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Octahedral Metal Carbonyls. XXV.[1a] Kinetics and Mechanism of Reactions of (Ethylenediphosphine)-tetracarbonylmolybdenum(0) with Lewis Bases[1b]

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Kinetic data for reactions of $(P\text{-}en)Mo(CO)_4$ *(P-en = ethylenediphosphine,* $H_2PC_2H_4PH_2$*) with phosphines and phosphites (L) in mesitylene solvent at 108-135° suggest three competing mechanisms, depending upon the Lewis base employed:* a, *rate-determining dissociation of CO;* b, *nucleophilic attack of L on the substrate and* c, *reversible dissociation of one end of the P-en ligand, followed by attack of L on the resulting five-coordinate intermediate. Of particular interest is the rate* via *path* b *for* $L = P(OC_2H_5)_3$ *which can be compared to rates for analogous reactions of other* cis-$L_2Mo(CO)_4$ *substrates, and to that for the hexacarbonyl itself. Attack in* $(P\text{-}en)Mo(CO)_4$ *occurs at a relatively slow rate, a result which is examined in terms of the nature of the interaction in the activated complex for these reactions.*

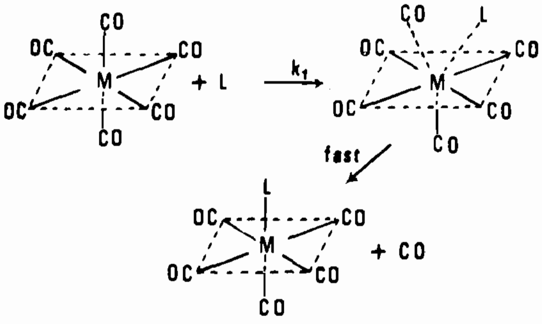
Introduction

Ligand-dependent behavior has been observed for a number of substitution reactions of Group VIb metal carbonyls and derivatives with Lewis bases,[2]

$$\begin{tikzcd} & L_xM(CO)_{6-x} \arrow[dl, "+xL'"'] \arrow[dr, "+L'"] & \\ L'_xM(CO)_{6-x}+xL & & L_xL'M(CO)_{5-x}+CO. \end{tikzcd}$$

(1)

For certain of these the kinetic data are consistent with an associative mechanism involving attack of the ligand on the substrate in the rate-determining step, *e.g.*,



(2)

while it would be desirable to examine rates *via* this mechanism as a function of the nature of the substituents in the metal carbonyl substrates, such results are difficult to obtain because other mechanism, *e.g.*, (3) and (6), below, have been found to compete with rate-determining ligand attack. The most extensive data for a given nucleophile are available for reactions of $(bidentate)Mo(CO)_4$ substrates with triethyl phosphite (bidentate = 2,2′-dipyridyl,[3] *o*-phenanthroline and substituted phenanthrolines,[4] 2,5-dithiahexane,[5] and $Mo(CO)_6$ itself.[6] Thus, data are available for ligands which coordinate through nitrogen or sulfur, for comparison to that for the unsubstituted molybdenum carbonyl. It would also be desirable to have analogous results for reaction of a substrate in which a phosphorus-containing bidentate ligand is the substituent. One such study, that of $(diphos)Mo(CO)_4$ (diphos = 1,2-bis(diphenylphosphino)ethane) with various phosphites,[7] revealed the reaction to proceed *via* rate-determining dissociation of CO. It was suggested that the failure to observe ligand-dependent behavior was the result of the stringent steric requirements posed by the diphos ligand. Accordingly, it was of interest to investigate another $(bidentate)Mo(CO)_4$ system in which the bidentate ligand is not sterically demanding. The complex chosen for study was $(ethylenediphosphine)Mo(CO)_4$;[8] the kinetic investigation of its reactions with phosphines and phosphites is the subject of this report.

Experimental Section

General. All preparative procedures involving metal carbonyl derivatives were carried out under an atmosphere of prepurified nitrogen. Infrared spectra were recorded on a Perkin Elmer Model 621 grating spectrophotometer and were calibrated against a band of water vapor at 1869.4 cm^{-1}.[9] The mass spectra were obtained on a Hitachi-Perkin Model RMU-6E

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(1) (a) Part XXIV: J.R. Paxson and G.R. Dobson, *J. Coord. Chem.*, *1*, 321 (1972). (b) Presented in part at the III *Inorganica Chimica Acta* Symposium, Venice, Italy, September, 1970.

