transitions. The intensities are quite sensitive to the energy separations between the allowed and forbidden bands.

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Substitution Reactions of Tetracarbonyl-1,5-cyclooctadienemolybdenum(0)

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Contribution from the Istituto di Chimica Generale dell'Università di Milano, Milan, Italy, and the Istituto di Chimica Generale dell'Università di Padova, Padua, Italy. *Received August 1, 1966.*

Abstract: The complex $Mo(CO)_4(C_8H_{12})$ undergoes substitution reactions with 1,2-bis(diphenylphosphino)-ethane, α,α'-dipyridyl, 1,10-phenanthroline, triphenylphosphine, triphenylarsine, and triphenylstibine to yield the products $Mo(CO)_4L_2$ or $Mo(CO)_4D$, where L is a monodentate ligand and D a bidentate ligand. The reactions proceed according to the two-term rate law: rate $= k_1[Mo(CO)_4(C_8H_{12})] + k_2[Mo(CO)_4(C_8H_{12})][L]$ (or [D] in the case of the bidentate ligands). The possible reaction mechanism and the reactivities of the entering groups toward molybdenum carbonyl complexes are discussed.

Extensive kinetic investigations on some octahedral complexes of group VI metal carbonyls (Cr, Mo, W) have shown that generally the replacement of weak basic groups by relatively strong bases (dipyridyl or substituted dipyridyl) increases the lability of the CO groups. As an example, $Cr(CO)_4$(dipy) reacts readily with phosphites to form *cis*-$Cr(CO)_3L$(dipy), whereas under the same conditions $Cr(CO)_6$ is quite inert.[1,2] However, the replacement of CO groups by phosphines or phosphites does not affect markedly the lability of the CO; *i.e.*, in the language of Pearson, the "harder" the base the more labile the CO groups are. As an example, $Re(CO)_4BrL$ undergoes a more rapid dissociation of a CO group when L is pyridine than in the case of the analogous complex in which L is triphenylphosphine.[3] This is consistent with the important conclusion of Jørgensen that a "soft" ligand coordinated to a metal ion can confer "softness" on it,[4] and this makes the release of a "soft" coordinated ligand, such as CO, more difficult.

In some ways, the kinetic behavior of metal carbonyl complexes of chromium, molybdenum, and tungsten is significantly different. Thus, the reaction of $Cr(CO)_4$(dipy) with phosphites (L) to yield *cis*-$Cr(CO)_3L$(dipy) proceeds according to a first-order rate law, whereas the analogous metal carbonyls of Mo and W (M) undergo, under the same conditions, substitution reactions with phosphites, which lead to both *cis*-$M(CO)_3L$(dipy) and *trans*-$M(CO)_4L_2$. For these reactions, a two-term rate law is followed.

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

This immediately suggests that the coordinated dipyridyl is much less inert in the latter complex than in the analogous chromium complex. The simple dissociative path (characterized by k_1) for the release of a carbon monoxide group depends slightly on the nature of the central atom, the rate of reaction varying in the order $Cr \simeq Mo > W$.[1] Moreover, on going from apolar to dipolar aprotic solvents, the values of k_1 do not depend appreciably upon the nature of the solvent, in agreement with the fact that neutral species arise from dissociation of the uncharged complexes.

This work is a development of a previous study on the substitution reactions of tetracarbonyl-1,5-cyclooctadienemolybdenum(0).[5] The present paper deals with kinetic investigations on substitution reactions of $Mo(CO)_4(C_8H_{12})$ with entering groups having nitrogen, phosphorus, arsenic, and antimony as donor atoms, in benzene or 1,2-dichloroethane solution. The object was to investigate, first, the possible reaction mechanism and, second, the factors which enhance the reactivity of the entering groups toward molybdenum carbonyl complexes.

Experimental Section

Materials. $Mo(CO)_4(C_8H_{12})$ was prepared following the method given in the literature.[6] The 1,2-bis(diphenylphosphino)ethane was prepared according to Chatt and Hart.[7] The method of Stiddard was used to prepare $Mo(CO)_4$(bipy).[8] The compounds *cis*-$Mo(CO)_4[P(C_6H_5)_3]_2$, *cis*-$Mo(CO)_4[As(C_6H_5)_3]_2$, and *cis*-$Mo(CO)_4[Sb(C_6H_5)_3]_2$ were prepared by adding, under nitrogen, a *n*-heptane solution of the ligand to a *n*-heptane solution of $Mo(CO)_4(C_8H_{12})$. The identity and purity of all these compounds were confirmed by their carbon, hydrogen, and nitrogen analyses and by their infrared spectra.

