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Octahedral Metal Carbonyls.[1a] X. Kinetics of the Reactions of [1,2-bis(Diphenylphosphino)ethane] Chromium- and Molybdenum Tetracarbonyls with Lewis Bases *

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Kinetic data for the reaction of Lewis bases (L) with (diphos)M(CO)₄ (diphos = 1,2-bis(diphenylphosphino)-ethane; M = Cr, Mo) support a mechanism in which reversible dissociation of CO is followed by attack of L on the resulting five-coordinate intermediate. Activation parameters for the carbonyl dissociation step have been calculated. The results suggest metal π-base and ligand π-acid interaction in the ligand association step. The results are compared to those previously obtained for reactions of L with (bidentate)-M(CO)₄ systems.

Introduction

It has long been known that reactions of (bidentate)-$M(CO)_4$ complexes (bidentate = *o*-phenanthroline (phen) and 2,2′-dipyridyl (dipy)) with Lewis bases (L) yield «mixed» products of the type *cis*-(bidentate)-(L)$M(CO)_3$:[2]

$$(\text{bidentate})M(CO)_4 + L \rightarrow cis\text{-}(\text{bidentate})(L)M(CO)_3 + CO \qquad (I)$$

Kinetic investigations of these reactions have recently been carried out by Angelici and Graham.[3] It has also recently been shown that (diphos)$Mo(CO)_4$ (diphos = 1,2-bis(diphenylphosphino)ethane) reacts similarly but under more drastic conditions to give, depending upon the steric nature of L, either *trans*- or *cis*-(diphos)(L)$Mo(CO)_3$ complexes.[4] Herein is reported a kinetic investigation of these reactions, and of the hitherto-unreported reactions of (diphos)$Cr(CO)_4$ with Lewis bases.

Experimental Section

Preparation of (diphos)Cr(CO)₄ and (diphos)Mo-(CO)₄. Equimolar amounts of diphos and either $Cr(CO)_6$ or $Mo(CO)_6$ were heated at reflux under nitrogen in xylene for five hours. The reaction solutions were filtered while hot and were then allowed to cool slowly, whereupon the products crystallized. They were recrystallized from hot toluene and dried *in vacuo*.

Purification of Ligands and Solvent. Triethylphosphite was distilled over sodium under nitrogen at reduced pressure. Mesitylene and *n*-octylamine were each fractionally distilled under nitrogen, mesitylene over sodium on a spinning band column. Triphenylphosphine was twice recrystallized from ethanol, while the constrained phosphite 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane, $CH_3C(CH_2O)_3P$, was prepared by the method of Verkade[5] and was five times vacuum sublimed. It was found to be identical (infrared spectrum) to an authentic sample kindly supplied by Professor Verkade. Other reagents were used as obtained from commercial sources.

Kinetic Runs. Kinetic runs were carried out in the solvent mesitylene under pseudo first order reaction conditions (at least a twenty-fold excess of L). The reaction vessel, from which light was excluded, was a volumetric flask fitted with a rubber septum through which samples were periodically withdrawn. The decay of a high energy carbonyl stretching absorption characteristic of (diphos)$Cr(CO)_4$ and (diphos)$Mo(CO)_4$ (*ca.* 2025 cm^{-1}) was monitored in a 1 mm. NaCl cell on a Beckman IR-10 infrared spectrophotometer equipped with an auxiliary recorder. Approximately 30 mg. of substrate in 25 ml. of solvent-ligand mixture was used for each run. The absorptions were found to obey Beer's law over the concentration range employed. Plots of $\ln(A_t - A_\infty)$ *vs.* t were linear to a least 75% of completion for those systems for which kinetic data are reported in Table I. No decomposition of the reaction solutions was noted over the longer reaction periods. Other methods employed in this investigation have previously been described.[6]

Identification of Products. Of the products of the reactions investigated, two, *trans*-(diphos)[$(C_6H_5)_3P$]-$Mo(CO)_3$ [4] and *trans*-(diphos)[$(C_2H_5O)_3P$)]$Mo(CO)_3$ [4,7]

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[1] (a) Part IX: G. C. Faber, T. D. Walsh, and G. R. Dobson, *J. Am. Chem. Soc.*, *90*, 4178 (1968); (b) N. D. E. A. Predoctoral Fellow (1967-1969).

