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Octahedral Metal Carbonyls. XXII.¹ Kinetics and Mechanism of the Reactions of Molybdenum Carbonyl Derivatives of Substituted *o*-Phenanthrolines with Mercuric Chloride

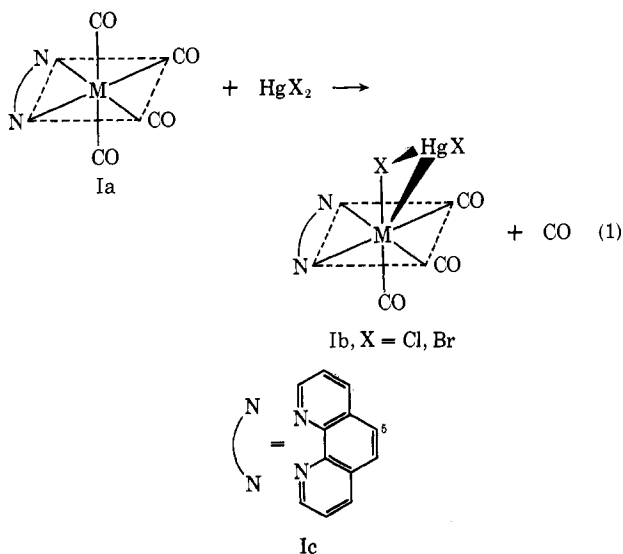
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The oxidative elimination reactions of (5-*X*-phen)Mo(CO)₄ complexes (*X* = H, CH₃, Cl, NO₂ substituted in the 5 position) with mercuric chloride in acetone to give (X-phen)Mo(CO)₃(Cl)HgCl have been investigated employing stopped-flow techniques. Kinetic data indicate the reactions to proceed *via* a mechanism involving "adducts" of stoichiometry (5-*X*-phen)Mo(CO)₄·HgCl₂ and (5-*X*-phen)Mo(CO)₄·2HgCl₂ and are consistent with previous preparative, equilibrium, and kinetic studies. From the data were extracted values of *k*₁, the rate of initial attack of HgCl₂ on the substrates. These rates increase as the charge-releasing abilities of the *X* substituents increase, a trend opposite to that observed for reactions of (X-phen)Mo(CO)₄ complexes with P(OCH₂)₃CCH₃. The implications of these results to reactivity trends in octahedral metal carbonyls are discussed.

Introduction

Oxidative elimination reactions of metal carbonyls involving replacement of a carbonyl by two univalent ligands with the attendant increase in the coordination number and formal oxidation state of the metal have been widely used as a means of synthesis of complexes containing metal-metal bonds. Mercuric halides have been the electrophilic reagents of choice for a number of these investigations, which have included a preparative study of reactions with various (bidentate ligand)-M(CO)₄ complexes (*M* = Mo, W)² and a very recent equilibrium and kinetic study of such reactions (bidentate ligand = *o*-phenanthroline (phen), 2,2'-dipyridyl (dipy); *M* = Mo, W),^{3,4} *e.g.*



A kinetic investigation of reactions of (5-*X*-phen)-

(1) Part XXI: R. A. Brown and G. R. Dobson, *Inorg. Chim. Acta*, in press.

(2) K. Edgar, B. F. G. Johnson, J. Lewis, and S. B. Wild, *J. Chem. Soc. A*, 2851 (1968).

(3) J. W. McDonald and F. Basolo, *Inorg. Chem.*, **10**, 492 (1971); this paper also contains other pertinent references to oxidative elimination reactions involving metal carbonyl complexes.

(4) The structure of Ib is inferred from that reported for (dipy)Mo(CO)₃(Cl)SnCH₂Cl₂, prepared from (dipy)Mo(CO)₄ and CH₃SnCl₃: M. Elder and D. Hall, *Inorg. Chem.*, **8**, 1268 (1969); the Cl bonded to Mo may or may not bridge Mo and Hg. A second structure, a capped trigonal prism, observed for (dipy)W(CO)₃(Br)GeBr₃, is also possible: E. M. Cradwick and D. Hall, *J. Organometal. Chem.*, **25**, 91 (1970).