Triphenylphosphine, triphenylarsine, and triphenylstibine, commercial reagent grade, were recrystallized from petroleum ether. α,α'-Dipyridyl and 1,10-phenanthroline, as reagent grade, were used without further purification. Thiophene-free benzene was refluxed over sodium wire and then fractionally distilled. Purification of 1,2-dichloroethane was effected by fractional distillation.

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[1] R. J. Angelici and J. R. Graham, *J. Am. Chem. Soc.*, **87**, 5586, 5590 (1965).

[2] T. A. Magee, C. N. Matthews, T. S. Wang, and J. H. Wotiz, *ibid.*, **83**, 3200 (1961).

[3] F. Zingales, unpublished data.

[4] C. K. Jørgensen, *Inorg. Chem.*, **3**, 1201 (1964), and references therein.

[5] F. Zingales, F. Canziani, and F. Basolo, *J. Organometal. Chem.* (Amsterdam), in press.

[6] E. O. Fischer and W. Fröhlich, *Ber.*, **92**, 2995 (1959).

[7] J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1378 (1960).

[8] M. H. B. Stiddard, *ibid.*, 4712 (1962).

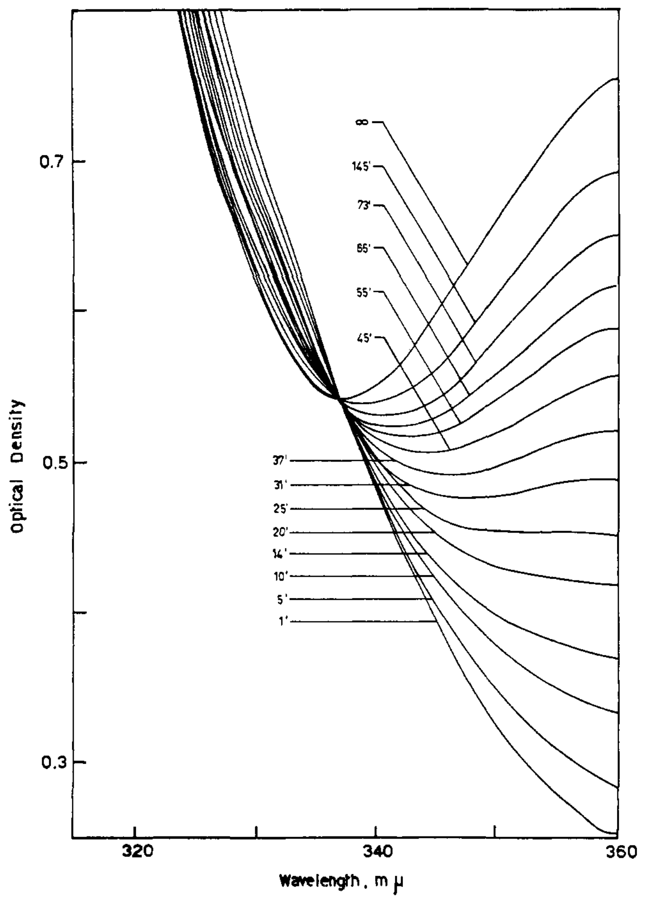

Figure 1. Spectral changes during the reaction of $Mo(CO)_4(C_8H_{12})$ with triphenylarsine (0.01 *M*) in benzene at 42.5° (complex concentration about 5×10^{-4} *M*).

Kinetics. The reactions were followed by measuring changes in optical density from time to time in the course of the reaction in the ultraviolet and visible regions (Figure 1).

All the experiments were carried out using both a Beckman-DK2 and an Optica CF 4 recording apparatus. Fresh solutions of the complex (generally about 5×10^{-4} *M*) in the appropriate solvent and the reagent were prepared and stored separately in a thermostat. The reaction was started by mixing known volumes of the two solutions in a 1-cm quartz cell in the thermostat-controlled (±0.1°) cell compartment. The reference cell contained the reagent blank. All the reactions were carried out in the presence of a large excess of the entering groups with respect to the complex in order to provide pseudo-first-order conditions. In each sequence of kinetic runs, the entering ligand concentration was changed at least 10-fold. The final spectra were in good agreement with those of the known products prepared independently, so that the reactions proceeded to completion. In most cases the spectra showed well-defined isosbestic points which are indicative of only two absorbing species, the starting material and the product. The experimental rate constants, k_{obsd} (sec^{-1}), were obtained graphically from the usual plot of log $(A_t - A_\infty)$ against time, where A_t and A_∞ are the optical densities of the reaction mixture at *t* seconds and after 7-10 half-lives at some selected wavelengths where the optical densities of the products are considerably larger than those of the initial complexes. Duplicate runs carried out under the same conditions showed that the values of k_{obsd} were generally reproducible to better than 5%. Activation parameters were obtained for some reactions, and the corresponding values are reported in Table III.

