since the corresponding DPE complex, prepared *via* the same method, exists in the cis form. Conversely the predominant DPE complex of Cr isolated is the trans rather than the cis isomer. Furthermore oxidation of the complex *cis*-$Mo(CO)_2(DPE)_2$ with iodine gives a Mo(I) complex whereas the same reaction with *trans*-$Mo(CO)_2(DPM)_2$ is reported to give the *trans*-$[Mo(CO)_2(DPM)_2]^{2+}$ complex.[2] Hence considerable differences in isomeric forms, reactions, and oxidation states appear to exist, between the DPM and DPE complexes of group VI metals.

In this paper, the preparation and characterization of the

Table I

	Analysis, %						Ir carbonyl region, cm^{-1}		Nmr (rel to TMS), τ	
	Calcd			Found						
	C	H	P	C	H	P	KBr disk	Nujol mull	Phenyl protons	Methylene protons
cis-$Cr(CO)_2(DPM)_2$	71.2	5.0	14.2	71.0	5.1	13.8	1834 1776	1835 1779	2.0–3.7	5.4[a]
cis-$Mo(CO)_2(DPM)_2$	67.7	4.8	13.5	66.8	5.1	13.3	1843 1786	1845 1784	2.0–3.7	5.4
cis-$W(CO)_2(DPM)_2$	61.9	4.4	12.3	60.5	4.6	12.1	1839 1782	1837 1783	2.0–3.8	4.8
DPM									2.1–3.3	7.2[b]

[a] Occurs as a triplet, J_{P-H} = 8 Hz. [b] Occurs as a very sharp triplet, $J_{P-H} \approx$ 1 Hz.

cis-$M(CO)_2(DPM)_2$ complexes is described. The electrochemistry of these complexes, both at room temperature and at low temperature, is studied and compared with that of the DPE complexes. From this information, it is possible to show which isomers, in given oxidation states, are the most thermodynamically and/or kinetically stable and to rationalize similarities and differences between the two series of complexes.

Experimental Section

General Data. A commercial sample of DPM (Strem Chemicals) was used without further purification. Ir spectra were recorded using a Perkin-Elmer 457 grating infrared spectrophotometer. The nmr spectra were obtained using a Perkin-Elmer NMRS R12 Instrument. All analyses were carried out by the Australian Microanalytical Service, Melbourne.

(i) Preparation of the Complexes. *cis*-$\mathbf{Cr(CO)_2(DPM)_2}$. $Cr(CO)_6$ and an excess of DPM were refluxed in *n*-decane for 47 hr. The cis dicarbonyl complex crystallized from the hot solution, as orange crystals. The solution remaining was decanted off and the crystals were washed thoroughly with *n*-hexane and dried under argon. Recrystallization was found to be unnecessary. The powdered complex has an orange-yellow rather than orange color. This complex has been prepared before, but only low yields were obtained.[3,4] However yields are high using the method described above and a complex of high purity is obtained directly.

cis-$\mathbf{Mo(CO)_2(DPM)_2}$. $Mo(CO)_6$ and an excess of DPM were refluxed in *n*-decane for 30 min. The *cis*-dicarbonyl complex crystallized out as the solution cooled. It was recrystallized from dichloromethane–*n*-hexane and dried under vacuum. The pure complex is yellow. No evidence of the previously reported *trans*-$Mo(CO)_2(DPM)_2$ was found,[2] although the identical synthetic procedure was followed.

cis-$\mathbf{W(CO)_2(DPM)_2}$. $W(CO)_6$ is inert toward substitution compared with $Mo(CO)_6$; hence a slightly different preparative procedure was used. Equimolar amounts of $W(CO)_6$ and DPM were refluxed in ethanol, in the presence of sodium borohydride, for 1 hr.[5] The precipitate contained a mixture of $W(CO)_5(DPM)$ and $W(CO)_4(DPM)$ (as identified by ir spectra[4]). These products and an excess of DPM were refluxed in *n*-decane for 66 hr. A new precipitate formed on cooling. The solution remaining was decanted off and the solid dried under argon. The impure compound was recrystallized several times from dichloromethane–hexane before pure, yellow *cis*-$W(CO)_2(DPM)_2$ was obtained. This complex does not appear to have been reported previously.

