

Another important consideration is whether the CO group is labilized as a result of a weakened metal-carbonyl bond or whether the transition state in the proposed CO dissociation mechanism is stabilized in some manner by the "hard" base. In phosphine-substituted nickel carbonyl complexes, infrared studies clearly indicate that the replacement of a CO by a phosphine increases the Ni-CO bond strength,¹⁵ and studies of the C-O stretching vibrations in Cr(CO)₆ and Cr(CO)₄(dipy) suggest that the Cr-CO bond strength is significantly stronger in the dipyriddy complex than in Cr(CO)₆.³ Since it therefore appears that both phosphine and pyridine bases actually increase the metal-carbonyl bond strength, the labilization of CO must be accounted for in terms of a stabilization of the transition state. While there are a number of possible reasons for a "hard" base stabilization of the transition state, none seems to offer an explanation which is consistent with all the data.

Activation Parameters. Since the data in Tables I and II indicate that the first-order rate constants depend slightly on the phosphite used, the activation parameters (Table III) were evaluated separately for each phosphite. The significant difference in activation parameters with the three phosphites is, as discussed in the Results section, not understood. While any interaction between the complex and ligand might be expected to depend on the basicities of the ligands, there is no correlation of ΔH^* with the basic properties of the phosphites which increase in the order: $P(OC_2H_5)_3 < P(OCH_2)_2CCH_3 < PO_3C_6H_9$.¹⁶

The ΔH^* values are relatively low and considerably lower than what one might have expected on the basis

(15) M. Bigorgne, *Bull. soc. chim. France*, 1986 (1960).

(16) J. G. Verkade and C. W. Heitsch, *Inorg. Chem.*, 2, 512 (1963).

of the C-O stretching frequencies of Cr(CO)₄(dipy).¹⁷ They are also significantly lower than the activation energy (39.3 kcal.) obtained for the gas phase ¹⁴CO exchange of Cr(CO)₆ also by way of a dissociative mechanism.¹⁸

The entropies of activation are generally positive or only slightly negative, which tends to support a dissociative mechanism in which the transition state is gaining some degree of freedom. It is also to be noted that ΔS^* decreases as ΔH^* decreases which implies that in the cases where the transition state energy is lowered by solvation there is an accompanying decrease in the over-all ΔS^* as a result of a decrease in the degrees of freedom of the solvating molecules. While these ideas explain the data, it should be added that in most systems ΔS^* usually decreases with ΔH^* .

Solvent Effects. To determine what role the solvent plays, the reaction of Cr(CO)₄(dipy) with P(OCH₂)₃-CCH₃ was studied in those solvents listed in Table IV. The rates were found to be independent of the phosphite and only affected to a small extent by the solvent. Small solvent effects have also been found in other carbonyl substitution reactions¹² and are to be expected for such nonionic reactions; but, while rates of reaction in chlorobenzene and 1,2-dichloroethane are much the same, the activation parameters are much more sensitive to the solvent.

Acknowledgment. Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

(17) A. T. Brault, E. M. Thorsteinson, and F. Basolo, *ibid.*, 3, 770 (1964).

(18) G. Pajaro, F. Calderazzo, and R. Ercoli, *Gazz. chim. ital.*, 90, 1486 (1960).

Kinetic Studies of Group VI Metal Carbonyl Complexes. II. Substitution Reactions of Dipyriddy Complexes of Molybdenum and Tungsten Hexacarbonyls

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The 2,2'-dipyriddy complexes of molybdenum and tungsten hexacarbonyls, $M(CO)_4(dipy)$, have been found under rather mild conditions to undergo substitution reactions with phosphites, L (where $L = P(OC_2H_5)_3$, $P(OCH_2)_2CCH_3$, and $PO_3C_6H_9$), to yield three products: $M(CO)_3(L)(dipy)$, $M(CO)_4(L)_2$, and $M(CO)_3(L)_3$. The reactions proceed according to the two-term rate law, $rate = k_1[M(CO)_4(dipy)] + k_2[L][M(CO)_4(dipy)]$. This rate law suggests that the reaction proceeds by two different mechanisms. On the basis of the products and their amounts formed during a particular reaction and with the aid of activation parameters, reaction mechanisms are proposed and discussed.

Introduction

Earlier Cr(CO)₄(dipy) was found to react readily with phosphites, L, under rather mild conditions to form *cis*-Cr(CO)₃(L)(dipy). Such behavior was unexpected in view of the inertness of Cr(CO)₆ under the same conditions. This labilizing effect of the 2,2'-dipyriddy was explained in terms of the greater "hardness" of 2,2'-dipyriddy relative to that of carbon monoxide.¹ The 2,2'-dipyriddy complexes of the other group VI metal carbonyls have now also been found to contain CO groups which have been substantially labilized by the

(1) R. J. Angelici and J. R. Graham, *J. Am. Chem. Soc.*, 87, 5586 (1965).

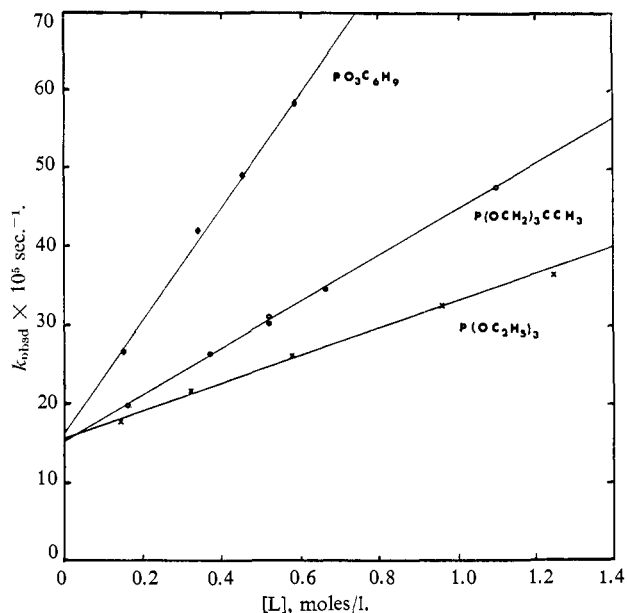


Figure 1. Plot of k_{obsd} for the reaction of $\text{Mo}(\text{CO})_4(\text{dipy})$ with phosphites at 47.9° in 1,2-dichloroethane.

presence of the bidentate ligand. The relative ease with which $\text{Mo}(\text{CO})_4(\text{dipy})$ and, to a lesser extent, $\text{W}(\text{CO})_4(\text{dipy})$ undergo substitution reactions with phosphites has allowed a thorough kinetic and mechanistic study of these systems to be carried out. The purpose of this paper is to present the results of this study.