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[3] (a) R. J. Angelici and J. R. Graham, *J. Am. Chem. Soc.*, *87*, 5586 (1965); (b) J. R. Graham and R. J. Angelici, *ibid.*, *87*, 5590 (1965); (c) R. J. Angelici and J. R. Graham, *Inorg. Chem.*, *6*, 988 (1967); (d) J. R. Graham and R. J. Angelici, *ibid.*, *6*, 992 (1967).

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[5] J. G. Verkade, T. J. Hutteman, M. K. Fung, and R. W. King, *Inorg. Chem.*, *4*, 83 (1965).

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Table I. Rates of Reaction of (Diphos)Cr(CO)$_4$ and (Diphos)Mo(CO)$_4$ with Phosphites in Mesitylene

Reaction, Temperature (°C)	[L], moles/liter	10^4k_{obsd}, sec.$^{-1}$
(diphos)Cr(CO)$_4$+CH$_3$C(CH$_2$O)$_3$P		
131.0	0.487	0.264
139.6	0.050	0.837
139.6	0.491	0.804
139.6	0.977	0.824
148.8	0.105	2.14
148.8	0.245	2.13
148.8	0.489	2.42
148.8	0.968	2.43
(diphos)Mo(CO)$_4$+(C$_2$H$_5$)$_3$P		
113.0	0.101	0.207
113.0	0.487	0.201
113.0	1.01	0.218
125.6	0.101	1.02
125.6	0.465	1.13
125.6	0.863	1.13
135.5	0.093	3.28
135.5	0.158	3.20
135.5	0.499	3.34
135.5	1.07	3.70
(diphos)Mo(CO)$_4$+CH$_3$C(CH$_2$O)$_3$P		
125.6	0.119	1.10
125.6	0.487	1.11
125.6	1.01	1.19

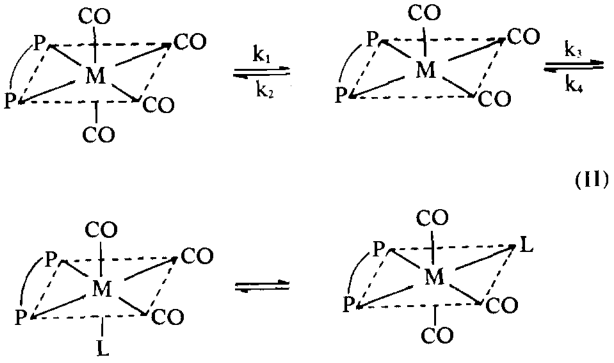
are known compounds, and were identified through their carbonyl stretching spectra. The product of the reaction between the constrained phosphite and (diphos)Cr(CO)$_4$, (diphos)[CH$_3$C(CH$_2$O)$_3$P]Cr(CO)$_3$ was prepared by heating (diphos)Cr(CO)$_4$ and a tenfold excess of phosphite at reflux under nitrogen in xylene for four hours. The reaction solution was then filtered and the solvent removed *in vacuo*. The crude product contained both *trans* and *cis* isomers (mostly *cis*). The pure *cis* product was obtained ofter two recrystallizations from toluene-hexane.

Anal. Calcd. for C$_{34}$H$_{33}$O$_6$P$_3$Cr: C, 59.83; H, 4.88. Found: C, 59.87; H, 4.94. Carbonyl stretching spectra (Beckman IR-12 infrared spectrophotometer, CHCl$_3$ solution): *trans*- 1974 (w), 1875 (s); *cis*- 1945 (vs), 1887 (s), 1853 (s) cm^{-1}.

Reaction of (diphos)Cr(CO)$_4$ with triethylphosphite under the conditions employed for kinetic runs gave, after five hours, a mixture of the corresponding *trans* and *cis* triethylphosphite complexes (mostly *trans*) as shown by the carbonyl stretching spectrum of the mixture (IR-12, CHCl$_3$); 1963 (w, *trans*), 1939 (w, *cis*), 1862 (vs, *trans, cis*), 1842 (sh, *cis*). The analogous reaction product of the constrained phosphite with (diphos)Mo(CO)$_4$ was also a mixture of isomers (mostly *cis*) with ν_{CO} (IR-12, CHCl$_3$) at 1988 (w, *trans*), 1962 (s, *cis*), 1887 (vs, *trans, cis*), 1862 (sh, *cis*). Reaction of *n*-octylamine and (diphos)Mo(CO)$_4$ for 72 hours in refluxing mesitylene in a flask fitted with a gas dispersion tube through which nitrogen was continually passed yielded *cis*-(diphos)(C$_8$H$_{17}$NH$_2$)Mo(CO)$_3$, as shown by comparison of its carbonyl stretching spectrum (IR-12; CHCl$_3$: 1929 (vs), 1836 (s), 1802 (s) cm^{-1}) to that of the known[4] *cis*-(diphos)(C$_6$H$_{11}$NH$_2$)Mo(CO)$_3$. Attempted reaction of *n*-octylamine or triphenylstibine with (diphos)Cr(CO)$_4$ gave no unequivocal evidence for the formation of (diphos)(L)Cr(CO)$_3$ products.