(ii) Electrochemistry. Reagents. Tetraethylammonium perchlorate was used as the supporting electrolyte at a concentration of 0.1 *M* in acetone. All solutions were degassed with argon.

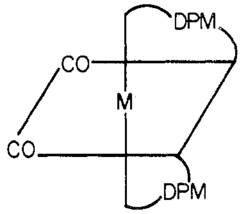
Instrumentation. Cyclic Voltammetry. Cyclic voltammograms were recorded at a platinum sheet working electrode using the PAR electrochemistry system, Model 170. The reference electrode was Ag–AgCl (0.1 *M* LiCl; acetone) separated from the test solution by a salt bridge containing 0.1 *M* tetraethylammonium perchlorate. A tungsten auxiliary electrode was used. Unless otherwise stated, measurements were made at 20°. Low-temperature electrochemistry at –75° was carried out using an acetone–Dry Ice mixture. Scan rates of dc potential up to 1 V/sec were used.

Results and Discussion

Table I shows the analyses, infrared spectra, and the nmr spectra of all three dicarbonyls. Molecular weight measurements were consistent with a monomeric formulation. The infrared spectra each show two strong absorptions in the carbonyl region. This is consistent with a cis structure for each complex. The wave number of each absorption increases in the order Mo > W > Cr.

The infrared spectrum of *cis*-$Mo(CO)_2(DPM)_2$ has carbonyl absorptions of 1843 and 1786 cm^{-1}. One would therefore expect that a *trans*-$Mo(CO)_2(DPM)_2$ complex would have a carbonyl absorption intermediate between these two values as is the case for the DPE complexes. However the value reported for the trans complex is 1980 cm^{-1}.[2] This seems to be extremely high, and the reported preparation of *trans*-$Mo(CO)_2(DPM)_2$ is doubtful. Hope[4] has also tried to reproduce the synthesis of the trans complex but, like us, only isolated the cis form.

The nmr spectrum of each complex consists of two parts—a very broad phenyl region and a broad methylene region. The low solubility of these complexes in $CDCl_3$ and the low signal to noise ratio made observation of any possible fine structure difficult. However the *cis*-$Cr(CO)_2(DPM)_2$ complex showed a triplet centered at τ 5.4, J_{P-H} = 8 Hz. Since only one methylene proton region is observed, both ligands should be bidentate. The structure is



The integrated ratio of phenyl protons to methylene protons was found to be (11 ± 2):1 in all cases. In the free ligand this ratio is 10:1.

The different τ values for the methylene proton region of the W and Mo complexes are consistent with those reported previously for oxidation state II complexes.[6]

Electrochemistry. All electrochemical data including a comparison with the DPE complexes are summarized in Table II. Discussion on each of the complexes is presented below.

cis-$\mathbf{Cr(CO)_2(DPM)_2}$. Figure 1 shows cyclic voltammograms at two different scan rates of *cis*-$Cr(CO)_2(DPM)_2$ at 20°. Three waves are seen on the first forward scan. On the reverse scan a new electrode process is observed at –0.61 V. On subsequent scans, four waves are observed in both directions. The waves are assigned below, starting with the most negative electrode process.

The first oxidation process occurring on the first scan (electrode process 2) is

$$\textit{cis}\text{-}Cr(CO)_2(DPM)_2 \underset{+e}{\overset{-e}{\rightleftharpoons}} \textit{cis}\text{-}[Cr(CO)_2(DPM)_2]^+ \xrightarrow{\text{fast}} \textit{trans}\text{-}[Cr(CO)_2(DPM)_2]^+ \qquad (1)$$

The *trans*-$[Cr(CO)_2(DPM)_2]^+$ species generated at the electrode surface in this step can then be reduced giving rise to electrode process 1, which occurs on the initial reverse scan

Table II[a]

