2820 *Inorganic Chemistry, Vol. 12, No. 12, 1973*

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Kinetic Study of Amine Substitution in $Mo(CO)_5$(amine) Complexes[1]

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Received June 5, 1973

The reactions of pentacarbonylaminemolybdenum(0) complexes, $Mo(CO_5)A$, with various ligands L to produce $Mo(CO)_5L$ have been studied. The reactions obey a two-term rate law of the form $-d[MA]/dt = (k_1/\gamma + k_2[L])[MA]$, where γ is a function of the ratio of A to L in the solution. The rate constant k_1 is related to a first-order dissociative process leading to an intermediate $Mo(CO)_5$. The relative rates of recombination of this species with A and L in hexane have been studied for A = piperidine and L = $P(OCH_3)_3$, $P(C_6H_5)_3$, and $As(C_6H_5)_3$. The competition ratios, *i.e.*, the relative rates of recombination, are all near unity. The results suggest that $\Delta G^\ddagger$ in the recombination reaction is small. In the reactions of $Mo(CO)_5A$ with $P(C_6H_5)_3$, k_1 varies in the order A = cyclohexylamine > piperidine > quinuclidine; $\Delta H_1^\ddagger$ and $\Delta S_1^\ddagger$ are about 25 kcal/mol and +3 eu, respectively. In the ligand-dependent process the same order in amine is observed; $\Delta H_2^\ddagger$ and $\Delta S_2^\ddagger$ are about 15 kcal/mol and in the range −20 to −40 eu, respectively. Increasing solvent polarity causes a slight increase in k_1 and a sharp decrease in k_2. It is concluded that the results are best accounted for in terms of concurrent dissociative (D) and dissociative interchange (I_d) pathways.

Introduction

$Mo(CO)_5$(amine) complexes undergo thermal decomposition thought to involve an initial dissociation of the amine to form a five-coordinate intermediate which abstracts a carbonyl from another $Mo(CO)_5$(amine) molecule to form $Mo(CO)_6$ and degradation products.[2,3] Substitution of amine by Lewis bases L such as phosphines follows a two-term rate law of the form

$$\text{rate} = (k_1 + k_2[L])[Mo(CO)_5A] \qquad (1)$$

The ligand-independent rate constant for reaction of $P(OPh)_3$ (Ph = C_6H_5) with $Mo(CO)_5$(piperidine), $k_1 = 2.75 \times 10^{-5}$ sec^{-1} at 40°, corresponds well with the observed rate constant for thermal decomposition of $Mo(CO)_5$(piperidine) in hexane at 40°, 3.15×10^{-5} sec^{-1}. The close correspondence in rates is taken to signify a common initial pathway for both processes. The ligand-independent term is proposed to involve a rate-determining dissociation of amine to form $Mo(CO)_5$, which then reacts with L to form $Mo(CO)_5L$ as product. The ligand-dependent term is postulated to involve attack by L on the metal center resulting in displacement of amine to form monosubstituted product. The rate is reported[2] to increase with increasing basicity, $P(OPh)_3 < P(OCH_3)_3 < P(n\text{-}C_4H_9)_3$, as expected for a nucleophilic displacement process.

The replacement of amine in $Mo(CO)_5$(amine) complexes represents a particularly simple and accessible instance of substitution at an octahedral center. In contrast to most octahedral substitutions which have been studied, the amine replacement can be carried out in nonpolar solvents. Reactants and products are uncharged and relatively nonpolar, and the transition state can be expected to be of low polarity whether the reaction proceeds *via* a dissociative or associative reaction pathway. For these reasons the reaction provides an especially attractive opportunity for discerning kinetic consequences of changes in either the leaving or attacking bases and solvent influences on the relative importance of dissociative and associative pathways. In addition, because the reaction can be studied in noninteractive solvents, it is possible to investigate in some detail the selectivity of the intermediate, generated when the reaction proceeds *via* a dissociative pathway, toward bases when more than one base is present.

There have been previous reports of the kinetic parameters for the first-order process involving loss of amines from $Mo(CO)_5$(amine) complexes,[2,3] notably the recent work by Dennenberg and Darensbourg.[3] Ingemanson and Angelici have reported[4] the first- and second-order activation parameters for substitution on $W(CO)_5$(morpholine) by PPh_3 in hexane. The variation in $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for the first-order processes with variation in amine are relatively small. Rather surprisingly, they report $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values for the second-order process in the $W(CO)_5$(morpholine)-PPh_3 reaction which are nearly identical with those for the first-order reaction.