Results and Discussion

Two different types of behavior, which will be discussed in turn, are noted for reactions of (diphos)M(CO)$_4$ with various Lewis bases in mesitylene solvent. These may best be reconciled in terms of a mechanism in which CO dissociates reversibly to give a five-coordinate intermediate which then reversibly reacts with L to give product:



(II)

Employing a steady-state approximation for the rate of formation of (diphos)M(CO)$_3$ the rate expression,

$$\text{rate}=k_1[(\text{diphos})\text{M}(\text{CO})_4]-k_2[\text{CO}]\,\frac{k_1[(\text{diphos})\text{M}(\text{CO})_4]+k_4[(\text{diphos})(\text{L})\text{M}(\text{CO})_3]}{k_2[\text{CO}]+k_3[\text{L}]} \qquad \text{(III)}$$

is applicable. Mechanisms involving initial dissociation of one end of the diphos ligand followed by subsequent steps and which are also consistent with the kinetic data are less plausible since no evidence for the replacement of diphos was observed under the reaction conditions employed for any kinetic run.

Reactions of (diphos)M(CO)$_4$ with CH$_3$C(CH$_2$O)$_3$P, and of (diphos)Mo(CO)$_4$ with triethylphosphite at 113-149° proceed according to a first order rate law,

$$\text{rate}=k_1[(\text{diphos})\text{M}(\text{CO})_4] \qquad \text{(IV)}$$

Table II. Activation Parameters for Some Metal Carbonyl Complexes of Cr and Mo

Complex	ΔH_1^* (kcal./mole)	ΔS_1^* (e.u.)
Cr(CO)$_6$ [a]	40.2±0.6	22.6±1.5
Mo(CO)$_6$ [a]	31.7±1.4	6.7±3.7
(diphos)Cr(CO)$_4$	40.3±2.4	19.8±5.8
(diphos)Mo(CO)$_4$	38.0±1.3	18.1±3.4
(phen)Cr(CO)$_4$ [b]	26.4±0.8	7.0±2.6
(phen)Mo(CO)$_4$ [c]	25.1±1.2	2.4±2.4

[a] J. R. Graham and R. J. Angelici, *Inorg. Chem.*, 6, 2082 (1967); decalin solvent. [b] Ref. 3c, 1,2-dichloroethane solvent. [c] Ref. 3d, 1,2-dichloroethane solvent.

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(7) S. O. Grim, D. A. Wheatland, and P. R. McAllister, *Inorg. Chem.*, 8, 161 (1968).

Rate data and activation parameters are given in Tables I and II. The observed rate law, together with the positive calculated entropies of activation, suggest a dissociative mechanism in which slow fission of M–C bonds is followed by the rapid attack of L on the resulting five-coordinate intermediate. Since the reactions proceed to completion it would seem reasonable to assume k_4 in (II), the existence of which is supported by the observed reversibility of the reactions under a CO atmosphere, to be negligible. For this condition, (III) becomes,

$$\text{rate} = k_1k_3[(\text{diphos})\text{M(CO)}_4][\text{L}]/k_2[\text{CO}] + k_3[\text{L}] \qquad (\text{V})$$

That plots of $\ln(A_t - A_\infty)$ *vs.* t are linear to at least 75% of completion of the reactions suggests that $k_2[\text{CO}]$ in (V) is negligible since an increase in CO concentration as the reactions progress would otherwise result in decreased rates at longer reaction times. When $k_2[\text{CO}] \ll k_3[\text{L}]$, (V) reduces to the observed first order rate expression.

Plots of $\ln(A_t - A_\infty)$ *vs.* t for the reaction of (diphos)Cr(CO)$_4$ with triethylphosphite were found to deviate significantly from linearity at reaction times longer than one half life, suggesting appreciable competition between CO and $P(OC_2H_5)_3$ as the reaction progresses. This reaction was also found to be ligand-indepedent, and the average initial rate for five runs was estimated to be $\sim 1.18 \times 10^{-4}$ sec^{-1}, compared to a value of 1.26×10^{-4} sec^{-1} obtained from the constrained phosphite data.