Mo(CO)₄ with HgCl₂ in acetone (5-*X*-phen = Ic; *X* = CH₃, H, Cl, NO₂) was undertaken independently in this laboratory; its results have proven to be complementary to those of McDonald and Basolo³ and are reported here.

Experimental Section

Preparation and Purification of Materials.—The ligands 5-*X*-phen (*X* = Cl, CH₃) were purchased from the G. Frederick Smith Chemical Co. The 5-NO₂-phen was obtained from Sigma Chemical Co. and was also employed as the precursor to 5-NH₂-phen, prepared by the method of Koft and Case.⁵ Molybdenum hexacarbonyl was purchased from Climax Molybdenum. Analytical reagent grade mercuric chloride was obtained from Mallinckrodt Chemical Works and was used as obtained. The solvent, reagent grade acetone (Matheson Coleman and Bell), was dried over anhydrous calcium chloride and then was fractionally distilled from calcium oxide and potassium permanganate.

The (phen)Mo(CO)₄ employed was some of that used in a previous study.⁸ The (5-*X*-phen)Mo(CO)₄ complexes (*X* = CH₃, NH₂) were prepared in a manner analogous to that employed in the preparation of (3-CH₃-phen)Mo(CO)₄.⁷ *Anal.*⁸ Calcd for C₁₇H₁₀N₂O₄Mo (for *X* = CH₃): C, 50.8; H, 2.51; N, 6.96. Found: C, 50.5; H, 2.60; N, 7.02. Calcd for C₁₆H₉N₂O₄Mo (for *X* = NH₂): C, 47.7; H, 2.25. Found: C, 48.1; H, 2.54.

The (5-*X*-phen)Mo(CO)₄ complexes (*X* = NO₂, Cl) were prepared through reaction of (norbornadiene)Mo(CO)₄, prepared by the literature method,⁹ and the appropriate phenanthroline. (5-NO₂-phen)Mo(CO)₄ had previously been synthesized by another procedure.⁷

(5-Cl-phen)Mo(CO)₄.—To 50 ml of toluene were added 1.57 g (5.2 mmol) of (norbornadiene)Mo(CO)₄ and 1.0 g (4.7 mmol) of 5-Cl-phen. The solution was stirred under nitrogen for 2 hr, after which the toluene was removed *in vacuo*. Excess (C₇H₅)Mo(CO)₄ was removed from the reaction residue by vacuum sublimation (100°, 0.1 Torr), and the crude product was then recrystallized from toluene-hexane at -20° to give 1.44 g (72% of theory) of puce crystals. *Anal.* Calcd for C₁₆H₇ClN₂O₄Mo: C, 45.5; H, 1.67. Found: C, 45.7; H, 1.85.

The (5-*X*-phen)Mo(CO)₃(Cl)HgCl products were prepared by the method previously described for (dipy)W(CO)₃(Cl)HgCl² and were identified through comparison of their infrared spectra to that of (dipy)Mo(CO)₃(Cl)HgCl² (Table I). The carbonyl stretching spectra of all the previously unreported complexes, obtained on a Perkin-Elmer Model 621 grating spectropho-

(5) E. Koft and F. H. Case, *J. Org. Chem.*, **27**, 865 (1962).

(6) D. Shrader, E. P. Ross, R. T. Jernigan, and G. R. Dobson, *Inorg. Chem.*, **9**, 1286 (1970).

(7) R. J. Angelici and J. R. Graham, *ibid.*, **6**, 988 (1967).

(8) Analyses performed by C. F. Geiger, Ontario, Calif.

(9) R. B. King, "Organometallic Syntheses," Vol. 1, Academic Press, New York, N. Y., 1965, pp 124-125.