Experimental Section

Preparation and Purification of Materials. Complexes of the type $\text{Mo}(\text{CO})_4(\text{X-X})$, where X-X is 2,2'-dipyridyl and 4,4'-dimethyl-2,2'-dipyridyl, were prepared and purified by the method used by Stiddard.² The $\text{W}(\text{CO})_4(\text{dipy})$ complex was prepared by the ultraviolet irradiation of 50 ml. of a THF solution containing 0.70 g. of tungsten hexacarbonyl and 0.35 g. of 2,2'-dipyridyl. The complex was recovered by evaporating the THF solution at room temperature, and purification was facilitated by crystallization of the compound from acetone and water. $\text{Mo}(\text{CO})_5\text{py}$ and $\text{W}(\text{CO})_5\text{py}$, where py = pyridine, were prepared and purified by the method outlined by Strohmeier and Gerlach.³ All of the complexes were identified by their infrared spectra.⁴

The ligands used in this study, 4-methyl-3,6,7-trioxal-1-phosphabicyclo[2.2.2]octane [$\text{P}(\text{OCH}_2)_3\text{CCH}_3$], 1-phospha-2,8,9-trioxadamantane ($\text{PO}_3\text{C}_6\text{H}_9$), and triethyl phosphite [$\text{P}(\text{OC}_2\text{H}_5)_3$], were prepared and the solvents purified in the same manner as described in the first paper of this series.¹

Determination of Rates. The techniques used in determining the reaction rate constants were the same as described in the previous paper.¹ All rates were determined by following the disappearance of the highest C-O stretching absorbance of $\text{Mo}(\text{CO})_4(\text{dipy})$ and $\text{W}(\text{CO})_4(\text{dipy})$ on a Beckman IR-8 infrared spectrophotometer. Because of the low solubility of the complexes, solution concentrations were approximately $6 \times 10^{-3} M$, and infrared cells of 1-mm. thickness were

(2) M. H. B. Stiddard, *J. Chem. Soc.*, 4712 (1962).

(3) W. Strohmeier and K. Gerlach, *Chem. Ber.*, **93**, 2087 (1960).

(4) C. S. Kraihanzel and F. A. Cotton, *Inorg. Chem.*, **2**, 533 (1963).

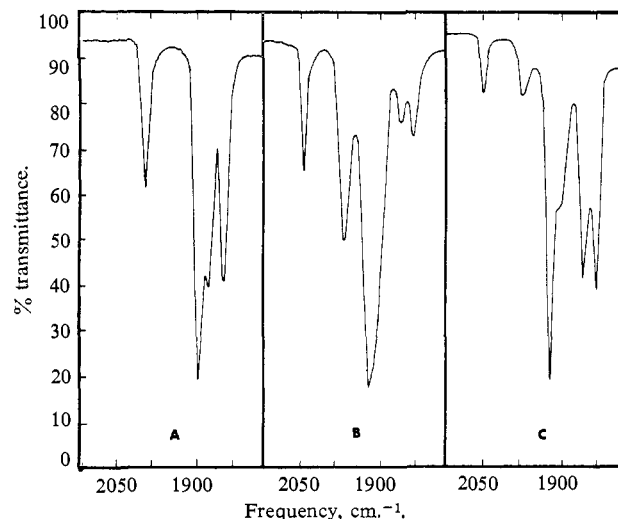


Figure 2. Infrared spectra: (A) $\text{Mo}(\text{CO})_4(\text{dipy})$; (B) and (C) products of the reaction of $\text{Mo}(\text{CO})_4(\text{dipy})$ with 0.717 and 0.047 M $\text{P}(\text{OCH}_2)_3\text{CCH}_3$, respectively, in 1,2-dichloroethane.

required to give satisfactory absorption intensities. Since the reactions were conducted with at least a tenfold excess of the phosphites, linear plots of $\ln(A - A_\infty)$ vs. time yielded pseudo-first-order rate constants. The average deviation of the rate constants for identical runs was almost always less than 2%. Blank runs containing no ligand showed that both $\text{Mo}(\text{CO})_4(\text{dipy})$ and $\text{W}(\text{CO})_4(\text{dipy})$ decomposed at a rate which was about 5% of that of the substitution reaction. This decomposition was accompanied by the formation of a brown precipitate. However, since there was no precipitate formation during the substitution reactions, it was therefore assumed that no decomposition was occurring under these conditions. The first- and second-order rate constants were determined from linear plots of the pseudo-first-order rate constants vs. the concentrations of the ligand used. The first-order rate constants were determined from the zero ligand concentration intercept of the line, the second-order rate constants from its slope. Figure 1 shows a typical plot of k_{obsd} vs. ligand concentration. The enthalpies and entropies of activation, along with their standard deviations, were determined by a least-squares computer program.⁵

Identification of Reaction Products. The infrared spectrum obtained after the reaction of $\text{Mo}(\text{CO})_4(\text{dipy})$ with $\text{P}(\text{OCH}_2)_3\text{CCH}_3$ in 1,2-dichloroethane had gone to completion consisted of five bands (Figure 2). The presence of *cis*- $\text{Mo}(\text{CO})_3[\text{P}(\text{OCH}_2)_3\text{CCH}_3](\text{dipy})$ as a product was immediately evident from the three bands at 1938, 1835, and 1790 cm^{-1} , which are almost identical in position and intensity with those previously identified as *cis*- $\text{Cr}(\text{CO})_3[\text{P}(\text{OCH}_2)_3\text{CCH}_3](\text{dipy})$.¹ The bands at 2050, 2000, and 1930 cm^{-1} correspond quite well to the compound *trans*- $\text{Mo}(\text{CO})_4[\text{P}(\text{OCH}_2)_3\text{CCH}_3]_2$,⁶ and the bands at 1998 and 1930 cm^{-1} indicated the presence of *cis*- $\text{Mo}(\text{CO})_3[\text{P}(\text{OCH}_2)_3\text{CCH}_3]_2$ ⁷ in the reaction mixture.

(5) R. H. Moore, based on a report from Los Alamos Scientific Laboratory, LA2367 and Addenda.

(6) J. G. Verkade, R. E. McCarty, D. G. Hendrick, and R. W. King, *Inorg. Chem.*, **4**, 228 (1965).

(7) F. A. Cotton, *ibid.*, **3**, 702 (1964).

Since during the kinetic runs a large excess of the ligand was used, the isolation of pure reaction products from the reaction mixtures was inconvenient. These products were therefore prepared in larger quantities as follows: $\text{Mo}(\text{CO})_3[\text{P}(\text{OCH}_2)_3\text{CCH}_3](\text{dipy})^8$ was obtained by refluxing in 10 ml. of 1,2-dichloroethane for about 1.5 hr. 0.72 g. of $\text{Mo}(\text{CO})_4(\text{dipy})$ and 0.35 g. of $\text{P}(\text{OCH}_2)_3\text{CCH}_3$. A reddish black solid precipitated from the reaction solution upon cooling to room temperature. This material was filtered, washed thoroughly with pentane, and dried under high vacuum. A yield of greater than 90% was obtained.

Anal. Calcd. for $\text{Mo}(\text{CO})_3[\text{P}(\text{OCH}_2)_3\text{CCH}_3](\text{dipy})$: C, 44.8; H, 3.54. Found: C, 44.9; H, 3.98.

The other products of the reaction were prepared by refluxing in 20 ml. of 1,2-dichloroethane for 12 hr. 1.1 g. of $\text{Mo}(\text{CO})_4(\text{dipy})$ and a fivefold excess (2.5 g.) of $\text{P}(\text{OCH}_2)_3\text{CCH}_3$. Upon cooling the reaction mixture to room temperature, a white crystalline solid was separated. The white crystals were washed thoroughly with pentane and dried under vacuum.