	Electrode process								
	1			2			3 and 4		
	Redn	Oxidn	$E_{1/2}$	Oxidn	Redn	$E_{1/2}$	Oxidn	Redn	$E_{1/2}$
cis-$Cr(CO)_2(DPM)_2$	−0.61	−0.55	−0.57	0.04	−0.02	0.01	0.88 0.98	0.82 0.90	0.84 0.91
cis-$Mo(CO)_2(DPM)_2$	−0.27	−0.21	−0.24	0.34	0.26	0.30	1.05		0.95
cis-$W(CO)_2(DPM)_2$	−0.29	−0.24	−0.27	0.33	0.24	0.30	0.90		0.86
trans-$Cr(CO)_2(DPE)_2$	−0.40	−0.34	−0.36	0.05		0.02	1.12	1.04	1.08
cis-$Mo(CO)_2(DPE)_2$	−0.03	+0.03	0.00	0.34	0.24	0.31	1.18		1.14
cis-$W(CO)_2(DPE)_2$	−0.04	−0.03	0.00	0.33	0.25	0.31	1.28		1.24

[a] DPE data from ref 1. Scan rate = 200 mV/sec. All values in volts.

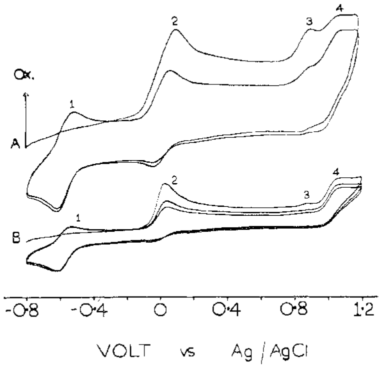


Figure 1. Cyclic voltammograms of *cis*-$Cr(CO)_2(DPM)_2$ at room temperature showing effect of varying scan rate. Curve A was run at 1 V/sec and curve B at 0.2 V/sec. The waves in A are slightly displaced because of recorder distortion. Electrode processes are numbered as in the text.

and all subsequent scans. Electrode process 1 can be written as

$$trans\text{-}[Cr(CO)_2(DPM)_2]^+ \underset{-e}{\overset{+e}{\rightleftharpoons}} trans\text{-}Cr(CO)_2(DPM)_2 \xrightarrow{\text{very slow}} cis\text{-}Cr(CO)_2(DPM)_2 \quad (2)$$

The most positive electrode processes are the following: electrode process 3

$$cis\text{-}[Cr(CO)_2(DPM)_2]^+ \underset{+e}{\overset{-e}{\rightleftharpoons}} cis\text{-}[Cr(CO)_2(DPM)_2]^{2+} \rightarrow \text{product(s)} \quad (3)$$

and electrode process 4

$$\begin{array}{l} trans\text{-}[Cr(CO)_2(DPM)_2]^+ \underset{+e}{\overset{-e}{\rightleftharpoons}} trans\text{-}[Cr(CO)_2(DPM)_2]^{2+} \rightarrow \text{product(s)} \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad \downarrow \\ \qquad\qquad\qquad\qquad\quad cis\text{-}[Cr(CO)_2(DPM)_2]^{2+} \rightarrow \text{product(s)} \quad (4) \end{array}$$

Electrode processes 3 and 4 were assigned on the basis of scan rate dependence on the current–potential curves. The use of fast scan rates decreases the extent of isomerism observed in electrode process 2. This means that the wave corresponding to the $cis^+ \rightarrow cis^{2+}$ oxidation predominates. However at slow scan rates the isomerism has more time to occur, so that the electrode process corresponding to the oxidation of the $trans^+$ species predominates and this wave is much larger than that observed for $cis^+ \rightarrow cis^{2+}$. Hence there is a thermodynamic preference for a particular isomer depending upon which oxidation state the metal atom is in.

Figure 2 shows a low-temperature cyclic voltammogram for *cis*-$Cr(CO)_2(DPM)_2$. The two chemically reversible processes are

$$cis\text{-}Cr(CO)_2(DPM)_2 \underset{+e}{\overset{-e}{\rightleftharpoons}} cis[Cr(CO)_2(DPM)_2]^+ \underset{+e}{\overset{-e}{\rightleftharpoons}} cis\text{-}[Cr(CO)_2(DPM)_2]^{2+} \quad (5)$$

i.e., the *cis*-$[Cr(CO)_2(DPM)_2]^+ \rightarrow$ *trans*-$[Cr(CO)_2(DPM)_2]^+$ isomerism is quenched at −75°.