TABLE I
 CARBONYL STRETCHING FREQUENCIES OF METAL CARBONYL DERIVATIVES

Complex	Solvent	Carbonyl str freq., $^{\circ}\text{cm}^{-1}$
(5-CH ₃ -phen)Mo(CO) ₄	Chloroform	2015 m, 1908 vs, 1879 s, 1831 s
(5-Cl-phen)Mo(CO) ₄	Chloroform	2015 m, 1910 vs, 1880 s, 1832 s
(5-NH ₂ -phen)Mo(CO) ₄	Acetone	2014 s, 1900 vs, 1878 s, 1833 s
(dipy)Mo(CO) ₃ (Cl)HgCl ^b	Mull	1990 s, 1935 m, 1880 s
(phen)Mo(CO) ₃ (Cl)HgCl	Acetone	1993 vs, 1920 s, 1879 s
(5-CH ₃ -phen)Mo(CO) ₃ (Cl)HgCl	Acetone	1990 vs, 1919 s, 1879 s
(5-Cl-phen)Mo(CO) ₃ (Cl)HgCl	Acetone	1993 vs, 1921 s, 1877 s
(5-NO ₂ -phen)Mo(CO) ₃ (Cl)HgCl	Acetone	1994 vs, 1923 s, 1881 s
(5-NH ₂ -phen)Mo(CO) ₃ (Cl)HgCl	Acetone	1988 vs, 1918 s, 1878 s
(dipy)Mo(CO) ₃ (Cl)SnCH ₃ Cl ₂ ^c	CH ₂ Cl ₂	2008 vs, 1918 m, 1898 s
(phen)W(CO) ₄ ^d	Chloroform	2010 m, 1901 vs, 1877 s, 1831 s
(phen)W(CO) ₄ ·2HgCl ₂ ^e	e	2070 s, 1985 s, 1950 m, 1925 s

^a Relative band intensities: s, strong; m, medium; w, weak; v, very. ^b Reference 2. ^c R. Kummer and W. A. G. Graham, *Inorg. Chem.*, **7**, 310 (1968). ^d Reference 7. ^e Reference 3; presumably mull spectrum.

tometer and calibrated against a band of water vapor at 1869.4 cm^{-1} ,¹⁰ are given in Table I.

Determination of Reaction Rates.—Reaction rates were studied employing an Aminco-Morrow stopped-flow spectrophotometric system coupled to the monochromator from either a Beckman DU-2 or Hitachi Perkin-Elmer 137 ultraviolet-visible spectrophotometer. The instrument was thermostated, and the temperature at the observation cell was determined through use of a thermocouple. Pseudo-first-order conditions were employed through use of at least a 40-fold excess of mercuric chloride; final substrate concentrations of $(4-9) \times 10^{-4} \text{ M}$ were employed. Solutions were stored in a constant-temperature bath at the reaction temperature, and after the driving syringes of the stopped-flow apparatus were filled, 20 min was allowed to ensure thermal equilibration before the kinetic runs were initiated. Changes in transmittance as a function of time were monitored at 530 nm for all substrates. That plots (k_{obsd}) of $\ln(A_t - A_{\infty})$ vs. time were linear to at least 2 half-lives demonstrated that only two colored species were present in significant quantity during the course of the reactions.

Rate constants were generally reproducible to within $\pm 5\%$ and were calculated through use of a nonlinear least-squares computer program.

Results and Discussion

Rate data for reactions of (5-X-phen)Mo(CO)₄ complexes (X = CH₃, H, Cl, NO₂) with mercuric chloride in acetone are given in Table II. For X = NH₂ it was

found that the reaction was catalyzed by traces of water in the acetone, and for this reason it was not further investigated. The plots of k_{obsd} vs. $[\text{HgCl}_2]$ at 25.0° are exhibited in Figure 1. It can be observed