Anal. Calcd. for $\text{Mo}(\text{CO})_3[\text{P}(\text{OCH}_2)_3\text{CCH}_3]_2$: C, 34.1; H, 4.26. Found: C, 34.1; H, 4.38.

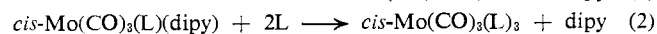
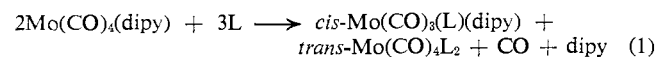
To the filtrate from the above reaction was added an equal volume of pentane. A white powder was obtained. This powder was recrystallized several times by dissolving the substance in hot acetone and precipitating with water.

Anal. Calcd. for $\text{Mo}(\text{CO})_4[\text{P}(\text{OCH}_2)_3\text{CCH}_3]_2$: C, 34.6; H, 4.33. Found: C, 35.1; H, 4.02.

Because of the high temperatures required for the $\text{W}(\text{CO})_4(\text{dipy})$ reactions, $\text{W}(\text{CO})_4(\text{dipy})$ was allowed to react with phosphites in chlorobenzene. In this solvent C-O absorptions below 2000 cm^{-1} are obscured by absorptions due to the solvent. Therefore the products of the $\text{W}(\text{CO})_4(\text{dipy})$ reactions were isolated from the chlorobenzene reaction solutions by precipitation with pentane. The infrared spectra of the products were then run in 1,2-dichloroethane. Except for the expected slight shift in frequencies, they were identical with the spectra obtained for the reactions of $\text{Mo}(\text{CO})_4(\text{dipy})$ with L. It was therefore concluded that analogous products, that is, *cis*- $\text{W}(\text{CO})_3(\text{L})(\text{dipy})$, *trans*- $\text{W}(\text{CO})_4(\text{L})_2$, and *cis*- $\text{W}(\text{CO})_3(\text{L})_3$ were also formed in these reactions.

Results

Kinetics and Products. The immediate products of the reaction of $\text{Mo}(\text{CO})_4(\text{dipy})$ with L, where L = $\text{P}(\text{OCH}_2)_3\text{CCH}_3$, $\text{PO}_3\text{C}_6\text{H}_9$, and $\text{P}(\text{OC}_2\text{H}_5)_3$, are *cis*- $\text{Mo}(\text{CO})_3(\text{L})(\text{dipy})$ and *trans*- $\text{Mo}(\text{CO})_4(\text{L})_2$. The 2,2'-dipyridyl group of *cis*- $\text{Mo}(\text{CO})_3(\text{L})(\text{dipy})$ is slowly replaced by two L groups to form *cis*- $\text{Mo}(\text{CO})_3(\text{L})_3$.



The assignment of the configuration of $\text{Mo}(\text{CO})_3(\text{L})(\text{dipy})$ as the *cis* isomer is the same as was made earlier by Stiddard⁹ for analogous complexes where L was triphenylphosphine and pyridine. The isomer assignment is consistent with the infrared spectrum which shows three strong CO absorbances at 1938, 1835, and 1790 cm^{-1} for L = $\text{P}(\text{OCH}_2)_3\text{CCH}_3$. The compound

$\text{Mo}(\text{CO})_3\text{L}_3$ was assigned the *cis* configuration from its infrared spectrum. The infrared spectrum consists of two strong equally intense absorptions at 1998 and 1930 cm^{-1} , again for L = $\text{P}(\text{OCH}_2)_3\text{CCH}_3$. This infrared spectrum is expected for the *cis* configuration and is the same assignment made by Poilblanc and Bigorgne for similar *cis* trisubstituted complexes.¹⁰

When the 2,2'-dipyridyl group in $\text{Mo}(\text{CO})_4(\text{dipy})$ is replaced by two L groups to form $\text{Mo}(\text{CO})_4(\text{L})_2$, the *cis* isomer would be expected. However, infrared and n.m.r. evidence indicates that the complex actually formed is *trans*- $\text{Mo}(\text{CO})_4(\text{L})_2$. The infrared spectrum, which shows three CO absorptions at 2050 (m), 2000 (w), and $1930\text{ (s)}\text{ cm}^{-1}$, is consistent with the *trans* assignment.⁷ The hydrogen n.m.r. spectrum of the complex shows the presence of phosphorus-phosphorus coupling, which is strong evidence that the complex has the *trans* configuration.⁶ If any *cis*- $\text{Mo}(\text{CO})_4(\text{L})_2$ is formed, its concentration must be very small or it must isomerize very quickly to the *trans* isomer since no evidence for the presence of this isomer can be found during a kinetic run.

The isomeric assignments of the products of the reaction of $\text{W}(\text{CO})_4(\text{dipy})$ with L are the same as those made for the analogous molybdenum complexes.

Both reactions 1 and 2 given above have been substantiated by changes in the infrared spectra and by isolating the intermediates of the reaction as described in the Experimental Section.

The rate of reaction for reaction 1 follows a two-term rate law (eq. 3) over a large range of concentrations as shown by the data in Tables I and II and Figure 1. In Figure 1 the pseudo-first-order rate con-

$$\text{rate} = k_1[\text{Mo}(\text{CO})_4(\text{dipy})] + k_2[\text{Mo}(\text{CO})_4(\text{dipy})][\text{L}] \quad (3)$$

stants, k_{obsd} , are plotted vs. the concentration of L. The graph shows that k_{obsd} depends on [L]; i.e., $k_{\text{obsd}} = k_1 + k_2[\text{L}]$. The value of k_{obsd} at [L] = 0 is k_1 , and the slope of the line is k_2 . As expected for a general rate law, k_1 is relatively independent of the nature of L while k_2 definitely depends on L. The values of k_1 and k_2 determined at different temperatures and in two different solvents are collected in Table III.

The rate of reaction 2 has also been found to follow a similar two-term rate law and is considerably slower than the rate of reaction 1. At 78.0° in 1,2-dichloroethane using $\text{P}(\text{OCH}_2)_3\text{CCH}_3$, concentrations of 0.365, 0.656, and 1.09 M rate constants of 2.22×10^{-4} , 2.98×10^{-4} , and $4.22 \times 10^{-4}\text{ sec}^{-1}$, respectively, have been determined. This accounts for the formation of a small amount of *cis*- $\text{Mo}(\text{CO})_3(\text{L})_3$ during a normal kinetic run.

The reaction of $\text{Mo}(\text{CO})_4(\text{dipy})$ with low concentrations of L does not go to completion but appears to form an equilibrium. If a threefold excess or less of L is used, the reaction proceeds at the expected rate for about the first 50% of the reaction. (Under these conditions of [L], the reaction is approximately first order.) After this point the rate falls off drastically. However, the rate never becomes equal to zero because of the slow decomposition of the main reaction product, $\text{Mo}(\text{CO})_4(\text{dipy})(\text{L})$. The presence of an equilib-

(8) All preparations were carried out under an N_2 atmosphere.