(2) References cited in G.R. Dobson and G.C. Faber, *Inorg. Chim. Acta*, *4*, 87 (1970).

(3) J.R. Graham and R.J. Angelici, *J. Amer. Chem. Soc.*, *87*, 5590 (1965).

(4) J.R. Graham and R.J. Angelici, *Inorg. Chem.*, *6*, 992 (1967).

(5) G.C. Faber and G.R. Dobson, *Inorg. Chem.*, *7*, 584 (1968).

(6) J.R. Graham and R.J. Angelici, *Inorg. Chem.*, *6*, 2082 (1967).

(7) G.C. Faber and G.R. Dobson, *Inorg. Chim. Acta*, *2*, 479 (1968).

(8) G.R. Dobson and A.J. Rettenmaier, *Inorg. Nucl. Chem. Letters*, *6*, 327 (1970).

(9) E.K. Plyler, A. Danti, R.L. Blaine, and E.D. Tidwell, *J. Res. Nat. Bur. Standards*, *64A*, 29 (1960).

Table I. Products of Reactions of (P-en)Mo$(CO)_4$ with L under Kinetic Conditions.

Complex (L)	ν_{CO}(cm^{-1}) [a]	Other data
$(P(OC_6H_5)_3)$		
cis-(P-en)(L)Mo$(CO)_3$	1893(s), 1957(sh), 1951(s)	[b]
cis-$(L)_3$Mo$(CO)_3$	[c]	
$(P(OC_2H_5)_3)$		
cis-$(L)_2$Mo$(CO)_4$	2038(w), 1955(s), 1944(s), 1920(vs)	[d]
cis-(P-en)(L)Mo$(CO)_3$	1973(vs), 1895(s), 1886(s)	[e]
cis-$(L)_3$Mo$(CO)_3$	1970(vs), 1884(s), 1871(s) [f]	[g]
trans-$(L)_3$Mo$(CO)_3$	[c]	
cis-(P-en)$(L)_2$Mo$(CO)_2$ [h]	1897(vs, 1840(vs)	[i]
$(P(n\text{-}C_4H_9)_3)$		
cis-$(L)_2$Mo$(CO)_4$	2016(w), 1911(m), 1897(m), 1884(s)	[j]
trans-$(L)_2$Mo$(CO)_4$	[k]	
cis-$(L)_3$Mo$(CO)_3$	[k]	

[a] n-hexane solvent unless otherwise noted; relative band intensities: s = strong; m = medium; w = weak, v very, sh = shoulder. [b] Major ions in mass spectrum at m/e = 586, 558, 530, 502: parent ion and ions corresponding to loss of three successive CO's from parent ion. [c] R. Poilblanc and M. Bigorgne, *Bull. Soc. Chim. France,* 1301 (1962). [d] See Experimental Section. [e] νP—H = 2330(m) cm^{-1}, toluene solvent. Major ions in mass spectrum at m/e = 442, 414, 386: parent ion and ions corresponding to successive loss of two CO's; 397, 369, 341: loss of $-OC_2H_5$ and two successive CO's from parent ion. [f] Spectrum recorded in toluene solution; prepared through reaction of an eight-fold excess of $P(OC_2H_5)_3$ with (P-en)Mo$(CO)_4$ in refluxing *n*-decane (30 min.). [g] Major ions in mass spectrum at m/e = 680, 652, 624, 596: parent ion and ions corresponding to successive loss of three CO's; 635, 607, 551: ions corresponding to loss of $-OC_2H_5$ from parent ion, followed by loss of one and three CO's. [h] This complex not found in kinetic solution at t_∞. [i] *Anal.* Calc'd for $C_{16}H_{38}P_4O_8Mo$: C, 33.22; H, 6.57. Found: C, 33.06; H, 6.56. Major ions in mass spectrum at m/e = 580, 545, 507: parent ion and ions corresponding to loss of OC_1H_5 and then loss of one CO. [j] Prepared from $[(CH_3)_2NC_3H_6N(CH_3)_2]Mo(CO)_4$ and two equivalents of $P(n\text{-}C_4H_9)_3$; Ref. 2. [k] Identity inferred from carbonyl stretching spectra of analogoussubstitution products of $P(C_2H_5)_3$; ref. *c*.

spectrometer employing a 70 ev election energy and a 2.7 kv accelerating potential. Chemical analyses were performed by the North Texas State University Analytical Service.