Results and Discussion

The reaction followed is

$$Mo(CO)_4(C_8H_{12}) + 2L \text{ (or D)} \longrightarrow cis\text{-}Mo(CO)_4L_2 \text{ (or } Mo(CO)_4D) + C_8H_{12} \quad (1)$$

The final products were characterized by infrared analyses. The four absorption bands observed in the range 2030–1800 cm^{-1} indicate a *cis* structure for the compounds $Mo(CO)_4L_2$ and $Mo(CO)_4D$. In fact, *cis*-$Mo(CO)_4L_2$ (or $Mo(CO)_4D$) has C_{2v} symmetry, which gives rise to four CO stretching frequencies ($2 A_1 + B_1 + B_2$) (Table V). Linear plots of k_{obsd} (Table I) *vs.* the concentrations of the entering groups were obtained with nonzero intercepts (Figure 2).

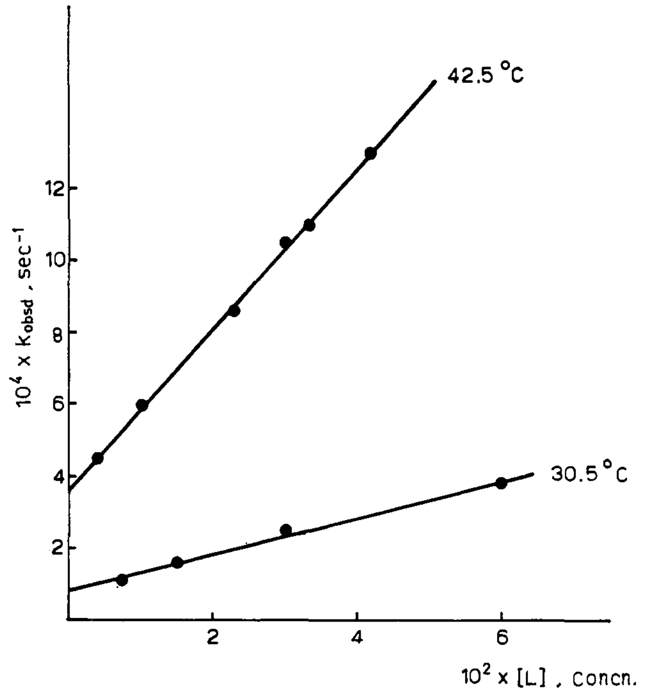

Figure 2. Plots of the experimental rate constants, k_{obsd}, *vs.* the concentration of 1,10-phenantroline in *s*-dichloroethane at two temperatures.

The rate data follow the two-term rate law

$$k_{obsd} = k_1 + k_2[L]^9 \quad (2)$$

Recorded in Tables II and III are the rate constants and the activation parameters of reaction 1. The extrapolated values of k_1, as determined following the reactions by measuring changes in optical density in the ultraviolet and visible regions, are slightly smaller than those estimated by making use of the infrared method.[5] It is likely that this is due to the fact that with the infrared method the concentrations of the entering group are markedly larger than those used with the method of the present work. However, this discrepancy seems to affect mainly the k_1 term rather than k_2, as verified in duplicate runs carried out with both methods.

The rate law (2) has the same form as that observed for four-coordinate planar complexes. The interpretation, indeed, cannot be the same in the two cases. In this case, in fact, not all the stages of the substitutions are bimolecular. The value of k_1 (the intercept) is about the same for all the entering groups in a given solvent (Table II). There is not, however, a satisfactory explanation for the different values of k_1 found for the examined entering groups in *s*-dichloroethane. There is some evidence to support the hypothesis that the k_1 term has to be ascribed to a simple dissociative pathway rather than to a reaction

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(9) Or [D] in the case of bidentate ligands.