In the absence of data on the activation parameters for amine substitution in $Mo(CO)_5$(amine) reactions it is impossible to characterize adequately the second-order, ligand-dependent process. There is no evidence in the experimental observations for a discrete seven-coordinate intermediate in the reaction. One is thus led to think in terms of an interchange (I) process.[5] But because the reaction of interest is carried out in relatively nonpolar solvents and involves low polarity reactants and products, it is to be expected that the relative importances of entering ligand and solvent will be very much different from those in octahedral substitutions involving charged species in polar media.

The interchange model, which has been discussed by Langford and Gray,[5] is expressed for the system of interest here by the equations

$$MA \underset{k_{-f}}{\overset{k_f}{\rightleftharpoons}} \langle MS, A\rangle \underset{k_{-10}}{\overset{k_{10}}{\rightleftharpoons}} MS + A \qquad (2)$$

$$MS + L \xrightarrow{k_{11}} ML \qquad (3)$$

$$L + MA \underset{k_{-i}}{\overset{k_i}{\rightleftharpoons}} \langle MA, L\rangle \xrightarrow{k_{20}} ML + A \qquad (4)$$

where S is solvent and the angular brackets enclose solvent-encased substrate and a species occupying a position favorable for interchange. But how important can the solvent be in

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(1) This research was supported in part by the Advanced Projects Research Agency through Contract ARPA-HC-15-67-C-0221 and the National Science Foundation through Grants NSF-GH-33634 and NSF-GP-30256X.

(2) D. J. Darensbourg and T. L. Brown, *Inorg. Chem.*, 7, 1679 (1968).

(3) R. J. Dennenberg and D. J. Darensbourg, *Inorg. Chem.*, 11, 72 (1972).

(4) C. M. Ingemanson and R. J. Angelici, *Inorg. Chem.*, 7, 2646 (1968).

(5) C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, New York, N. Y., 1965, Chapter 1.

stabilizing the coordinatively unsaturated metal carbonyl intermediate? There is evidence from matrix isolation studies[6] that rare gas atoms or CH_4 can in fact interact with the $M(CO)_5$ intermediate, as evidenced from the geometry maintained by the species in the matrix and by spectral shifts. The energetics of such interactions are unlikely to be very large, *i.e.*, not more than perhaps 2-3 kcal/mol, but the solvent may play a role in maintaining a nominally six-coordinate geometry at the metal in solution.

The rate law derived from eq 2-4 is

$$-\mathrm{d}[\mathrm{MA}]/\mathrm{d}t = \left[\frac{k_{10}k_f}{\gamma k_{-f} + k_{10}} + \frac{k_{20}k_i}{k_{-i} + k_{20}}[\mathrm{L}]\right][\mathrm{MA}] \qquad (5)$$

$$\gamma = 1 + k_{-10}[\mathrm{A}]/k_{11}[\mathrm{L}] \qquad (6)$$

The expression can be reduced by consideration of the relative magnitudes of the rate constants involved. Because of the presumed weak interaction of solvents of low basicity with the five-coordinate species, $k_{-f} >> k_{10}$. Conversely, we expect that $k_{-i} >> k_{20}$. With these assumptions the rate law reduces to

$$-\mathrm{d}[\mathrm{MA}]/\mathrm{d}t = \left[\frac{k_{10}k_f}{\gamma k_{-f}} + \frac{k_{20}k_i}{k_{-i}}[\mathrm{L}]\right][\mathrm{MA}] \qquad (7)$$

For convenience we write this in the form

$$-\mathrm{d}[\mathrm{MA}]/\mathrm{d}t = (k_1/\gamma + k_2[\mathrm{L}])[\mathrm{MA}] \qquad (8)$$

For $[A] \approx 0$, as is the case when the substitution is carried out in the absence of added A, $\gamma \rightarrow 1$. Equation 8 thus reduces to the familiar eq 1, in which the constant k_1 is $(k_{10} \cdot k_f/k_{-f})$, reflecting a dissociative process modified by separation and recombination processes. The energetics of the first-order process are dominated by dissociation, eq 2. The k_2 term of eq 1 and 8 corresponds to $k_{20}k_i/k_{-i}$; it reflects an interchange process modified by the equilibrium for formation of the associated species with L in a favorable position for the interchange. The energy requirement for the interchange depends on the degree of participation of L in formation of the transition state. The degree of participation of L in the transition state in the ligand-dependent process is reflected also in the manner in which variations in the electronic and steric properties of L and changes in solvent affect the enthalpy and entropy of activation.