Preparation and purification of materials. The preparation and purification of the substrate, (P-en)-Mo$(CO)_4$ have been described.[8] Purification of the solvent, mesitylene, has also been given, as has that of the ligand, $P(OC_2H_5)_3$;[7] $P(n\text{-}C_4H_9)_3$ and $P(OC_6H_5)_3$ were purified similarly. Preparation of *cis*$[(C_2H_5)_3P]_2$Mo-$(CO)_4$: (N,N,N',N'-tetramethy1-1,3-propanediamine)-Mo$(CO)_4$[2] (6.0 g, 17.8 mmole), 175 ml of *n*-hexane and 59.1 g (356 mmole) of triethy1 phosphite were placed in a 300 ml round bottom flask, which was then fluxed with nitrogen and sealed with a rubber septum. The reaction solution was stirred at room temperature for 30 min and poured onto a hexane-filled silica column. After elution with *n*-hexane, the solvent was removed from the eluant on a rotovac, a small quantity of *n*-hexane was added to the residue, and the resulting solution was cooled in a dry ice-acetone bath. White crystals separated, were recovered by decantation of the solvent and excess triethyl phosphite, and were immediately washed with several small portions of cold pentane. The crystals melted to a colorless oil at room temperature. Carbonyl stretching data for this complex are exhibited in Table I.

Determination of reaction rates. The reaction rates in mesitylene were determined employing methods described previously[5,7] by monitoring the disappearance of a carbonyl stretching absorption belonging to the substrate (2030.5 cm^{-1}) in 1 mm NaCl cells on the Perkin Elmer 621; kinetics of *cis*-$[P(OC_2H_5)_3]_2$Mo-$(CO)_4$ were monitored at 2035.5 cm^{-1}. Substrate concentrations of *ca.* 4 x 10^{-3} *M* were employed, and pseudo first order reaction conditions were achieved through use of at least a twenty-fold excess of the appropriate ligand. Plots (k_{obsd}) of $\ln(A_t - A_\infty)$ *vs.* time were linear to at least two half lives except as noted. All rates, which were reproducible to about ± 5%, were determined through use of a non-linear least squares computer program.

Identification of reaction products. Depending upon the ligand employed, the reaction products were those resulting from loss of P-en and/or carbonyl ligands (see Eq. 1). They were identified through comparison of the carbonyl stretching spectra of reaction solutions at t_∞ with those of complexes previously reported in the literature, or with those of complexes prepared in this investigation and/or through mass spectral analysis of the t_∞ solutions. The products, together with relevant data with regard to their characterization are listed in Table I. Among the complexes prepared were the « mixed » derivatives, *cis*-(P-en)(L)Mo$(Co)_3$ (L = $P(OC_6H_5)_3$, $P(OC_2H_5)_3$), and *cis*-(P-en)$(L)_2$Mo$(CO)_2$ (L = $P(OC_2H_5)_3$. Preparation of (P-en)$[P(OC_6H_5)_3]$Mo$(CO)_3$: (P-en)Mo-$(CO)_4$ (0.5 g, 1.7 mmole) and $P(OC_6H_5)_3$ (0.5 g, 1.6 mmole) were dissolved in 50 ml of a 2: 1 mixture of *n*-decane and 2,2,5-trimetylhexane and were heated at reflux for 40 min. The solution was cooled and the precipitate was collected by suction filtration. The off-white crystalline product was then obtained by recrystallization from toluene-hexane at −20°. The white, crystalline *cis*-(P-en)$[P(OC_2H_5)_3]$Mo$(CO)_3$ complex was obtained similarly, using 0.25 g (0.83 mmole) of (P-en)Mo$(CO)_4$ and 0.22 g (1.33 mmole) $P(OC_2H_5)_3$ in refluxing 1:2 *n*-decane - 2,2 5,-trimethylhexane (25 min).

Cis-(P-en)$[P(OC_2H_5)_3]_2$Mo$(CO)_2$ was obtained in an analogous manner from 0.5 g (1.7 mmole) of (P-en)Mo-

$(CO)_4$ and 0.3 g (1.8 mmole) $P(OC_2H_5)_3$ in *n*-decane for 23 hr at 140°. All three complexes exhibit appreciable air-stability.