(9) M. H. B. Stiddard, *J. Chem. Soc.*, 756 (1963).

(10) R. Poilblanc and M. Bigorgne, *Bull. soc. chim. France*, 1301 (1962).

rium can be shown by bubbling CO through a solution of $\text{Mo}(\text{CO})_3(\text{dipy})(\text{L})$. After a short time at 48° , an infrared spectrum of the solution shows the presence of both $\text{Mo}(\text{CO})_4(\text{dipy})$ and $\text{Mo}(\text{CO})_3(\text{dipy})(\text{L})$. If N_2 is passed through the solution containing both complexes to remove the CO from the reaction equilibrium, the equilibrium is shifted in favor of the formation of $\text{Mo}(\text{CO})_3(\text{dipy})(\text{L})$.

Table I. Rates of Reaction of $\text{Mo}(\text{CO})_4(\text{dipy})$ with Phosphites in 1,2-Dichloroethane

Phosphite L	[L], moles/l.	Temp., $^\circ\text{C}$.	$10^3 k_{\text{obsd}}$, sec^{-1}	
$\text{P}(\text{OCH}_2)_3\text{CCH}_3$	0.156	37.8	6.56	
	0.656	37.8	11.6	
	1.41	37.8	19.8	
	1.82	37.8	24.6	
	0.00592	47.9	15.7	
	0.0182	47.9	16.3	
	0.156	47.9	19.6	
	0.365	47.9	26.1	
	0.518	47.9	30.1	
	0.518	47.9	31.3	
	0.656	47.9	34.4	
	1.09	47.9	47.7	
	0.156	58.1	66.3	
	0.365	58.1	82.9	
	0.656	58.1	109	
	1.09	58.1	155	
	1.41	58.1	178	
	1.64	58.1	198	
	$\text{PO}_3\text{C}_6\text{H}_5$	0.0873	37.8	7.86
		0.270	37.8	11.8
0.451		37.8	17.4	
0.676		37.8	22.2	
0.00394		47.9	16.8	
0.0170		47.9	17.1	
0.148		47.9	26.4	
0.338		47.9	42.1	
0.452		47.9	49.3	
0.580		47.9	58.2	
0.0873		58.1	65.6	
0.338		58.1	103	
0.541		58.1	138	
0.676		58.1	167	
$\text{P}(\text{OC}_2\text{H}_5)_3$		0.111	37.8	5.12
	0.569	37.8	8.07	
	0.779	37.8	10.0	
	1.00	37.8	10.7	
	1.30	37.8	12.6	
	0.00562	47.9	15.9	
	0.0228	47.9	16.3	
	0.136	47.9	17.5	
	0.319	47.9	21.4	
	0.574	47.9	26.0	
	0.956	47.9	32.6	
	1.243	47.9	36.5	
	0.136	58.1	61.8	
	0.136	58.1	62.2	
	0.318	58.1	69.4	
	0.574	58.1	84.3	
	1.21	58.1	119	
	1.55	58.1	144	
1.81	58.1	164		

Ratio of Products. The infrared spectra of the products of several kinetic runs in which a different concentration of ligand was used showed that the amount of each product formed depended on the concentration of the ligand (Figure 2). To determine exactly what effect the ligand concentration had on the amount of each product formed during a particular reaction, the concentration of each product was determined as a function of the ligand concentration. This was done

by first determining the molar extinction coefficients for each reactant and product. They were found for $\text{Mo}(\text{CO})_4(\text{dipy})$, $\text{Mo}(\text{CO})_4[\text{P}(\text{OCH}_2)_3\text{CCH}_3]_2$, $\text{Mo}(\text{CO})_3[\text{P}(\text{OCH}_2)_3\text{CCH}_3]_3$, and $\text{Mo}(\text{CO})_3(\text{dipy})[\text{P}(\text{OCH}_2)_3\text{CCH}_3]$ to be 1130, 1620, 2630, and 1900 l./cm. mole, respectively. (The highest frequency CO absorption of each compound was used, except for $\text{Mo}(\text{CO})_3(\text{dipy})[\text{P}(\text{OCH}_2)_3\text{CCH}_3]$ for which the band at 1335 cm^{-1} was used, for this determination.)

Five kinetic runs were carried out in 1,2-dichloroethane at 58.1° . In each run the same concentration of $\text{Mo}(\text{CO})_4(\text{dipy})$ (0.00344 M) was used, while the ligand concentrations were varied from 0.117 to 0.943 M . The reactions were allowed to proceed until all of the $\text{Mo}(\text{CO})_4(\text{dipy})$ had completely reacted. The infrared spectrum of each reaction solution was carefully recorded, and the absorbance of each product band was measured. When the infrared spectra were recorded, the solution used in the solvent cell of the double-beam spectrophotometer contained the same concentration of ligand as was used in the reaction. This technique cancelled out all of the extraneous absorbances due to the ligand. From the absorbance of each product band and its molar extinction coefficient, the concentration of each product was determined using Beer's law. The results are shown in Table IV.

The two-term rate law shown in eq. 3 suggests that $\text{Mo}(\text{CO})_4(\text{dipy})$ reacts with phosphites by two mechanisms. The first-order mechanism leads to the formation of only *cis*- $\text{Mo}(\text{CO})_3(\text{L})(\text{dipy})$ as found in the analogous Cr system,¹ and the second-order mechanism leads to the formation of both *cis*- $\text{Mo}(\text{CO})_4(\text{dipy})(\text{L})$ and *trans*- $\text{Mo}(\text{CO})_4(\text{L})_2$. (This will be discussed in more detail in the Discussion section.) The ratio of the amounts of these products obtained from the two reaction paths must be proportional to the ratio of the first-order rate constants describing the rate of formation of these products. Therefore¹¹

$$\frac{k_1}{k_2[\text{L}]} = \frac{[\text{Mo}(\text{CO})_3(\text{dipy})(\text{L})]_1}{[\text{Mo}(\text{CO})_4(\text{L})_2]_2 + [\text{Mo}(\text{CO})_3(\text{dipy})(\text{L})]_2}$$

Since the initial $[\text{Mo}(\text{CO})_4(\text{dipy})] = 0.00344 \text{ M} =$
[products]

and

$$[\text{products}] = [\text{Mo}(\text{CO})_4(\text{L})_2]_2 + [\text{Mo}(\text{CO})_3(\text{dipy})(\text{L})]_1 + [\text{Mo}(\text{CO})_3(\text{dipy})(\text{L})]_2$$

then

$$[\text{Mo}(\text{CO})_3(\text{dipy})(\text{L})]_1 = \frac{k_1(0.00344)}{k_1 + k_2[\text{L}]}$$

and

$$[\text{Mo}(\text{CO})_3(\text{dipy})(\text{L})]_2 = \frac{[\text{Mo}(\text{CO})_3(\text{dipy})(\text{L})]_{1,2} - [\text{Mo}(\text{CO})_3(\text{dipy})(\text{L})]_1}{[\text{Mo}(\text{CO})_3(\text{dipy})(\text{L})]_1}$$