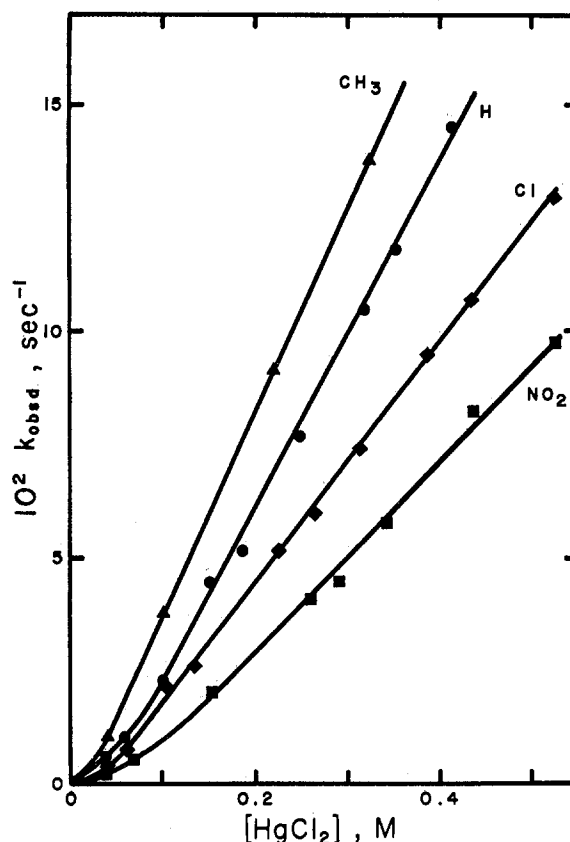


Figure 1.—Plots of k_{obsd} vs. $[\text{HgCl}_2]$ for reactions of (5-X-phen)-Mo(CO)₄ complexes with mercuric chloride in acetone at 25.0°.

that at high mercuric chloride concentrations these plots are linear, indicative of a limiting rate law

$$\text{rate} = k[(5\text{-X-phen})\text{Mo}(\text{CO})_4][\text{HgCl}_2] \quad (2)$$

This is the region of the plot of k_{obsd} vs. $[\text{HgCl}_2]$ not accessible to McDonald and Basolo³ in their investigation, which employed conventional kinetic techniques. Their results at lower mercuric chloride concentrations, with which data obtained in this study are fully consistent, show a limiting rate law

$$\text{rate} = k[(\text{phen})\text{Mo}(\text{CO})_4][\text{HgCl}_2]^2 \quad (3)$$

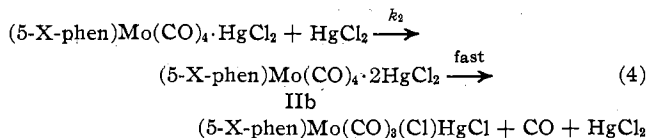
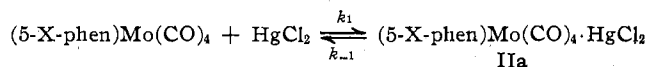
TABLE II
OBSERVED RATES FOR THE REACTION OF
(5-X-phen)Mo(CO)₄ WITH HgCl₂ IN ACETONE

[HgCl ₂], M	10 ² k _{obsd} , sec ⁻¹	[HgCl ₂], M	10 ² k _{obsd} , sec ⁻¹	[HgCl ₂], M	10 ² k _{obsd} , sec ⁻¹
NO ₂ (25.0) ^a		CH ₃ (25.0) ^a		H (25.0) ^a	
0.0372	0.179	0.0408	1.07	0.251	7.65
0.0670	0.535	0.0612	1.85	0.318	10.5
0.153	2.02	0.100	3.80	0.353	11.8
0.259	4.04	0.220	9.16	0.413	14.5
0.290	4.40	0.327	13.8		
0.342	5.76				
0.435	8.24	H (20.0) ^a		H (30.2) ^a	
0.528	9.73	0.0589	0.688	0.0638	1.66
		0.104	1.32	0.106	3.93
		0.147	2.36	0.159	7.52
		0.205	3.59	0.247	12.9
		0.248	4.82	0.303	15.4
		0.298	6.16	0.355	19.0
		0.343	7.15		
		0.400	8.26		
Cl (25.0) ^a		H (25.0) ^a		H (35.5) ^a	
0.0403	0.350	0.0401	0.561	0.0638	2.47
0.615	0.744	0.0604	1.01	0.106	6.03
0.104	2.17	0.102	2.29	0.159	11.7
0.135	2.62	0.150	4.47	0.247	18.9
0.227	5.20	0.187	5.10	0.303	26.6
0.266	5.97			0.355	28.8
0.316	7.40			0.411	34.7
0.386	9.50				
0.436	10.7				
0.529	13.0				

^a 5-X-phen (°C).