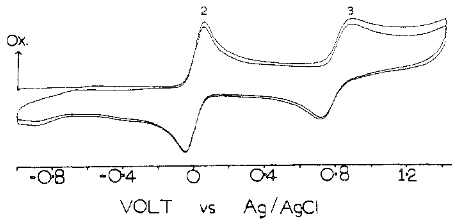


Figure 2. Cyclic voltammogram of *cis*-$Cr(CO)_2(DPM)_2$ at low temperature (−75°). The scan rate is 200 mV/sec. Electrode processes are numbered as in the text.

Several interesting points arise from this work.

(i) There is a very large thermodynamic difference between the cis^0–cis^+ and $trans^+$–$trans^0$ couples; *i.e.*, $E_{1/2}$ values differ by almost 600 mV. The $E_{1/2}$ values, despite the presence of follow-up chemical reactions, were shown to be close to the $E°$ values. In terms of free energies, the equilibrium constant (K) for the reaction

$$cis^0 + trans^+ \overset{K}{\rightleftharpoons} trans^0 + cis^+$$

can be calculated from the difference in $E_{1/2}$ ($\simeq E°$) values. Such calculations show that thermodynamically only the cis^0 and $trans^+$ complexes are expected since the equilibrium lies far to the left. Cis^+ or $trans^0$ species should therefore only be isolated *via* kinetic inertness, *i.e.*, very slow isomerism after the electron-transfer step.

The electrochemistry reveals that the $trans^0$ species is in fact isomerized much more slowly than the cis^+ species. At low temperatures, isomerism rates are much slower and low-temperature redox reactions may provide a synthetic route to this complex. However, at least in acetone, results suggest either of these complexes would be difficult to isolate. The $trans^0$ complex could also be very air sensitive because of the negative potentials at which it is oxidized. However there appears to be no reason why the $trans^+$ complex should not be stable both kinetically and thermodynamically to give the analogous complex formed with DPE.

(ii) The electrochemistry also proves unambiguously the existence of *cis*-$[Cr(CO)_2(DPM)_2]^{2+}$ at low temperatures. The data are also consistent with the presence of *trans*-$[Cr(CO)_2(DPM)]^{2+}$ at room temperature. The equilibrium for the reaction

$$trans^+ + cis^{2+} \rightleftharpoons trans^{2+} + cis^+$$

lies to the left and thermodynamically the $trans^+$ and cis^{2+} species are expected to be the thermodynamically stable isomers. However, in oxidation state II, Cr appears to be unstable and reactions in addition to isomerism occur. Possible alternative reactions include the ligand(s)'s becoming monodentate. This commonly arises with group VI oxidation state II DPM complexes.[2,6] Thus evidence for cis and trans isomers in each of oxidation state 0, I, and II has been found.

(iii) The comparison with the analogous DPE complexes shows a remarkable difference in the $E_{1/2}$ value for the

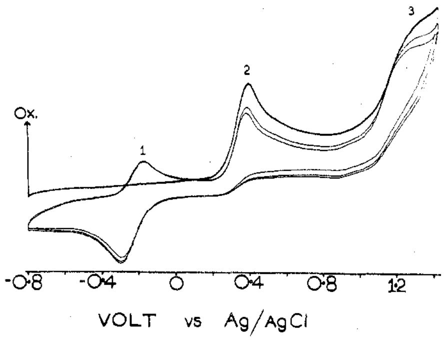


Figure 3. Cyclic voltammogram of *cis*-$Mo(CO)_2(DPM)_2$ at room temperature. The scan rate is 200 mV/sec and the electrode processes are numbered as in the text.

trans^0–trans$^+$ couple. The $E_{1/2}$ value is 210 mV more negative for the DPM complex, while for the cis^0–cis$^+$ couple, the $E_{1/2}$ values are almost identical for both complexes. This means thermodynamically that the cis^0 complex is favored to a much greater extent with DPM as the ligand than is the case with DPE, and the fact that only the cis isomer is isolated in this work whereas both cis and trans Cr complexes are produced in the DPE case can be understood.