The ratio of the amounts of the two products formed only by the second-order path is therefore

$$\frac{[\text{Mo}(\text{CO})_3(\text{dipy})(\text{L})]_2}{[\text{Mo}(\text{CO})_4(\text{L})_2]_2} = \frac{[\text{Mo}(\text{CO})_3(\text{dipy})(\text{L})]_{1,2} - \frac{k_1(0.00344)}{k_1 + k_2[\text{L}]}}{[\text{Mo}(\text{CO})_4(\text{L})_2]_2}$$

The concentration of $[\text{Mo}(\text{CO})_3(\text{dipy})(\text{L})]_{1,2}$ is taken as the sum of $[\text{Mo}(\text{CO})_3(\text{dipy})(\text{L})]_1$ and $[\text{Mo}(\text{CO})_3(\text{L})_3]$ since $\text{Mo}(\text{CO})_3(\text{dipy})(\text{L})$ is the initial product in the reaction, and $\text{Mo}(\text{CO})_3(\text{L})_3$ is formed by the further

(11) Explanation of subscripts used: 1 is rate constant or product of first-order process; 2 is rate constant or product of second-order process; 1 and 2 is total product formed by both processes. All concentrations are in moles per liter.

Table II. Rates of Reaction of $\text{M}(\text{CO})_4(\text{dipy})$ with Phosphites in Chlorobenzene

Phosphite L	[L], moles/l.	Temp., °C.	$10^5 k_{\text{obsd}}$, sec. ⁻¹	Phosphite L	[L], moles/l.	Temp., °C.	$10^5 k_{\text{obsd}}$, sec. ⁻¹
$\text{P}(\text{OCH}_2)_3\text{CCH}_3$	$\text{Mo}(\text{CO})_4(\text{dipy})$			$\text{PO}_3\text{C}_6\text{H}_9$	$\text{W}(\text{CO})_4(\text{dipy})$		
	0.0576	37.8	2.38		0.451	37.8	14.5
	0.105	37.8	2.93		0.580	37.8	16.6
	0.120	37.8	3.26		0.150	47.9	19.1
	0.198	37.8	4.10		0.214	47.9	23.8
	0.238	37.8	4.37		0.271	47.9	27.3
	0.276	37.8	4.82		0.451	47.9	39.2
	0.394	37.8	5.87		0.580	47.9	44.2
	1.36	37.8	17.0		0.0727	58.1	43.4
	0.156	47.9	9.84		0.0908	58.1	44.0
	0.365	47.9	15.4		0.104	58.1	48.2
	0.656	47.9	21.0		0.311	58.1	79.2
	1.094	47.9	29.6		0.395	58.1	84.8
	1.41	47.9	35.6				
	1.64	47.9	40.0				
	0.0662	58.1	34.8				
	0.161	58.1	38.2				
	0.307	58.1	45.4				
	0.440	58.1	51.9				
	0.563	58.1	56.0				
	0.780	58.1	69.7				
	0.965	58.1	71.8				
	1.266	58.1	84.6				
1.688	58.1	100.0					
$\text{P}(\text{OC}_2\text{H}_5)_3$	0.114	37.8	2.86	$\text{P}(\text{OC}_2\text{H}_5)_3$	0.362	100.0	12.3
	0.174	37.8	3.52		0.671	100.0	19.2
	0.266	37.8	3.90		1.09	100.0	27.7
	0.479	37.8	6.18		1.40	100.0	33.6
	0.798	37.8	8.72		1.63	100.0	39.6
	1.02	37.8	10.4		0.266	110.0	27.2
	0.114	47.9	9.84		0.378	110.0	35.2
	0.266	47.9	12.1		0.479	110.0	43.5
	0.479	47.9	17.4		1.02	110.0	76.7
	0.798	47.9	24.7		1.20	110.0	92.0
	1.025	47.9	28.4		0.362	120.0	71.4
	1.20	47.9	30.7		0.514	120.0	86.5
	0.317	58.1	42.2		0.671	120.0	109
	0.492	58.1	49.3		1.09	120.0	151
	0.982	58.1	61.4		1.81	120.0	236
	1.41	58.1	74.8				
	$\text{PO}_3\text{C}_6\text{H}_9$	0.150	37.8		6.27	$\text{PO}_3\text{C}_6\text{H}_9$	0.128
0.214		37.8	8.42	0.271	100.0		22.4
0.271		37.8	9.64	0.451	100.0		28.9
				0.580	100.0		34.7
				0.150	110.0		36.4
			0.271	110.0	49.4		
			0.338	110.0	58.2		
			0.451	110.0	65.4		
			0.541	110.0	74.2		
			0.150	120.0	89.0		
			0.214	120.0	101		
			0.271	120.0	112		
			0.451	120.0	142		
			0.580	120.0	160		

reaction of $\text{Mo}(\text{CO})_4(\text{dipy})(\text{L})$ with excess L. Since all of the terms in the above expression for the ratio of second-order product concentrations are known, it is a simple matter to calculate the ratio for different [L]. The values of this ratio calculated from experimental points are listed in Table IV. The fact that the relative concentrations of the second-order products is independent of the concentration of $\text{P}(\text{OCH}_2)_3\text{CCH}_3$ used in the reaction firstly supports the assumptions as to what products are formed by each reaction path and secondly indicates that the initial intermediate formed in the second-order mechanism reacts to yield the two products by paths which do not depend on the concentration of $\text{P}(\text{OCH}_2)_3\text{CCH}_3$. These results will be discussed in relation to the possible mechanisms in the Discussion section.

$\text{W}(\text{CO})_4(\text{dipy})$, like $\text{Mo}(\text{CO})_4(\text{dipy})$, was found to react with $\text{P}(\text{OCH}_2)_3\text{CCH}_3$, $\text{PO}_3\text{C}_6\text{H}_9$, and $\text{P}(\text{OC}_2\text{H}_5)_3$ to form a mixture of products. Infrared data indicated that the products were *cis*- $\text{W}(\text{CO})_3(\text{dipy})(\text{L})$, *cis*- $\text{W}(\text{CO})_3(\text{L})_3$, and *trans*- $\text{W}(\text{CO})_4(\text{L})_2$. These reactions also followed a two-term rate law as shown by the data in Table II. A summary of k_1 and k_2 constants obtained at three different temperatures is given in Table III. Because the kinetic study of the reactions of

$\text{W}(\text{CO})_4(\text{dipy})$ had to be carried out at temperatures of 100° and greater, the reproducibility of the kinetic data was not as good as it was for the $\text{Mo}(\text{CO})_4(\text{dipy})$ system. This is pointed out by some of the high standard deviations obtained for the activation parameters as listed in Table V. In the case where the ligand was $\text{P}(\text{OCH}_2)_3\text{CCH}_3$, the ligand appeared to be subliming from the reaction mixture during a kinetic run making it impossible to obtain reproducible rate constants for this ligand.