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

These observations, together with results of the detailed preparative² and kinetic and equilibrium³ studies of reactions of (bidentate ligand)W(CO)₄ complexes with mercuric halides support the mechanism



Assuming a steady-state concentration of intermediate IIa (see Experimental Section), the rate law

$$\text{rate} = \frac{k_1 k_2 [(5\text{-X-phen})\text{Mo}(\text{CO})_4] [\text{HgCl}_2]^2}{k_{-1} + k_2 [\text{HgCl}_2]} \quad (5)$$

is obtained. It is evident that the limiting expressions (2) and (3) are readily obtainable from (5). Rearrangement of (5) in terms of k_{obsd} gives

$$[\text{HgCl}_2]/k_{\text{obsd}} = 1/k_1 + \frac{k_{-1}}{k_1 k_2 [\text{HgCl}_2]} \quad (6)$$

and thus it can be seen that a plot of $[\text{HgCl}_2]/k_{\text{obsd}}$ vs. $1/[\text{HgCl}_2]$ is expected to be linear, with intercept $1/k_1$ and slope $k_{-1}/k_1 k_2$. Such plots, for the reaction of the four (5-X-phen)Mo(CO)₄ substrates with HgCl₂ at 25.0° are exhibited in Figure 2. In practice, a more

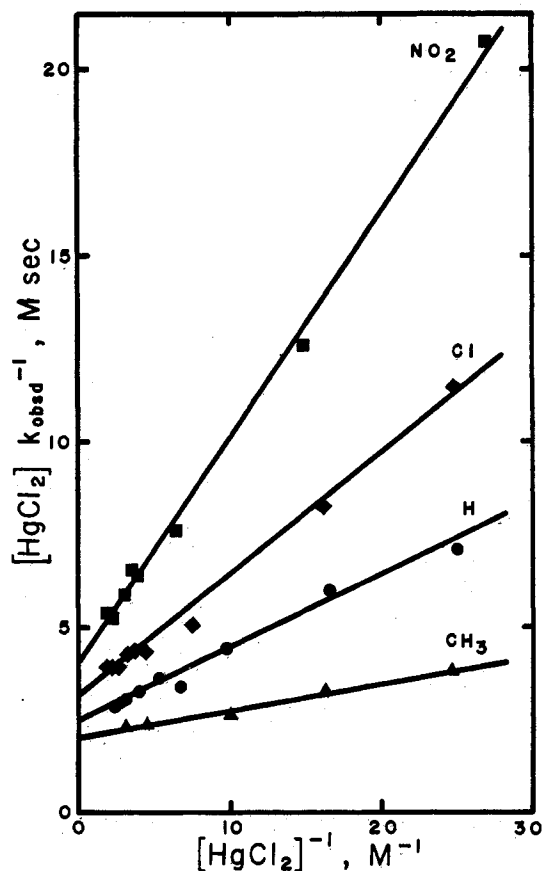


Figure 2.—Plots of $[\text{HgCl}_2](k_{\text{obsd}})^{-1}$ vs. $[\text{HgCl}_2]^{-1}$ for reactions of (5-X-phen)Mo(CO)₄ complexes with mercuric chloride in acetone at 25.0°.

accurate value for the rate constant of greatest interest, k_1 , can be obtained from the limiting slope of the plot of k_{obsd} vs. $[\text{HgCl}_2]$ at high $[\text{HgCl}_2]$. It is found ex-

perimentally that the values of k_1 extracted from the slope of this plot agree with those obtained from the intercept of the reciprocal plot within an average of 15%. Rate constants, together with activation parameters obtained from data at four temperatures for the reaction of (phen)Mo(CO)₄ are presented in Table III. It is to be noted, in particular, that the en-

TABLE III
RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE REACTION OF (5-X-phen)Mo(CO)₄ AND HgCl₂ IN ACETONE

X	pK _a ^a	Temp, °C	k ₁ , M ⁻¹ sec ⁻¹	k ₋₁ /k ₂ , M
NO ₂	3.57	25.0	0.214	0.151
Cl	4.26	25.0	0.261	0.105
CH ₃	5.23	25.0	0.446	0.0336
H	4.86	20.0	0.240	0.0687
		25.0	0.387	0.0758
		30.2	0.592	0.0906
		35.5	0.933	0.0986

$$\Delta H^\ddagger_1 = 15.1 \pm 0.6 \text{ kcal/mol}; \Delta S^\ddagger_1 = -9.9 \pm 1.9 \text{ eu}^\dagger$$

$$\Delta H^\ddagger_1 - \Delta H^\ddagger_2 = 3.7 \pm 1.0 \text{ kcal/mol}; \Delta S^\ddagger_1 - \Delta S^\ddagger_2 = 7.5 \pm 3.4 \text{ eu}$$

^a Values as reported by W. W. Brandt and D. K. Gullstrom, *J. Amer. Chem. Soc.*, **74**, 3532 (1952), or A. A. Schilt and G. F. Smith, *J. Phys. Chem.*, **60**, 1546 (1956). [†] Limits of error, one standard deviation.

trophy of activation for the step involving attack of HgCl₂ on (phen)Mo(CO)₄ is negative, consistent with an associative mechanism.