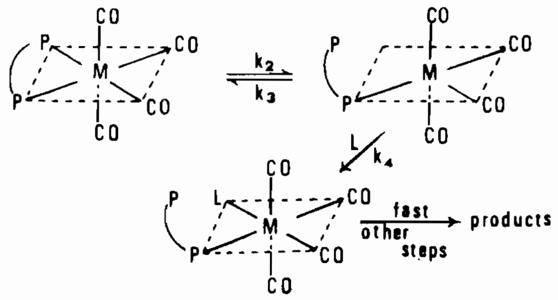
Table II. Rates of Reaction of $(P\text{-en})Mo(CO)_4$ with Lewis B in Mesitylene Solvent at Various Temperatures

Ligand (T, °C)	[L], *M*	10^4 k_{obsd} (sec^{-1})
$P(OC_6H_5)_3$		
(135.1)	1.014	13.8
	0.761	11.7
	0.504	9.13
	0.256	5.92
	0.255	5.63
	0.143	4.00
	0.113	3.40
	0.111	3.32
$P(n\text{-}C_4H_9)_3$		
(108.5)	1.033	4.90
	0.895	4.26
	0.641	3.04
	0.513	2.57
	0.257	1.25
	0.133	0.663
(118.5)	1.074	11.42
	0.777	8.73
	0.501	6.08
	0.256	3.65
	0.177	2.32
	0.138	1.82
$P(n\text{-}C_4H_9)_3$		
(128.5)	1.032	25.8
	0.863	22.5
	0.702	17.6
	0.509	11.8
	0.245	7.65
	0.180	5.93
	0.129	4.31
	0.113	3.97
$P(OC_2H_5)_3$		
(115.0)	0.999	1.61
	0.759	1.47
	0.502	1.40
	0.400	1.21
	0.308	1.06
	0.253	0.945
(125.0)	0.501	3.92
	0.249	2.76
	0.168	2.19
	0.126	1.75
	0.101	1.57
$P(OC_2H_5)_3$		
(135.1°)	1.001	14.5
	0.759	12.1
	0.499	11.0
	0.249	7.39
	0.168	5.86
	0.125	5.00
	0.100	4.01
$[P(OC_2H_5)_3]_2Mo(CO)_4+P(OC_2H_5)_3$		
(135.1)	0.983	2.33
	1.503	2.48
	2.012	2.62

Results and Discussion

Rate (k_{obsd}) data for reaction of $(P\text{-en})Mo(CO)_4$ with the three Lewis bases, $P(OC_6H_5)_3$, $P(n\text{-}C_4H_9)_3$ and $P(OC_2H_5)_3$ are given in Table II. Rate constants and activation parameters are exhibited in Table III. Since different kinetic behavior was observed for each ligand, the three reactions will be discussed in turn.

a. *Triphenyl Phosphite.* The reaction solution at t_∞ was found to contain two products, *cis*-(P-en)-$[P(OC_6H_5)_3]Mo(CO)_3$ and *cis*-$[P(OC_6H_5)_3]_3Mo(CO)_3$ (Table I). The plot of k_{obsd} *vs.* [L] for this reaction at 135.1° Figure 1-A) shows a slight curvature, suggestive of a mechanism (3):



(3)

The steady-state rate expression for this mechanism is,

$$\text{rate} = k_2k_4[(P\text{-en})Mo(CO)_4][L]/(k_3+k_4[L]). \tag{4}$$

The curvature is expected for $k_3 \sim k_4[L]$, and rearrangement of (4) in terms of k_{obsd} yields,

$$1/k_{obsd} = 1/k_2 + k_3/k_2k_4[L]. \tag{5}$$

Thus a plot of $1/k_{obsd}$ *vs.* [L] is expected to be linear. However, it can be seen that this reciprocal plot deviates significantly from linearity (Figure 2-A).