Table I. Pseudo-First-Order Rate Constants, k_{obsd}, for the Reaction $Mo(CO)_4(C_8H_{12}) + 2L \text{ (or D)} \longrightarrow Mo(CO)_4L_2$ (or $Mo(Co)_4D$) + C_8H_{12} in Different Solvents, at Two Temperatures

Entering group, *M*	Solvent	Temp, °C	10^4k_{obsd}, sec^{-1}
	α,α′-Dipyridyl		
0.008	C_6H_6	30.5	0.9
0.03			1.0
0.08			1.3
0.1			1.45
0.16			1.7
0.2			1.9
0.02		42.5	4.5
0.05			5.0
0.1			6.4
0.14			7.0
0.2			8.4
0.02	$ClCH_2CH_2Cl$	30.5	1.5
0.037			1.7
0.07			2.0
0.075			2.1
0.12			2.45
0.15			2.6
0.15			3.0
0.2			3.1
0.24			3.2
0.02		42.5	5.7
0.037			6.3
0.068			7.2
0.075			8.1
0.136			10.5
0.272			15.5
	1,2-Bis(diphenylphosphino)ethane		
0.0015	C_6H_6	30.5	0.7
0.005			0.9
0.025			1.2
0.050			1.6
0.070			1.85
0.005		42.5	3.6
0.02			4.3
0.05			5.2
0.07			6.4
0.1			7.8
0.012	$ClCH_2CH_2Cl$	30.5	0.5
0.025			0.54
0.051			1.4
0.103			2.8
0.01		42.5	2.3
0.02			3.0
0.05			6.6
0.05			6.8
0.1			13.0
	Triphenylphosphine		
0.02	C_6H_6	30.5	0.8
0.047			0.9
0.08			1.2
0.09			1.3
0.106			1.45
0.14			1.[illegible]
0.01		42.5	3.0
0.02			3.4
0.05			4.0
0.10			6.1
	Triphenylarsine		
0.036	C_6H_6	30.5	0.8
0.090			1.25
0.12			1.5
0.24			2.5
0.01		42.5	3.2
0.021			3.5
0.042			4.0
0.043			3.8
0.074			5.1
0.10			5.5
	Triphenylstibine		
0.01	C_6H_6	30.5	0.75
0.028			0.9
0.040			0.96
0.048			1.15
0.087			1.45
0.095			1.50
0.010		42.5	3.8
0.028			4.25
0.06			5.15
0.087			6.0
0.10			6.15
	1,10-Phenanthroline		
0.0075	$ClCH_2CH_2Cl$	30.5	1.1
0.015			1.6
0.03			2.5
0.05			3.8
0.004		42.5	4.5
0.01			6.0
0.022			8.6
0.03			10.5
0.033			11.0
0.042			13.0

Table II. Rate Constants at 30.5° for the Reaction $Mo(CO_4)(C_8H_{12}) + 2L \text{ (or D)} \longrightarrow Mo(CO)_4L_2$ (or $Mo(Co)_4D$) + C_8H_{12} in Different Solvents

Entering group	10^4k_1, sec^{-1}	10^4k_2, M^{-1} sec^{-1}	Solvent
α,α′-Dipyridyl	0.8	6.5	C_6H_6
1,2-Bis(diphenylphosphino)ethane	0.7	18	
$P(C_6H_5)_3$	0.5	8.5	
$As(C_6H_5)_3$	0.6	8	
$Sb(C_6H_5)_3$	0.65	9	
α,α′-Dipyridyl	1.0	8.5	$ClCH_2CH_2Cl$
1,10-Phenanthroline	0.7	55	
1,2-Bis(diphenylphosphino)ethane	0.2	25	

with the solvent. Thus, the positive activation entropies for the path independent of the entering group strongly suggest a transition state in which some degree of freedom is gained. Moreover, the activation energies for this pathway are about 25 kcal/mole and are very close to those obtained earlier for the dissociative mechanism of $Cr(CO)_4$(dipy). This behavior seems to be of general validity, and it has been observed also in the reactions of similar chromium, molybdenum, and tungsten carbonyl complexes. Furthermore, a dissociative pathway is found also in the ^{14}CO exchange of the hexacarbonyls of the above three group VI metals.[10] For the ligand independent path (k_1), the implicit assumption is made that the cleavage of the first metal–diene π bond is the rate-determining step, followed by the rapid release of the diene ligand. This model is in agreement with the mechanism previously proposed for the substitution reaction of (arene)$Mo(CO)_3$ with various entering groups.[11]

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[10] (a) G. Pajaro, F. Calderazzo, and R. Ercoli, *Gazz. Chim. Ital.*, **90**, 1486 (1960); (b) G. Cetini and O. Gambino, *Atti Accad. Sci. Torino, Classe Sci. Fis. Mat. Nat.*, **97**, 757 (1963).