Reactions of (diphos)Cr(CO)$_4$ with *n*-octylamine and triphenylstibine, and of (diphos)Mo(CO)$_4$ with *n*-octylamine and triphenylphosphine do not proceed at measurable rates under these reaction conditions despite the fact that the expected products of the reactions of (diphos)Mo(CO)$_4$, *cis*-(diphos)($C_8H_{17}NH_2$)-Mo(CO)$_3$ and *trans*-(diphos)[$(C_6H_5)_3P$]Mo(CO)$_3$ are prepared through use of conditions under which carbon monoxide is removed from the reaction flask as it is formed. In experiments in which carbon monoxide was removed from the reaction vessel with a nitrogen stream, but in which other reaction conditions were those employed in the kinetic runs, it was observed that both reactant and product were present at very long reaction times. This would seemingly indicate that $k_3[\text{L}]$ and k_4 are comparable in magnitude. The failure of the two ligands to react under the kinetic conditions may thus, at least in part, be attributed to smaller $k_3[\text{L}]$ values than for the phosphites. For $k_2[\text{CO}] \gg k_3[\text{L}]$ and k_4 appreciable, the rate from (III) would approximate zero.

On the basis of the relative bonding properties of P and CO, it would appear probable that in each case a carbonyl *cis* to diphos is lost, and that isomerism then follows. However, no supporting evidence was obtained. Rate data for the constrained phosphite and for triethylphosphite show the rate to be independent of the product isomer, or mixture of isomers obtained, and it would seem reasonable that the isomerization would occur under much milder conditions than are required for carbonyl replacement. Preparative data for these systems (Experimental Section) indicate that the isomer or isomer mixture obtained is a function of the steric properties of the metal and the ligand.

The results also indicate that strongly π-accepting phosphites are evidently better able to compete with CO than are triphenylstibine, triphenylphosphite and *n*-octylamine. For triphenylphosphine and triphenylstibine the reasons may largely be steric. Steric arguments cannot, however, explain the failure of *n*-octylamine, which is strongly basic and which possesses favorable steric properties (as in shown by the formation of the *cis* rather than the *trans*-(diphos)-(amine)Mo(CO)$_3$ product) to replace CO under the reaction conditions employed. It would seem, therefore, that the π-accepting ability of a ligand is of major importance in determining the relative rates of ligand attack on the intermediate in these systems Thus the mechanism may be envisioned as one in which, to a considerable degree, the metal acts as a π-base and the ligand a π-acid in the step governed by k_3.

It would also appear that the stringent steric requirements of diphos in (diphos)Mo(CO)$_4$ would best explain the absence of a second order term in the rate law as was observed for the (bidentate)Mo-(CO)$_4$ complexes investigated by Angelici and Graham.[3b,3d] It has been shown that the magnitude of the k_2 term in the rate expression,

$$\text{rate} = k_1[(\text{Xphen})\text{Mo(CO)}_4] + k_2[(\text{Xphen})\text{Mo(CO)}_4][\text{L}] \qquad (\text{VI})$$

(Xphen = substituted *o*-phenanthroline)

decreases with the increasing basicity of the particular Xphen.[3d] In the absence of steric complications it thus might reasonably be expected that a larger second order term would be noted for (diphos)Mo(CO)$_4$ than for the analogous Xphen systems.

Rates of reaction for Group VIb metal carbonyl systems usually vary Mo > Cr > W, and it is therefore somewhat surprising that (diphos)Cr(CO)$_4$ and (diphos)Mo(CO)$_4$ react with phosphites under essentially the same reaction conditions. A comparison of first order activation parameters for M(CO)$_6$, (phen)M(CO)$_4$, and (diphos)Mo(CO)$_4$ is given in Table II. It is seen that activation parameters for the corresponding Cr and Mo complexes of phen and diphos are quite similar, while there are significant differences in these values for the parent carbonyls. No explanation is offered for this seeming anomaly. With the exception of Cr(CO)$_6$ and Mo(CO)$_6$, it would seem, from the available data[8] that activation parameters do not differ appreciably between corresponding Cr and Mo complexes, and thus the relative ease of reaction of Mo carbonyl derivatives relative to the corresponding Cr complexes would appear to be due to the greater size of Mo, which facilitates nucleophilic attack.

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[8] R. J. Angelici, *Organometal. Chem. Rev.*, 3, 173 (1968).