Variation in k_1 with Different Ligands. The first-order rate constant, k_1 , in eq. 3 should be independent of the nature of the entering ligand. However, k_1 does seem to depend slightly on the ligand used in the reaction as shown by the rate constants listed in Table III. For the analogous $\text{Cr}(\text{CO})_4(\text{dipy})$ reactions, complex solubilities and initial rate constants determined at low ligand concentrations seemed to indicate that association between the complex and ligand was probably not responsible for the variation in first-order rate constants.¹ In an effort to ascertain if this is the case for the Mo- and $\text{W}(\text{CO})_4(\text{dipy})$ reactions, the following were determined: the solubility of $\text{Mo}(\text{CO})_4(\text{dipy})$ in pure 1,2-dichloroethane and in 1,2-dichloroethane containing varying amounts of L, initial rates

Table III. Rate Constants for the Reaction of $M(\text{CO})_4(\text{dipy})$ with Phosphites in 1,2-Dichloroethane and Chlorobenzene

$M(\text{CO})_4(\text{dipy})$	Phosphite L	Temp., °C.	$10^5 k_1$, sec. ⁻¹	$10^5 k_2$, l./mole sec.
In 1,2-Dichloroethane				
$\text{Mo}(\text{CO})_4(\text{dipy})$	$\text{PO}_3\text{C}_6\text{H}_5$	37.8	5.50	25.4
		47.9	16.7	67.8
		58.1	49.0	173
	$\text{P}(\text{OC}_2\text{H}_5)_3$	37.8	4.30	6.34
		47.9	15.6	19.4
		58.1	52.1	55.7
	$\text{P}(\text{OCH}_2)_3\text{CCH}_3$	37.8	4.43	10.6
		47.9	15.3	31.9
		58.1	49.2	89.2
In Chlorobenzene				
$\text{Mo}(\text{CO})_4(\text{dipy})$	$\text{PO}_3\text{C}_6\text{H}_5$	37.8	2.78	24.8
		47.9	10.0	61.3
		58.1	32.4	143
	$\text{P}(\text{OC}_2\text{H}_5)_3$	37.8	1.86	8.74
		47.9	7.80	18.1
		58.1	30.0	36.0
	$\text{P}(\text{OCH}_2)_3\text{CCH}_3$	37.8	1.74	10.8
		47.9	7.80	20.9
		58.1	32.8	38.9
$\text{W}(\text{CO})_4(\text{dipy})$	$\text{PO}_3\text{C}_6\text{H}_5$	100.0	9.80	42.8
		110.0	25.1	88.8
		120.0	48.7	205
	$\text{P}(\text{OC}_2\text{H}_5)_3$	100.0	6.10	20.8
		110.0	13.3	51.7
		120.0	39.0	112

Table IV. The Concentration of Products Formed in the Reaction of $\text{Mo}(\text{CO})_4(\text{dipy})$ with Varying Concentrations of $\text{P}(\text{OCH}_2)_3\text{CCH}_3$

[L]	$[\text{Mo}(\text{CO})_4\text{L}_2]$	$[\text{Mo}(\text{CO})_3\text{L}_3]$	$[\text{Mo}(\text{CO})_2(\text{dipy})\text{L}]$	$[\text{Mo}(\text{CO})_4(\text{dipy})\text{L}]_2$
0.943	0.00106	0.00067	0.00160	0.95
0.717	0.00095	0.00075	0.00172	1.03
0.470	0.00078	0.00062	0.00199	0.97
0.235	0.00046	0.00046	0.00253	1.08
0.117	0.00027	0.00031	0.00284	1.22

at low ligand concentrations, and the molecular weight of $\text{W}(\text{CO})_4(\text{dipy})$ in a solution containing a known amount of $\text{PO}_3\text{C}_6\text{H}_5$.

The solubility of $\text{Mo}(\text{CO})_4(\text{dipy})$ in 1,2-dichloroethane was determined spectrophotometrically and was found to be 0.00935 mole/l. at 25°. This solubility increased only very slightly upon the addition of ligand to the 1,2-dichloroethane solutions. For ligand concentrations between 0.006 and 0.10 M, the solubility increased

Table V. Entropies and Enthalpies of Activation for the Reaction of $M(\text{CO})_4(\text{dipy})$ with Phosphites in 1,2-Dichloroethane and Chlorobenzene

$M(\text{CO})_4(\text{dipy})$	Phosphite L	ΔH_1^* , kcal./mole	ΔS_1^* , e.u.	ΔH_2^* , kcal./mole	ΔS_2^* , e.u.
In 1,2-Dichloroethane					
$\text{Mo}(\text{CO})_4(\text{dipy})$	$\text{PO}_3\text{C}_6\text{H}_5$	21.5 ± 0.9	-9.1 ± 2.8	18.6 ± 0.7	-15.4 ± 2.3
	$\text{P}(\text{OC}_2\text{H}_5)_3$	24.6 ± 0.7	0.48 ± 2.1	21.3 ± 0.8	-9.4 ± 2.6
	$\text{P}(\text{OCH}_2)_3\text{CCH}_3$	23.7 ± 0.9	-2.3 ± 2.9	20.8 ± 0.7	-10.0 ± 2.1
In Chlorobenzene					
$\text{Mo}(\text{CO})_4(\text{dipy})$	$\text{PO}_3\text{C}_6\text{H}_5$	23.9 ± 1.1	-2.5 ± 3.4	17.0 ± 0.7	-20.5 ± 2.2
	$\text{P}(\text{OC}_2\text{H}_5)_3$	27.3 ± 1.3	7.5 ± 4.0	13.6 ± 1.2	-33.4 ± 3.6
	$\text{P}(\text{OCH}_2)_3\text{CCH}_3$	28.9 ± 0.7	12.5 ± 2.2	12.3 ± 0.7	-37.2 ± 2.3
$\text{W}(\text{CO})_4(\text{dipy})$	$\text{PO}_3\text{C}_6\text{H}_5$	24.6 ± 6.1	-12.5 ± 15.8	24.2 ± 2.2	-10.9 ± 5.7
	$\text{P}(\text{OC}_2\text{H}_5)_3$	26.1 ± 1.3	-7.5 ± 3.4	20.0 ± 1.2	-20.8 ± 3.2

by about 1.5 to 4% for the three ligands used in the study. This small increase in solubility suggests that there is very little if any association between the complex and the ligand.

Initial rate constants for the reaction of $\text{Mo}(\text{CO})_4(\text{dipy})$ with ligand concentrations of 0.004 to 0.02 M were determined at 47.9° (Table I). At these low ligand concentrations the second term, $k_2[\text{L}][\text{Mo}(\text{CO})_4(\text{dipy})]$ in eq. 3, becomes very small and affects the reaction rate by less than 2%. Therefore eq. 3 reduces to a first-order rate law. As shown by the data in Table I, the rate constants determined at low [L] are very close to the previously determined first-order rate constants. Even at ligand concentrations which are less than the $\text{Mo}(\text{CO})_4(\text{dipy})$ concentration, slight differences are still observed in the first-order rate constants. If association of the $\text{Mo}(\text{CO})_4(\text{dipy})$ complex by excess ligand were responsible for the variations in k_1 , it should be expected that k_1 for the different ligands should approach a common value at very low ligand concentrations. This, however, does not seem to be the case.

The molecular weight of a 1,2-dichloroethane solution containing known amounts of $\text{W}(\text{CO})_4(\text{dipy})$ and $\text{PO}_3\text{C}_6\text{H}_5$ was determined by means of a vapor pressure osmometer. The molecular weight obtained for the solution of the ligand and the complex was within 1% of the value predicted if there was no association taking place between the complex and the ligand.