[11] F. Zingales, A. Chiesa, and F. Basolo, *J. Am. Chem. Soc.*, **88**, 2707 (1966).

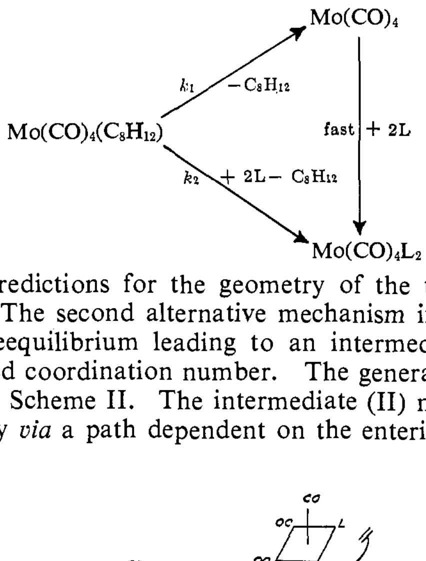
Table III. Activation Parameters for the Reaction $Mo(CO)_4C_8H_{12} + 2L$ (or D) $\longrightarrow$ $Mo(CO)_4L_2$ or (Mo(Co)D) + C_8H_{12} in Different Solvents[a]

Entering group	Solvent	$\Delta H_1^{\ddagger}$, kcal/mole	$\Delta S_1^{\ddagger}$, eu/mole	$\Delta H_2^{\ddagger}$, kcal/mole	$\Delta S_2^{\ddagger}$, eu/mole
α,α'-Dipyridyl	C_6H_6	25	+5	19	−11
1,2-Bis(diphenylphosphino)ethane		24	+2	14	−25
$P(C_6H_5)_3$		25	+4	21	−3
$As(C_6H_5)_3$		25	+4	17	−17
$Sb(C_6H_5)_3$		25	+4	19	−10
α-α'-Dipyridyl	$ClCH_2$-CH_2Cl	25	+5	22	−1
1,10-Phenanthroline		27	+11	20	−3
1,2-Bis(diphenylphosphino)ethane		28	+12	22	0
Pyridine[b]	$CHCl_3$	24	+3	18	−12
$PCl_2C_6H_5$[b]		24	+3	20	−10

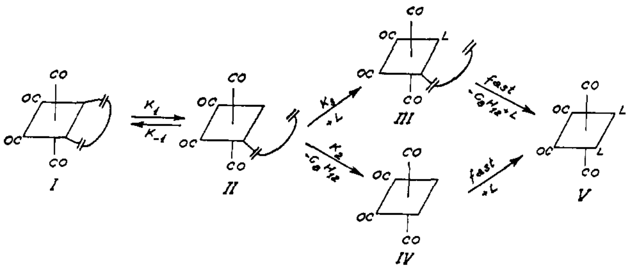
[a] Temperatures examined 30.5 and 42.5° [b] Temperatures examined 25 and 40°. Data from ref 5.

As far as the second-order term k_2 is concerned, at least two mechanisms can adequately account for the kinetic data. The first mechanism involves a direct attack by the entering group upon the reaction center forming an activated complex of increased coordination number.[12] This then rapidly releases the C_8H_{12} molecule to give the products. Accordingly, the general scheme for the substitution is therefore that shown as Scheme I. No information is available to permit predictions for the geometry of the transition state.[13] The second alternative mechanism involves a rapid preequilibrium leading to an intermediate (II) of reduced coordination number. The general form is shown in Scheme II. The intermediate (II) may react selectively *via* a path dependent on the entering group (k_3[L]) and/or also *via* a simple dissociative mechanism (k_2). For the two-step mechanism, one may apply the steady-state approximation for the concentration of the postulated intermediate (II).[14]