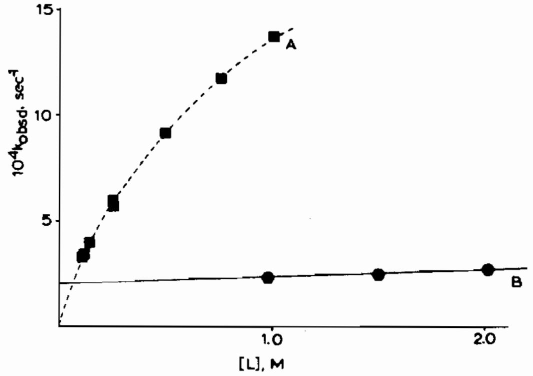


Figure 1. Plots of k_{obsd} *vs.* [L] at 135.1° for, A. the reaction of $(P\text{-en})Mo(CO)_4$ with $P(OC_6H_5)_3$; B. the reaction of $[P(OC_2H_5)_3]_2Mo(CO)_4$ with $P(OC_2H_5)_3$.

The reversible dissociation mechanism (3) is one commonly observed for reactions of (bidentate)$M(CO)_4$ complexes with Lewis bases.[2] Where this mechanism has been observed the product has been found invariably to be one in which the bidentate ligand has been replaced. The detection of the *cis*-(P-en)[P(OC$_6$-

Table III. Rate Constants and Activation Parameters for Reactions of (P-en)Mo(CO)$_4$ with Lewis Bases.

(T,°C)	k ^{a}	ΔH^{*b} (kcal/mole)	ΔS^{*b} (e. u.)
(P(n-C$_4$H$_9$)$_3$	10^4k$_1$ (M^{-1}sec^{-1})	ΔH$_1$*	ΔS$_1$*
(108.5)	4.70	23.9 ± 1.4	−11.7 ± 3.6
(118.5)	10.2		
(128.5)	23.7		
	10^4k$_5$ (sec^{-1})	ΔH$_5$*	ΔS$_5$*
(108.5)	0.0626	44.7 ± 22.2	+35.0 ± 56.8
(118.5)	0.719		
(128.5)	1.28		
P(OC$_2$H$_5$)$_3$	10^4k$_2$ (sec^{-1})	ΔH$_2$*	ΔS$_2$*
(115.0)	2.16	32.9 ± 1.2	+8.9 ± 2.9
(125.0)	6.16		
(135.1)	18.5		
	10^4k$_2$k$_4$/k$_3$ (M^{-1}sec^{-1})	ΔH$_2$* + ΔH$_4$* − ΔH$_3$*	ΔS$_2$* + ΔS$_4$* − ΔS$_3$*
(115.0)	6.80	31.1 ± 1.4	+6.6 ± 3.5
(125.0)	20.3		
(153.1)	52.2		

^{a} For identification of subscripts, see equations in text. ^{b} Limits of error: one standard deviation.

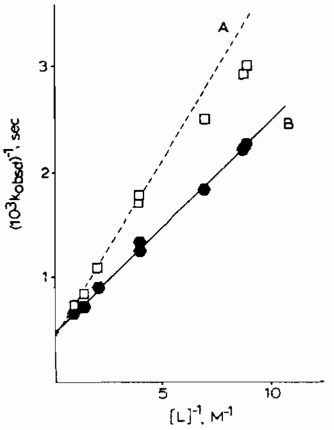
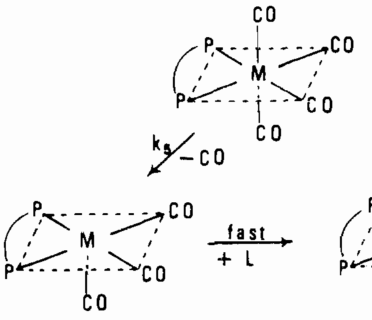


Figure 2. Reciprocal Plots for, A. the reaction of (P-en)Mo(CO)$_4$ with P(OC$_6$H$_5$)$_3$; B. Same plot under assumption of a first order term *ca.* 8 × 10^{-5} sec^{-1}.

H$_5$)$_3$]Mo(CO)$_3$ product in the t$_\infty$ reaction solutions thus strongly indicates that a second mechanism competes with (3), the most likely of which would be (6).