The reason for the variations in the first-order rate constants for different ligands is not known. Although the kinetic data, solubility studies, and molecular weight study seem to indicate that the variations in k_1 are not due to ligand-complex association, they do not offer any explanation for the observed phenomenon.

Solvent Effects. The rates of reaction of $\text{Mo}(\text{CO})_4(\text{dipy})$ with $\text{P}(\text{OCH}_2)_3\text{CCH}_3$ in various solvents increases irregularly with increasing dielectric constant of the solvent (Table VI). The reaction rate is accelerated only by a factor of three in the more polar solvents such as acetone and nitrobenzene. The nature

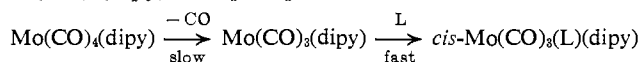
Table VI. Rates of Reaction of $\text{Mo}(\text{CO})_4(\text{dipy})$ with $\text{P}(\text{OCH}_2)_3\text{CCH}_3$ in Various Solvents at 37.9°

Solvent	Dielectric constants	$10^5 k_1$, sec. ⁻¹	$10^5 k_2$, l./mole sec.
Chlorobenzene	5.62	1.74	10.8
1,2-Dichloroethane	10.36	4.43	10.6
Acetone	20.7	5.30	9.67
Nitrobenzene	34.8	5.20	10.4

of the solvent appears to play a relatively minor role in determining the rate of reaction.

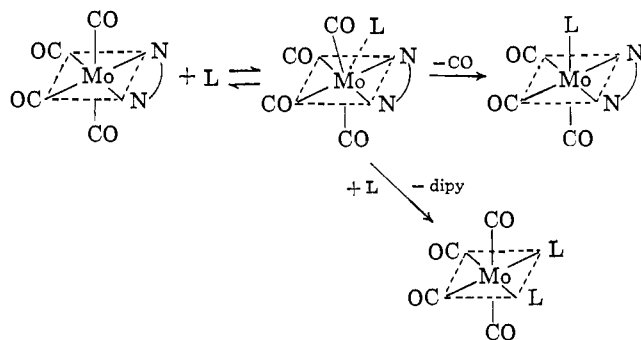
Discussion

The two-term rate law shown in eq. 3 indicates that the reaction of $\text{Mo}(\text{CO})_4(\text{dipy})$ with phosphites occurs by two mechanisms. The first term, $k_1[\text{Mo}(\text{CO})_4(\text{dipy})]$, which is dependent only on the concentration of $\text{Mo}(\text{CO})_4(\text{dipy})$, suggests a simple dissociation mechanism which is analogous to that for the reaction of $\text{Cr}(\text{CO})_4(\text{dipy})$ with phosphites.¹



The activation energies of about 25 kcal./mole and the positive or slightly negative entropies of activation (Table V) for these reactions are very close to those obtained earlier for the dissociative mechanism of $\text{Cr}(\text{CO})_4(\text{dipy})$ and support the same mechanism for the first-order portion of the $\text{Mo}(\text{CO})_4(\text{dipy})$ reaction. Moreover, the formation of *cis*- $\text{Mo}(\text{CO})_3(\text{L})(\text{dipy})$ as one of the reaction products also suggests this mechanism is the correct one.

The second term of eq. 3, $k_2[\text{Mo}(\text{CO})_4(\text{dipy})][\text{L}]$, is an unusual rate law term for octahedral complexes and immediately suggests a mechanism which involves a nucleophilic attack by the ligand upon the molybdenum atom forming a seven-coordinated activated complex, which then releases either a CO group or 2,2'-dipyridyl to form the observed products. The relative amounts of the two products would be independent of the concentration of L as found experimentally. The seven-coordinated intermediate must react rapidly to form the products since no intermediates were detected in the infrared spectral studies. The displacement mech-



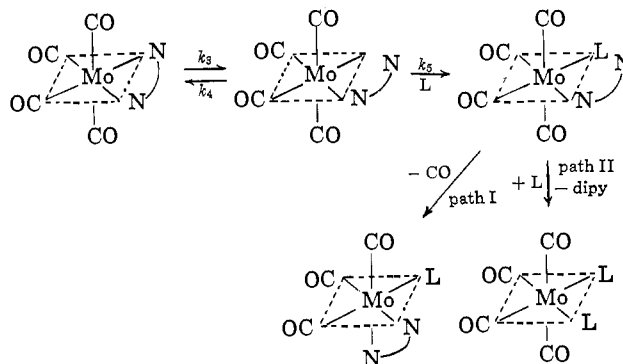
anism is strongly supported by the generally large negative values of the second-order entropies of activation. This indicates that the system is losing some degree of freedom in going to the activated complex which would indeed be the case if the activated complex were a seven-coordinated species.

The displacement mechanism therefore adequately accounts for all of the data. However, a special type of dissociation mechanism (see Scheme I) will also explain the kinetic data. A steady-state treatment for the reaction of $\text{Mo}(\text{CO})_4(\text{dipy})$ by the mechanism shown in Scheme I yields the following rate expression.

$$\text{rate} = \frac{k_3 k_5 [\text{Mo}(\text{CO})_4(\text{dipy})][\text{L}]}{k_4 + k_5[\text{L}]}$$

When $k_4 \gg k_5[\text{L}]$ the equation reduces to a second-order rate law. Since it is likely that k_4 is much larger than $k_5[\text{L}]$, this mechanism offers another possible interpretation of the observed rate law. The rate expression predicts that at high concentrations of L,

Scheme I



i.e., when $k_5[\text{L}] \gg k_4$, the rate law should reduce to a first-order equation. Even at concentrations of L as high as 1.7 M, the reaction rate shows no decrease in its dependence on [L]. Since the rates of paths I and II would very likely be independent of [L], the relative amounts of the two products would be independent of [L] in this mechanism also.

The second-order rate law supports both mechanisms, but the fact that $\text{Cr}(\text{CO})_4(\text{dipy})$ reactions show no second-order term¹ suggests that the larger central atom in $\text{Mo}(\text{CO})_4(\text{dipy})$ may encourage an attack to form a seven-coordinated activated complex. Moreover, seven-coordinated carbonyl complexes of Mo and W are known to be more stable than those of Cr as evidenced, for example, by the existence of $[\text{Mo}(\text{CO})_4\text{I}_3]^-$ and $[\text{W}(\text{CO})_4\text{I}_3]^-$ and the nonexistence of $[\text{Cr}(\text{CO})_4\text{I}_3]^-$.¹²