Scheme I



Scheme II



It is appropriate at this point to summarize the relative influences of different ligands acting as entering and leaving groups for the reactions in which the reactants and the products are of comparable stability. We can consider the cases in which P–P and N–N are the entering and the leaving groups. In the reactions of $Mo(CO)_4$(P–P) and $Mo(CO)_4$(N–N) (where P–P is 1,2-bis(diphenylphosphino)ethane and N–N is α,α'-dipyridyl), we have found that, under the same experimental conditions, the N–N group is replaced by the same entering group (triphenyl phosphite) dramatically faster than the P–P group, the ratio of the observed rate constants being roughly larger than 10^3:1. On the other hand, for the reactions of $Mo(CO)_4(C_8H_{12})$ with P–P and N–N, k_2(P–P) is larger than k_2(N–N) by a factor of only 3. This illustrates the greater importance of the leaving group in these reactions, and it argues for an "intimate" mechanism in which the activation is of dissociative type (I_d mechanism). In fact, as shown above, these substrates are more sensitive to the nature of the leaving group than to the nature of the entering group.[13d] As far as the activation entropies are concerned, it may be noted that the negative values found for the path dependent on entering groups are expected for bimolecular displacement processes.[15] Generally speaking, one of the most important requirements of a mechanism, in which bond formation in the transition state is the driving force for the substitution, is the existence of large differences in the reactivities of different entering groups. In other, words, whatever the finer details of the mechanism are, the larger the discrimination ability of the reaction center and the more extensively developed is the extent of bond formation in the transition state. This may be the case for systems where the changes in bond energy with change in ligand are relatively small (usually "soft" centers, *e.g.*, Pt(II)). For "harder" centers (*e.g.*, hydrogen, carbon, phosphorus) the discrimination ability first increases and then decreases with the extent of bond formation in the transition state.[16,17]

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(12) J. R. Graham and R. J. Angelici, *J. Am. Chem. Soc.*, **88**, 3658 (1966).

(13) For a general discussion concerning the possible structures of transition states in displacements on octahedral complexes, see (a) F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1967; (b) S. Asperger and C. K. Ingold, *J. Chem. Soc.* 2862 (1956); (c) D. D. Brown, C. K. Ingold, and R. S. Nyholm, *ibid.*, 2674 (1953). For a recent review, see (d) C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin Inc., New York, N. Y., 1965.

(14) The experimental rate constant is

$$k_{\text{obsd}} = \frac{\text{rate}}{[\text{I}]} = \frac{k_1}{k_{-1} + k_2 + k_3[\text{L}]}\ \{k_2 + k_3[\text{L}]\} \qquad \text{(i)}$$

Assuming that k_3[L] is negligible in comparison to k_{-1} at the concentrations of L used in these experiments and that k_2 is comparable to k_3[L], one can get the approximately two-term rate law

$$k_{\text{obsd}} = \frac{\text{rate}}{[\text{I}]} = k' + k''[\text{L}] \qquad \text{(ii)}$$

There is no real evidence supporting the assumption that the terms k_2 and k_3[L] are of comparable magnitude, so that the mechanism of Scheme II actually may be believed to be operating only on the basis of the previously proposed reaction mechanisms for analogous metal carbonyl complexes. However, no decrease of the reaction rate in its dependence on L was observed at the higher concentrations of the entering groups, as one may expect on the basis of eq i.

If the mechanism of Scheme II is the operative one in the case in which k_2 is much larger than the k_3[L] term, no [L]-dependent path should be found. It is pertinent to note that $Mo(CO)_4(C_8H_{12})$ reacts with PCl_3 only by a dissociative mechanism; see ref 5.

(15) (a) F. Basolo in "Mechanisms of Inorganic Reactions," Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965, p 81, and references therein; (b) P. B. Chock and J. Halpern, *J. Am. Chem. Soc.*, **88**, 3511 (1966).

(16) R. F. Hudson in "Structure and Bonding," Vol. I, Springer-Verlag, Heidelberg, 1966.

(17) J. F. Bunnett, *Ann. Rev. Phys. Chem.*, 271 (1963).