The additional wave observed with the DPM complex is explained in terms of the different kinetics. Thus the DPM and DPE complexes exhibit considerable differences both thermodynamically and kinetically. The steric differences associated with the two different ligands have been discussed.[6] This is now reflected in kinetic and thermodynamic observations. The above discussion derived from consideration of differences in $E_{1/2}$ values is generally applicable to Cr, Mo, and W and need not be repeated when discussing the latter two series of complexes.

cis-**$Mo(CO)_2(DPM)_2$**. Figure 3 shows a cyclic voltammogram of *cis*-$Mo(CO)_2(DPM)_2$ at 20°. Two waves are observed on the first forward scan and a new electrode process is seen at −0.27 V on the reverse scan. Three waves are observed on subsequent scans. The first oxidation process on the first scan (electrode process 2) is assigned as

$$\textit{cis}\text{-}Mo(CO)_2(DPM)_2 \underset{+e}{\overset{-e}{\rightleftharpoons}} cis[Mo(CO)_2(DPM)_2]^+ \xrightarrow{\text{fast}} trans[Mo(CO)_2(DPM)_2]^+ \quad (6)$$

The trans$^+$ species formed can be reduced to give the trans^0 complex (electrode process 1).

$$\textit{trans}\text{-}[Mo(CO)_2(DPM)]^+ \underset{-e}{\overset{+e}{\rightleftharpoons}} \textit{trans}\text{-}Mo(CO)_2(DPM)_2 \xrightarrow{\text{slow}} \textit{cis}\text{-}Mo(CO)_2(DPM)_2 \quad (7)$$

Electrode process 3 involves the irreversible oxidation of Mo(I) to Mo(II). The wave is broad and drawn out. This is possibly the result of the cis$^+$ → cis^{2+} → products and trans$^+$ → trans^{2+} → products waves overlapping with the latter process being the predominant one.

Figure 4 shows a low-temperature cyclic voltammogram of *cis*-$Mo(CO)_2(DPM)_2$. The first oxidation wave is now

$$\textit{cis}\text{-}Mo(CO)_2(DPM)_2 \underset{+e}{\overset{-e}{\rightleftharpoons}} \textit{cis}\text{-}[Mo(CO)_2(DPM)_2]^+ \xrightarrow{\text{slow}} \textit{trans}\text{-}[Mo(CO)_2(DPM)_2]^+ \quad (8)$$

i.e., the cis$^+$ → trans$^+$ isomerism is much slower at low temperatures. Unlike chromium, however, the isomerism is not quenched on the electrochemical time scale, even at −75°. The Mo(I) → Mo(II) step at low temperature is analogous to the Cr(I) → Cr(II) oxidation at room temperature. Thus, the two series of complexes are different kinetically. Thermodynamic differences are clearly shown by the considerably different $E_{1/2}$ values. The $E_{1/2}$ values of the DPM and DPE series of complexes suggest that their chemical reactions with oxidants could be different. This, in fact, has been observed. The reaction of I_2 with *cis*-$Mo(CO)_2(DPE)_2$ gives the paramagnetic *trans*-$[Mo^I(CO)_2(DPE)_2]I_3$ complex.[7] However, on treating *cis*-$Mo(CO)_2(DPM)_2$ with iodine in dichloromethane we found that the diamagnetic *cis*-$[Mo^{II}(CO)_2(DPM)_2I]I_3$ complex is produced. This complex has been reported previously[2] but *via* a different synthetic route. Thus with DPM as a ligand Mo(0) is oxidized to Mo(II) whereas in the DPE case Mo(0) is oxidized to only Mo(I).