If the reaction does follow a displacement mechanism, then the rate of reaction of $\text{Mo}(\text{CO})_5\text{py}$ with $\text{P}(\text{OCH}_2)_3\text{CCH}_3$, which is somewhat analogous to the $\text{Mo}(\text{CO})_4(\text{dipy})$ reactions, should also show a dependence on the ligand concentration. Indeed this has been found to be the case. Using $\text{P}(\text{OCH}_2)_3\text{CCH}_3$ concentrations of 0.121, 0.400, and 0.848 M, rate constants of 9.96×10^{-4} , 11.6×10^{-4} , and $13.5 \times 10^{-4} \text{ sec}^{-1}$, respectively, were found at 47.9° in 1,2-dichloroethane. The mechanism of this reaction appears to be quite complicated since three products have been identified by their infrared spectra in the final reaction solution. They are $\text{Mo}(\text{CO})_5\text{L}$, $\text{Mo}(\text{CO})_4(\text{L})_2$, and $\text{Mo}(\text{CO})_4(\text{py})(\text{L})$, where $\text{L} = \text{P}(\text{OCH}_2)_3\text{CCH}_3$, $\text{P}(\text{C}_6\text{H}_5)_3$, and $\text{P}(\text{C}_6\text{H}_5)_3$. Only in the case where $\text{L} = \text{P}(\text{C}_6\text{H}_5)_3$, a weaker base than pyridine, could $\text{Mo}(\text{CO})_4(\text{L})(\text{py})$ be isolated after the reaction. The dependence of the reaction rate on the ligand concentration can be easily explained by a displacement mechanism which proceeds *via* the formation of a seven-coordinated activated complex. No plausible mechanism can be proposed for this reaction that explains the second-order character which involves a dissociative process.

Preliminary results from a study of the reaction of molybdenum hexacarbonyl with various ligands at 112° using decalin as the solvent show that the reaction rate is strongly dependent on the ligand concentration. The fact that the rate of reaction of $\text{Mo}(\text{CO})_6$ with L shows a dependence on the ligand concentration lends strong support to a displacement mechanism for this reaction as well as for the $\text{Mo}(\text{CO})_4(\text{dipy})$ reaction.

Experimental evidence which supports both mechanisms was obtained from a study of the effect of a

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change in the basicity of the ligand on the rate of reaction. The second-order rate constant k_2 increased in the following order for the different ligands used in the study: $\text{P}(\text{OC}_2\text{H}_5)_3 < \text{P}(\text{OCH}_2)_3\text{CCH}_3 < \text{PO}_3\text{C}_6\text{H}_9$. The basicity of these ligands toward BH_3 and $\text{B}(\text{CH}_3)_3$ increases in the same order.^{13,14}

If 2,2'-dipyridyl ($\text{p}K_a = 4.50$) is replaced in the Mo complex by a stronger base, 4,4'-dimethyl-2,2'-dipyridyl ($\text{p}K_a = 5.45$), the result should be an increase in the formal negative charge on the Mo atom. Therefore if the reaction does proceed by a displacement mechanism (this would also be consistent with the dissociation mechanism), then the second-order rate constant for the reaction of $\text{Mo}(\text{CO})_4(\text{dipy})$ with L should be greater than the second-order rate constant for the reaction of $\text{Mo}(\text{CO})_4(4,4'\text{-dimethyl-dipy})$ with L. Using ligand concentrations of 0.262, 0.786, and 1.18 M, rate constants of 3.41×10^{-4} , 4.18×10^{-4} , and $5.00 \times 10^{-4} \text{ sec}^{-1}$, respectively, were found for the reaction of $\text{Mo}(\text{CO})_4(4,4'\text{-dimethyl-dipy})$ with $\text{P}(\text{OCH}_2)_3\text{CCH}_3$ at 47.9°. The first- and second-order rate constants are $2.94 \times 10^{-4} \text{ sec}^{-1}$ and $1.64 \times 10^{-4} \text{ l./mole sec.}$, respectively. If k_2 for this reaction is compared with k_2 for the corresponding $\text{Mo}(\text{CO})_4(\text{dipy})$ reaction (Table III) in 1,2-dichloroethane, it can be seen that k_2 does decrease as the basicity of the bidentate ligand is increased. It is also to be noted that k_1 for $\text{Mo}(\text{CO})_4(4,4'\text{-dimethyl-dipy})$ is about twice that for $\text{Mo}(\text{CO})_4(\text{dipy})$. This trend was observed for the analogous Cr complexes and discussed in detail in an earlier publication.¹

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$\text{W}(\text{CO})_4(\text{dipy})$ in its reactions with $\text{PO}_3\text{C}_6\text{H}_9$ and $\text{P}(\text{OC}_2\text{H}_5)_3$ also obeys a two-term rate law of the form given in eq. 3. The values of k_1 and k_2 at three different temperatures given in Table III show the same trends as for the reactions of $\text{Mo}(\text{CO})_4(\text{dipy})$, and the mechanisms corresponding to the two terms of the rate law are presumably the same as those discussed for the analogous Mo complex. Again k_2 increases with increasing basicity of L in the order $\text{P}(\text{OC}_2\text{H}_5)_3 < \text{PO}_3\text{C}_6\text{H}_9$.

Because W is a slightly larger atom than Mo, the displacement mechanism would predict that k_2 might be greater for the W complex than the Mo complex, if the Mo-CO and W-CO bond energies were the same. However, this is not immediately evident from the second-order activation energies since the $\text{W}(\text{CO})_4(\text{dipy})$ reactions have considerably higher second-order activation energies than do the corresponding $\text{Mo}(\text{CO})_4(\text{dipy})$ reactions in the same solvent. The higher activation energies for the W reactions may be accounted for by the presence of not only a stronger W-L bond as compared to the Mo case but also a stronger W-CO bond in the activated complex. The stronger W-CO bond may more than compensate for a stronger W-L bond, thus increasing the activation energy to a point where it is actually greater than the activation energies for the $\text{Mo}(\text{CO})_4(\text{dipy})$ reactions.

The activation energies of the first-order path are remarkably similar for the complexes of Cr, Mo, and W. They do not reflect trends in the M-CO bond strengths¹⁵ of the hexacarbonyls of these metals. The differences in the rates of these reactions depend largely on differences in the entropies of activation.

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Electron-Transfer Reactions Involving Chelating Bridging Groups¹

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When α -hydroxy acids act as bridging groups in the reduction of carboxylatopentaamminecobalt(III) ions by Cr^{2+} , the specific rates are significantly higher than for previously reported systems involving simple adjacent attack. With glycolate as bridging group, the initial chromium(III) product is metastable and reverts to a species identical with the glycolatochromium(III) ion prepared by conventional methods; this evidence, together with the fact that the initial Cr(III) product has a higher extinction coefficient, indicates that the chromium is chelated by the bridging group in the activated complex. The rates of the oxidation-reduction reactions are independent of acid in the range 0.05 to 1.0 N H^+ , and in each case the reaction is described by the rate law

$-d(\text{Co}^{III})/dt = k(\text{Co}^{III})(\text{Cr}^{II})$. When alkyl-substituted malonates are the ligands, the rate law is of the general form $-d(\text{Co}^{III})/dt = k_1(\text{Co}^{III})(\text{Cr}^{II}) + k_2(\text{Co}^{III})(\text{Cr}^{II})/(\text{H}^+)$. No acid-catalyzed path is observed for these reactions, in contrast to the case of the malonato complex, presumably because the inductive effect of the alkyl group makes the loss of the methylene hydrogen more difficult.

Introduction

The subject of electron transfer through organic bridging groups has been explored in considerable detail.²⁻⁶

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