Table IV. Discrimination Ability, $k_2(\text{I})/k_2(\text{II})$, for Bimolecular Substitution Reactions of Some Metal Carbonyl Complexes Reacting with Different Entering Groups

Metal carbonyl	Entering groups I	Entering groups II	$k_2(\text{I})/k_2(\text{II})$	Solvent	Ref
(mesitylene)$Mo(CO)_3$	$P(n\text{-}C_4H_9)_3$	PCl_3	40	*n*-Heptane	11
(*p*-xylene)$Mo(CO)_3$	$P(n\text{-}C_4H_9)_3$	PCl_3	100	*n*-Heptane	11
(toluene)$Mo(CO)_3$	$P(n\text{-}C_4H_9)_3$	PCl_3	150	*n*-Heptane	11
$(C_8H_{12})Mo(CO)_4$	$P(n\text{-}C_4H_9)_3$	$PCl_2C_6H_5$	10	Chloroform	5
(dipy)$Mo(CO)_4$	$PO_3C_6H_9$	$P(OC_2H_5)_3$	5	1,2-Dichloroethane	1
(dipy)$Mo(CO)_4$	$PO_3C_6H_9$	$P(OC_2H_5)_3$	3	Chlorobenzene	1
$(C_5H_5)Rh(CO)_2$	$P(C_2H_5)_3$	$P(OC_6H_5)_3$	110	Toluene	19
$[Re(CO)_4I]_2$	γ-Picoline	α-Chloropyridine	30	Carbon tetrachloride	*a*

[a] F. Zingales, U. Sartorelli, F. Canziani, and M. Raveglia, *Inorg. Chem.*, **6**, 154 (1967).

One of the most significant features of bimolecular substitution reactions in metal carbonyl complexes is the lack of large discrimination between different entering groups; as an example, see data in Table IV.

Table V. CO Stretching Frequencies (cm^{-1})

Compound			Solvent	Ref
cis-$Mo(CO)_4[P(C_6H_5)_3]_2$	2023	1929	Hydrocarbon	*a*
	1911	1899		
cis-$Mo(CO)_4[As(C_6H_5)_3]_2$	2023	1929	Hydrocarbon	*b*
	1915	1899		
cis-$Mo(CO)_4[Sb(C_6H_5)_3]_2$	2024	1935	Hydrocarbon	*c*
	1921	1909		
cis-$Mo(CO)_4C_2H_4[P(C_6H_5)_2]_2$	2020	1919	$CHCl_3$	*d*
	1907	1881		
cis-$Mo(CO)_4$(dipy)	2017	1909	$CHCl_3$	*e*
	1878	1829		

[a] R. Poilblanc and M. Bigorgne, *Bull. Soc. Chim. France*, 1301 (1962). [b] G. Bouquet and M. Bigorgne, *ibid.*, 433 (1962). [c] D. Benlian and M. Bigorgne, *ibid.*, 1583 (1963). [d] J. Chatt and H. R. Watson, *J. Chem. Soc.*, 4980 (1961). [e] C. S. Kraihanzel and F. A. Cotton, *Inorg. Chem.*, **2**, 533 (1963).

As shown, the values of the discrimination abilities (*i.e.*, the changes in k_2 with the entering group) are relatively small. It is pertinent to note that in the cases of the metal carbonyl complexes examined, the reactivity of the heterocyclic amines (pyridine and substituted pyridines) ranges between the reactivities of PCl_3 and of $P(n\text{-}C_4H_9)_3$. In contrast, the ratio between the rate constants for the slowest (amine) and the fastest (phosphine) entering groups is about 10^6 in the case of substitution reactions of four-coordinate planar platinum(II) complexes, and about 10^4 in the case of methyl iodide as substrate.[13a] From these observations, the assumption is reasonable that, for the reactions of $Mo(CO)_4(C_8H_{12})$, of the two possible mechanisms the more probable one is a bimolecular substitution[18] in which the bond breaking prevails on the bond making.

As far as the entering group reactivity is concerned, rate constants listed in Table II show that ligands having phosphorus, arsenic, and antimony as donor atoms react at practically the same rate toward $Mo(CO)_4(C_8H_{12})$. This may be interpreted as due to a balance of compensating influences of the basicity and the polarizability of the donor atom upon its reactivity toward this substrate. The same conclusion has been reached for the reactions of $Rh(CO)_2C_5H_5$[19] and strongly suggests that group VI metal carbonyl complexes may be considered as borderline in the classification of "soft" and "hard" acids.[20,21]

Acknowledgments. The present work was financially supported by the Italian Consiglio Nazionale delle Ricerche (C. N. R., Roma). We thank Professor R. F. Hudson and Dr. P. Uguagliati for discussions.

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(18) It is of interest that the substitution reactions of molybdenum hexacarbonyl depend upon the concentrations of both the reacting species; see ref 12.

(19) H. G. Schuster-Woldan and F. Basolo, *J. Am. Chem. Soc.*, **88**, 1657 (1966).

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