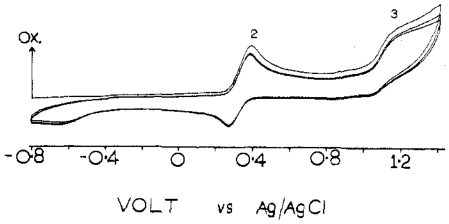


Figure 4. Cyclic voltammogram of *cis*-$Mo(CO)_2(DPM)_2$ at low temperature (−75°). The scan rate is 200 mV/sec and the electrode processes are numbered as in the text.

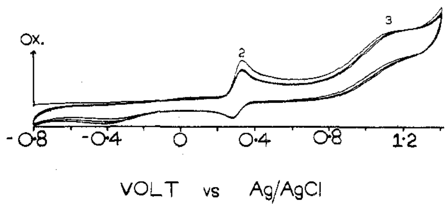


Figure 5. Cyclic voltammogram of *cis*-$W(CO)_2(DPM)_2$ at low temperature (−75°). The scan rate is 200 mV/sec and the electrode processes are numbered as in the text.

The electrochemistry of *cis*-$Mo(CO)_2(DPM)_2$ supports the ir evidence that the reported formation of *trans*-$Mo(CO)_2(DPM)_2$[2] *via* a direct synthetic route is highly unlikely. This also means that the complex *trans*-$[Mo(CO)_2(DPM)_2]I_2$ reported to be formed by oxidation with iodine[2] is probably incorrect. The electrochemistry does not support the claim that this latter complex is formed, as $[Mo(CO)_2(DPM)_2]^{2+}$ species are seen to be unstable.

cis-**$W(CO)_2(DPM)_2$**. The general electrochemistry of *cis*-$W(CO)_2(DPM)_2$ is similar to that found for Mo and is therefore not discussed in detail. However the rates of cis$^+$ and trans^0 isomerism are faster than for Mo. At low temperatures the W(I) → W(II) electrode process(es) still gives (give) rise to a very drawn-out wave. This is shown in Figure 5, and this step shows no evidence of reversibility under any conditions. This inability to form stable $[M(CO)_2(DPM)_2]^{2+}$ complexes at room temperature is most interesting.

General Trends and Kinetic Stability. The rate of the cis$^+$ → trans$^+$ isomerism increases in the order W > Mo > Cr. This same order is also evident for the trans^0 → cis^0 isomerism and the Cr^{2+} species is also far more kinetically stable than either Mo^{2+} or W^{2+}. Thus in every oxidation state Cr appears to possess the greatest kinetic stability. This trend also exists in the DPE complexes and was observed previously in studies of group VI halocarbonyls.[8]

Thermodynamically, the Mo and W DPM complexes are very similar; however, the Cr complex is much more readily oxidized. In all cases the trans$^+$ and cis^0 complexes are favored thermodynamically over the trans^0 and cis$^+$ species. In general DPM complexes are more readily oxidized than DPE complexes and from this point of view chemical redox reactions could produce products in different oxidation states.

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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*-$Cr(CO)_2(DPM)_2^+$, 53152-35-5; *trans*-$Mo(CO)_2(DPM)_2^+$, 53154-29-3; *trans*-$W(CO)_2(DPM)_2^+$, 53152-41-3.

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Carbon-13 Nuclear Magnetic Resonance Studies of Organometallic Compounds. VI. Phenylthiocarbene Derivatives[1]

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^{13}C nuclear magnetic resonance parameters for a series of transition metal carbene complexes of the type p-$XC_6H_4S(CH_3)CW(CO)_5$ are presented. Comparisons of the σ^n and σ^+ substituent constants for X with the carbene carbon shieldings reveal that both σ and π interactions between the aromatic ring and carbene carbon are occurring. This idea is also supported by quantitative evidence derived from the shieldings of the aromatic carbons of the carbene complexes and para-substituted benzenethiols. A direct relationship is revealed by comparisons of the carbene carbon shieldings of a series of complexes of the type $R(R')CW(CO)_5$, where R = p-C_6H_4X and R' = OCH_3, and the central carbon shieldings for carbonium ions of the type $(p\text{-}XC_6H_4)_3C^+$.