(6)

Fig. 2-B shows the reciprocal plot obtained through the assumption that there is such a competing first-order process (k$_5$ ~ 8 × 10^{-5} sec^{-1}); the linearity of this plot, together with the product data is strong evidence that the overall reaction proceeds *via* the two competing mechanisms, as described. However, the relative rates for the two competing processes are such that accurate values of the respective rate constants cannot be obtained.

b. *Tri*(n-*butyl*)*phosphine.* Plots of k$_{obsd}$ *vs.* [L] for this reaction at three temperatures are exhibited in Figure 3. These plots are essentially linear with non-zero intercepts, suggesting two competing mechanisms. It is most reasonable to assume that the ligand-dependent reaction largely involves nucleophilic attack of P(n-C$_4$H$_9$)$_3$ on the substrate (Mechanism 2).[10] This mechanism is to be favored over the limiting form of (3) where k$_3$ ≫ k$_4$[L], since tri(n-butyl)-phosphine is known to be a strong nucleophile.[11] It is unlikely that for this reaction k$_3$ ≫ k$_4$[L], while

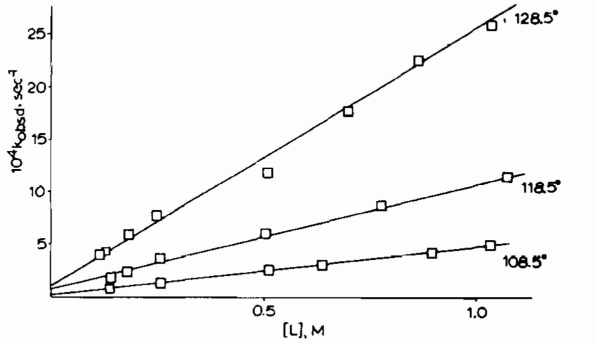


Figure 3. Plots of k$_{obsd}$ *vs.* [L] at various temperature for reaction of P(n-C$_4$H$_9$)$_3$ with (P-en)Mo(CO)$_4$.

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(10) For the present it will be assumed that attack of L occurs at the metal atom, rather than at a carbonyl carbon; see later discussion.

for the weaker nucleophile $P(OC_6H_5)_3$ (discussed above) that $k_3 \sim k_4[L]$. Also consistent with mechanism (2) for the ligand-dependent path is the negative entropy of activation calculated from rate data at three temperatures (Table III).

The finite intercept is indicative of a ligand-independent term which is most probably ascribable to mechanism (6). While the agreement between the first order rate constants obtaind there and that obtained for $L = P(OC_6H_5)_3$ is not partucularly good, it is not unexpected considering the method employed in the estimation of k_5 (Eq. 6) for $L = P(OC_6H_5)_3$ and the small values of k_5 relative to those of k_1 (Eq. 2) obtained for $L = P(n\text{-}C_4H_9)_3$ (*cf.* ΔH_5^*, ΔS_5^*, Table III).

c. *Triethyl Phosphite.* The investigation of the kinetics of reaction of this ligand with $(P\text{-en})Mo(CO)_4$ was complicated by the fact that the highest energy band of one product, *cis*-$[P(OC_2H_5)_3]_2Mo(CO)_4$, absorbs at 2035.5 cm^{-1} in mesitylene solvent, very close to the position of absorption of the substrate (at 2030.5 cm^{-1}). Accordingly, the kinetics of the reaction of this product with triethyl phosphite were also briefly investigated. At 135.1° this reaction was found to proceed at an initial fast rate, after which good linear plots of $\ln(A_t - A_{bl})$ *vs.* t were obtained over two or more half lives. A plot of k_{obsd} *vs.* [L] for this reaction is shown in Figure 1B. The initial rapid rate may be attributed to *cis* to *trans* isomerization of the substrate; the *cis-trans* equilibration is complete in *ca.* 40 minutes. After this time, what is being observed is the disappearance of the *cis* equilibrium concentration of substrate as a function of time. Since equilibration is rapid and the mixture contains a large percentage of the *trans* isomer which does not absorb at 2030.5 cm^{-1}, it was decided that initial rates of reaction of the $(P\text{-en})Mo(CO)_4$ substrate with $P(OEt)_3$ would yield a fairly accurate measure of the rates of reaction. Indeed, it was found that plots of $\ln(A_t - A_{bl})$ *vs.* t were linear to about one half life. These data at three temperatures are given in Table II.