Rate data for reactions of the four (5-X-phen)Mo(CO)₄ complexes with HgCl₂ reveal a pattern consistent with electrophilic attack of HgCl₂ on (5-X-phen)Mo(CO)₄ in the k_1 step, in that the values of k_1 decrease with increasing electron withdrawal from X-phen by the X substituent. The ratios k_{-1}/k_2 obtained for the four substrates are also consistent with this trend.

Since the 5-X-phen ligands chosen for study were selected so as to minimize steric differences from one substrate to another, the trend may be ascribed primarily to electronic effects. In this regard it is worth noting that the reaction of (3,4,7,8-(CH₃)₄-phen)Mo(CO)₄ with HgCl₂ was found to proceed at a rate too slow to measure.

An excellent linear free energy plot (of $-\log k_1$ vs. the pK_a of the 5-X-phen ligand), which may be compared to that reported by Graham and Angelici¹¹ for the ligand-dependent reactions of various (X-phen)Mo(CO)₄ substrates with the Lewis base P(OCH₂)₃CCH₃, is obtained. For these reactions, rates increase with increasing charge-withdrawing power of X. Both plots are given in Figure 3. They nicely demonstrate that (X-phen)Mo(CO)₄ substrates function as biphilic¹² reagents.

Presumably the initial interaction *via* an associative path in these systems involves approach of the attacking group at an octahedral face of the substrate.¹³

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

(12) R. G. Pearson, H. B. Gray, and F. Basolo, *J. Amer. Chem. Soc.*, **82**, 787 (1960).

(13) In this regard it is worth noting that X-ray studies of two oxidative elimination products of (bidentate ligand)M(CO)₄ substrates, the (dipy)Mo(CO)₃(Cl)SnCH₂Cl₂ mentioned earlier⁴ and (DTH)W(CO)₃(Cl)SnCH₂Cl₂ (DTH = 2,5-dithiahexane (M. Elder and D. Hall, *Inorg. Chem.*, **8**, 1273 (1969)), have shown them to be capped octahedra and, frequency shifts notwithstanding, that the carbonyl stretching spectra for (bidentate ligand)M(CO)₄ complexes and the corresponding (bidentate ligand)M(CO)₄·2HgCl₂ adducts (see, e.g., Table I) are very similar, which should indicate (roughly similar (C_{2v}) geometries for the M(CO)₄ moieties in both types of complex.