Introduction

Numerous reports[3-10] of ^{13}C nuclear magnetic resonance parameters derived from the nmr spectra of transition metal carbene derivatives have appeared in the literature. For complexes of the type $R(R')CCr(CO)_5$, where R = CH_3 or C_6H_5 and R' = OCH_3, OC_2H_5, $NH(CH_3)$, $N(CH_3)_2$, etc., there has been considerable discussion concerning the bonding factors which give rise to alterations in the carbene carbon shieldings when R and/or R' is varied. For example, the upfield shift of the carbene carbon, when R' is varied from an alkoxyl to an amino group, has been attributed to the greater ability of the amino substituent to participate in dative π-bonding with the carbene carbon[3b,6-8] and/or the overall difference in electron release between the alkoxyl and amino groups.[3b,6]

Moreover, when R is a meta- or para-substituted phenyl ring, there is some controversy as to whether[6,8,9] or not[7] distinct π-p-carbene carbon–aryl interactions result in carbene carbon shielding variations as the phenyl substituent is changed. While a qualitative relationship[9] between the increase of the π-donor ability of a p-phenyl substituent and the carbene carbon shielding exists, no *quantitative* attempts have been made to assess this relationship, nor have comparisons been made with analogous systems. In addition, there have been no reports of ^{13}C-nmr studies of carbene derivatives in which the effects of variations of substituents on the *hetero* atom have been extensively examined.

A new, facile route to a series of phenylthiocarbene complexes of the type p-$XC_6H_4S(CH_3)CW(CO)_5$ has been recently reported,[3a] and we now wish to present the complete set of ^{13}C-nmr parameters derived from six of these derivatives. We will compare these data with the ^{13}C-nmr parameters obtained from the parent thiophenols and two series[9] of transition metal carbene complexes which have para-substituted phenyl groups directly attached to the carbene carbon. Finally, the ^{13}C-nmr data for the last series of complexes will be carefully reexamined; a striking relationship between the carbene carbon shieldings and the shieldings of the central carbon atoms of a series of related carbonium ions of the type $(p\text{-}XC_6H_4)_3C^+$ [11] is noted.

Experimental Section

Samples of the carbene complexes and para-substituted thiophenols and the ^{13}C-nmr parameters of these compounds were obtained as described previously.[3a,12]

Results

The ^{13}C-nmr shieldings obtained from the phenylthio(methyl)carbene complexes **1–6** and the parent thiophenols are provided in Table I.

The assignments of the carbon resonances of the carbene methyl carbons, *cis*- and *trans*-carbonyl carbons, and carbene carbons were carried out by comparisons with related derivatives.[9] However, the assignments of all the aromatic carbons were not as straightforward. The signals arising from the *quaternary* carbons C_1 and from the para carbons C_4 could be distinguished from the ortho and meta carbons on the basis of their relative intensities. In theory, the ortho and meta carbons of **5** can be differentiated by the proton-coupled method described by Scott.[13] However, the appropriate proton-coupled experiments carried out on both **5** and **11** yielded only broad, unresolved signals for the ortho and meta carbons. Since it is well known that meta-carbon shieldings are relatively insensitive to the presence of a substituent in monosubstituted benzenes,[14] the meta carbons of **5** and **11** were arbitrarily assigned to those signals closest to 128.7 ppm, the shielding of the carbons in benzene.[14b] Once the complete assignments were made for **5** and **11**, the signals of the aromatic carbons of the remaining compounds **1–4**, **6–10**, and **12** were assigned by assuming additivity of the individual substituent effects[14c] on the aryl carbon shieldings. The average deviation between the observed and predicted shieldings of all the aromatic carbons is 0.9 ppm.

Discussion

(a) Qualitative Shielding Trends. The shieldings of the *cis*- and *trans*-carbonyl carbons of **1–6** are almost invariant, fluctuating randomly in the ranges 196.8–197.4 and 207.4–207.8 ppm, respectively. The shieldings of the carbene-methyl carbons also undergo slight variations (0.5 ppm). The carbene carbons are apparently more sensitive to alterations in the para-aryl substituent and they vary from 331.1 to 333.3 ppm, over a range of *ca.* 2 ppm. Finally, the