The plots of k_{obsd} *vs.* [L] at three temperatures are shown in Figure 4. They suggest mechanism (3); the reciprocal plots (Figure 5) are also consistent with this mechanism, as are the predominant reaction products found at t_∞, *cis*- and *trans*-$[P(OC_2H_5)_3]_3Mo(CO)_3$. While it is possible, or even probable, that mechanisms (2) and/or (6) compete to a limited extend with (3), they are not observed, within the limits of accuracy of the rate determinations. Further, any "mixed" product which might have arisen through (6) would not be detectable in the t_∞ solutions as the result of masking of its carbonyl stretching bands by those of the *cis*-$[P(OC_2H_5)_3]_3Mo(CO)_3$ product (see Table I).

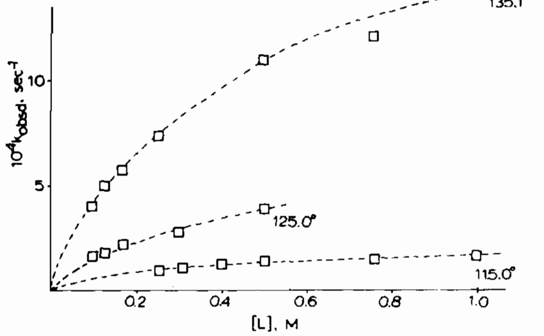

Fig. 4. Plots of k_{obsd} *vs.* [L] at various temperatures for reaction of $P(OC_2H_5)_3$ with $(P\text{-en})Mo(CO)_4$.

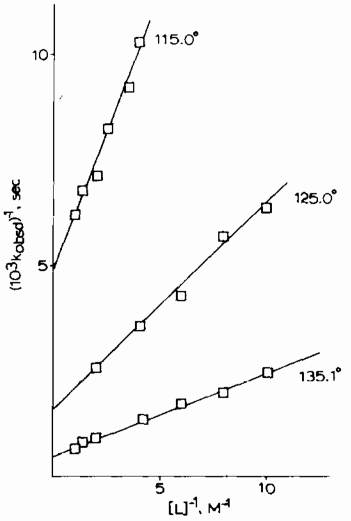

Figure 5. Reciprocal plots at various temperatures for reaction of $P(OC_2H_5)_3$ with $(P\text{-en})Mo(CO)_4$.

The fact that an associative mechanism is indicated for $P(n\text{-}C_4H_9)_3$ but not for $P(OC_2H_5)_3$ or $P(OC_6H_5)_3$ is not unexpected since, of the three ligands, the first has been found to be the strongest nucleophile in reactions with metal carbonyls;[11] however, the ratio (k_5 for $P(n\text{-}C_4H_9)_3$)/(k_5 for $P(OC_2H_5)_3$) must be quite large, a perhaps unexpected result.

The rate data for $P(OC_2H_5)_3$ may be compared to those for reactions of this ligand with $Mo(CO)_6$ and with various *cis*-$L_2Mo(CO)_4$ complexes (Table IV). While it would have been preferable to report all data at the same temperature, or to be able to cite enthalpies of activation, unfortunately such data are available for few substrates. The data in Table IV provide evidence with regard to the site of attack in these complexes. Two possible sites of attack, at the metal atom, or at the carbonyl carbon, are indistinguishable on the basis of the second order rate law alone (Figure 6).[10] Reactions of strong nucleophiles such as the azide ion and organolithium reagents most probably proceed *via* attack at the carbonyl carbon, as is indicated by the carbonylation products obtained.[12] Darensbourg and Darensbourg have suggested the rates of these reactions should increase with the increasing magnitude of the carbonyl stretching force constant of the carbonyl attacked;[13] a recent kinetic study of reactions of $W(CO)_6$ and $LW(CO)_5$ ($L = P(OC_6H_5)_3$, $As(C_6H_5)_3$, $P(C_6H_5)_3$) with methyl-

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[11] See, *e. g.*, R.J. Angelici, *Organometal. Chem. Rev.*, 3, 273 (1968).

[12] For a brief discussion, see K.G. Caulton and R.F. Fenske, *Inorg. Chem.*, 7, 1273 (1968).

Table IV. Rates of Reaction with Triethyl Phosphite *via* Ligand-Dependent Paths and Carbonyl Stretching Data for *cis*-$L_2Mo(CO)_4$ Complexes.