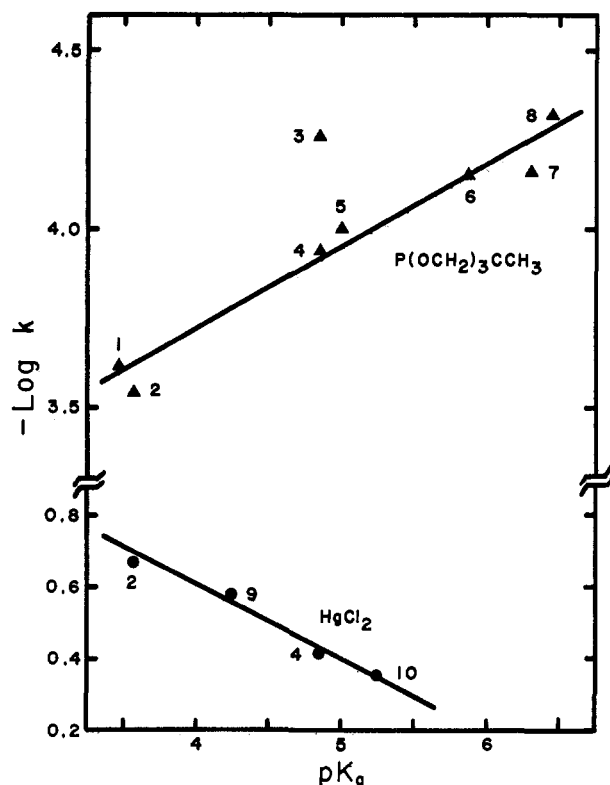


Figure 3.—Linear free energy plots for the reaction of (X-phen)Mo(CO)₄ with mercuric chloride in acetone at 25.0° and with 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane in 1,2-dichloroethane at 47.9°. X substituents: 1, 5,6-dichloro; 2, 5-nitro; 3, 4,7-diphenyl; 4, unsubstituted; 5, 3-methyl; 6, 3,5,7-trimethyl; 7, 3,4,7,8-tetramethyl; 8, 3,4,6,7-tetramethyl; 9, 5-chloro; 10, 5-methyl.

With electrophilic reagents such as HgCl₂, this approach would involve interaction of filled d_π orbitals on Mo with vacant orbitals of appropriate symmetry, presumably p orbitals, on Hg. That the process involves electron removal from the transition metal atom is indicated not only by the kinetic results but also by the higher carbonyl stretching frequencies found in the (phen)M(CO)₄·2HgCl₂ intermediates (isolated for M = W)^{2,8} and in the (phen)Mo(CO)₃(Cl)HgCl products than in the corresponding (phen)M(CO)₄ substrates (Table I); increased carbonyl stretching frequencies are closely related to decreased transition metal d_π electron density.

The variation of the associative rate constants as a function of the pK_a of the X-phen substituents observed by Graham and Angelici¹¹ for reactions of (X-

phen)Mo(CO)₄ complexes with P(OCH₂)₃CCH₃ is consistent with an S_N2 mechanism involving donation of electronic charge from the lone pair on phosphorus to the transition metal. However, the present data would strongly indicate that interaction of the filled metallic d_π orbitals with the available vacant d_π orbitals on phosphorus in the transition state is also possible. Such a stabilization of the transition state would help to explain anomalously fast rates observed for reactions *via* associative paths of substituted group VIb metal carbonyls with phosphines and phosphites. For example, the rate of the ligand-dependent reaction of (phen)Mo(CO)₄ with P(OC₂H₅)₃¹¹ is faster than is the corresponding reaction of Mo(CO)₆ with the same base,¹⁴ despite the fact that the higher carbonyl stretching frequencies observed for the latter substrate would indicate lower electron density at the metal. In this regard, it is of interest to note that complexes such as (DTH)Mo(CO)₄,¹⁵ (phen)Mo(CO)₄,¹¹ and (dipy)Mo(CO)₄,¹⁶ which exhibit anomalously fast rates *via* associative paths with phosphites,¹⁷ are also those complexes which have entered into oxidative elimination reactions with electrophilic reagents.^{2,8,18} There is, in fact, a considerable body of evidence, which has been summarized elsewhere,¹⁹ which indicates that the biphilic nature of octahedral metal carbonyls and derivatives has an important bearing on observed reactivities in ligand replacement reactions *via* associative paths.

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

(15) G. C. Faber and G. R. Dobson, *ibid.*, **7**, 584 (1968).

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

(17) A second mechanism, involving initial reversible dissociation of one end of the bidentate chelating ligand and subsequent attack of the Lewis base on the resulting five-coordinate intermediate can, under certain conditions, also give a rate law which is first order in the concentration of the Lewis base. However, for the (phen)Mo(CO)₄ complex in particular this mechanism would appear to be highly improbable, because of the negative entropy of activation observed and because there is no evidence for replacement of the phen ligand by the Lewis base; in all instances of reactions of (bidentate ligand)M(CO)₄ complexes with Lewis bases for which this mechanism is known to be operative (for references, see G. C. Faber and G. R. Dobson, *Inorg. Chim. Acta*, **4**, 87 (1970)), the bidentate ligand is replaced during the reaction.

(18) R. Kummer and W. A. G. Graham, *Inorg. Chem.*, **7**, 310 (1968).

(19) G. R. Dobson, *Proc. S. Dak. Acad. Sci.*, in press.