L_2	T, °C	10^4k_2, $M^{-1}sec^{-1}$	Carbonyl Stretching Frequencies,[a] cm^{-1}
$H_2PC_2H_4PH_2$	125.0	0	2037, 1948, 1927,[b]
$(CO)_2$	112.0	6.69[c]	2119, 2019, 1986[d]
dipy[e]	47.9	1.81[e]	2014, 1911, 1882, 1830[f]
phen[g]	47.9	0.94[g]	2014, 1910, 1881, 1833[h]
4,7-Ph_2-phen[g]	47.9	0.55[g]	2013, 1909, 1879, 1831[h]
DTH[i]	45.1	44.5[i]	2030, 1919, 1905, 1868[j]

[a] $CHCl_3$ solvent unless otherwise specified. [b] Ref. 8; *n*-hexane solvent. [c] Ref. 6; decalin solvent. [d] R. Poiblanc and M. Bigorgne, *Bull. Soc. Chim. France,* 1301 (1962); hydrocarbon solvent. The two highest frequencies obtained from the Raman spectrum. [e] Ref. 3; dipy = 2,2′-dipyridyl; 1,2-dichloroethane solvent. [f] M.H.B. Stiddard, *J. Chem. Soc.*, 4712 (1962; [g] Ref. 4; 1,2-dichloroethane solvent; phen = *o*-phenanthroline. [h] R.J. Angelici and J.R. Graham, *Inorg. Chem.*, *6* 988 (1967). [i] Ref. 5; 1,2-dichloroethane solvent; DHT = 2,5-dithiahexane. [j] H.C.E. Mannerskantz and G. Wilkinson, *J. Chem. Soc.*, 4454 (1962).

lithium[1a] is consistent with their proposal.* The rates of reactions proceeding *via* attack at the carbonyl may thus be contrasted to those of Lewis bases which, as is indicated in Table IV, are faster for substrates exhibiting the lower carbonyl stretching frequencies.[14] This contrasting reactivity strongly indicates that the attack site differs for the two types of reaction, *i.e.*, that second-order reactions of octahedral metal carbonyls with Lewis bases such as triethyl phosphite proceed *via* attack at the metal atom.

For attack at the metal atom it should be expected that as carbonyl stretching frequencies for the complexes decrease, the rate *via* nucleophilic attack of the base at the metal should also decrease, since lower carbonyl stretching frequencies imply greater metallic d_π electron density, and these metallic orbitals are directed along the presumed paths of ligand attack. The data in Table IV indicate, however, that this is not observed, and, to the contrary, the faster reacting substrates are noted to possess the lower carbonyl stretching frequencies. However, faster reaction rates as observed for substrates such as $(phen)Mo(CO)_4$ would be consistent with stabilization of the transition state through interaction of filled d_π metallic orbitals with vacant d_π ligand orbitals, since lower carbonyl stretching frequencies imply a greater metallic d_π electron density. There is considerable additional evidence, which has been summarized elsewhere,[15] which suggests such stabilization to be important in reactivity *via* ligand dependent paths of metal carbonyls and derivatives of octahedral symmetry, especially for more highly substituted complexes, for which metallic d_π electron density is greater.

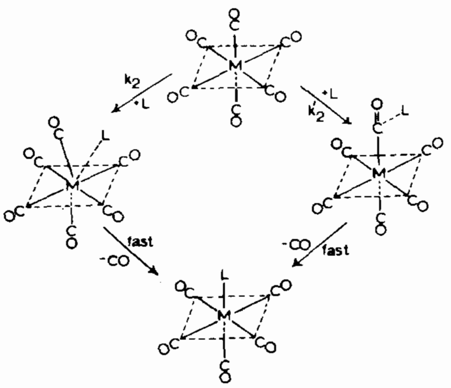

Figure 6. Possible mechanisms for reaction of octahedral metal carbonyls and derivatives with Lewis bases.

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[13] D.J. Darensbourg and M.Y. Darensbourg, *Inorg. Chem.*, *9*, 1691 (1970).

[14] Strict ordering of rates and ν(CO) are not to be expected since other factors, *e.g.*, steric influences and the ground state energies of the substrates also will influence rates.

(*) *Note added in proof*: Further such studies (J.R. Paxson and G.R. Dobson, manuscript in prepaation), suggest differences in rate as a function of L to be attributable to both steric and electronic effects, the former evidently being of greater importance.

[15] G.R. Dobson, *Proc. S. Dak. Acad. Sci.*, *51*, 244 (1971).