In this contribution we describe detailed studies of the substitution reactions of $Mo(CO)_5$(amine) complexes with various bases, mostly phosphorus containing. By observing the effects of added amine on the rates of substitution it has been possible quantitatively to evaluate the selectivity of the presumed five-coordinate intermediate toward different bases. The $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values for substitution of the quinuclidine, piperidine, and cyclohexylamine complexes by triphenylphosphine (PPh_3) and the effect of solvent on the rate constants for the $Mo(CO)_5$(piperidine)-PPh_3 system have been carefully evaluated.

Results

A. Concentration Dependence. Substitution of piperidine by triphenylphosphine on $Mo(CO)_5$(piperidine) was studied in hexane at 35°. The sole product after long reaction times was shown from ir analysis to be the monosubstitution product $Mo(CO)_5(PPh_3)$, provided the reagent ligand had been present initially in at least eightfold molar excess over substrate. Otherwise, $Mo(CO)_6$ was also formed.

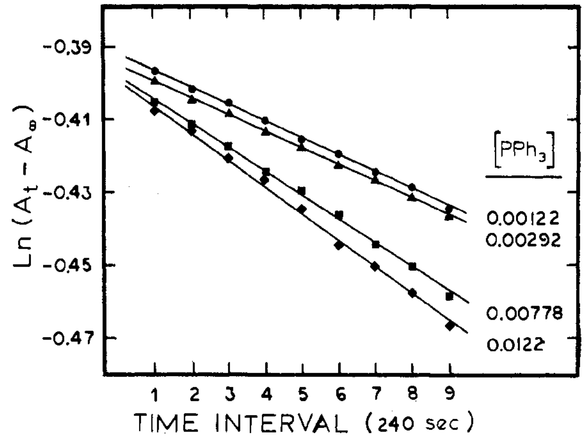

Figure 1. Typical absorbance-time data for reaction of $Mo(CO)_5$-(pip) with PPh_3 in hexane at 35°.

Typical absorbance-time data are presented in Figure 1. As expected from eq 8, the slope is L dependent and increases with an increase in L concentration. (Different intercepts in Figure 1 arise because different initial $Mo(CO)_5$(piperidine) concentrations were used.) k_{obsd} varies linearly with L concentration. The slope is k_2, the L-dependent rate constant, and the intercept is k_1, the L-independent rate constant.

According to eq 8, k_1 is L independent only when experimental conditions are such that the A concentration is essentially nil. With increasing concentration of added A, k_1 is expected to diminish. Variation in k_{obsd} as a function of A/L is shown in Figure 2. The intercept diminishes as the molar ratio increases. (Note: each point in this figure corresponds to a complete rate constant determination.) A complete tabulation of k_{obsd}-L concentration-molar ratio data is included in the microfilm edition.[7]

B. The Competition Ratio. According to eq 6, a graph of calculated γ values plotted against A/L should be linear with unit intercept and (k_{-10}/k_{11}) as the slope. The quantity (k_{-10}/k_{11}) is the ratio of the rates with which A and L react with the intermediate, according to eq 2 and 3; we term it the *competition ratio.* It reflects the discriminatory behavior of the intermediate in combining with A or L.

The observed intercept values (k_1/γ), obtained as in Figure 2, evaluate the competition ratio (see Discussion). An exemplary graph of inverse intercept *vs.* molar ratio is shown in Figure 3. (Note: each point in Figure 3 represents an entire series of kinetics runs to obtain a single intercept, as in Figure 2.) The quotient of the intercept in Figure 3, $(1/k_1)$, divided into the slope, $(k_{-10}/k_{11}k_1)$, is the competition ratio. This procedure incidentally provides check on the L-independent rate constant. k_1 is most readily obtained from k_{obsd} *vs.* L concentration data when the molar ratio A/L is zero. It is obtained also as the inverse intercept in Figure 3. The value of 1.71×10^{-5} sec^{-1} for k_1, calculated from the latter data set, is in good agreement with $k_1 = (1.84 \pm 0.12) \times 10^{-5}$ sec^{-1}, calculated from the former.[8]

The experiments were repeated with triphenylarsine and trimethyl phosphite as reagent ligands. Calculated competi-

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[6] M. A. Graham, R. N. Perutz, M. Poliakoff, and J. J. Turner, *J. Organometal. Chem.*, 34, C34 (1972).

[7] See paragraph at end of paper regarding supplementary material.

[8] Dennenberg and Darensbourg's data[3] for $Mo(CO)_5$(pip), when extrapolated to 35° using their reported temperature dependence, yield a value for k_1 of 3.73×10^{-5} sec^{-1}. But these authors apparently defined the rate in terms of disappearance of starting material. In the thermal decomposition reaction two molecules of starting material are consumed for each loss of amine, thus accounting for the factor of two difference in rates.

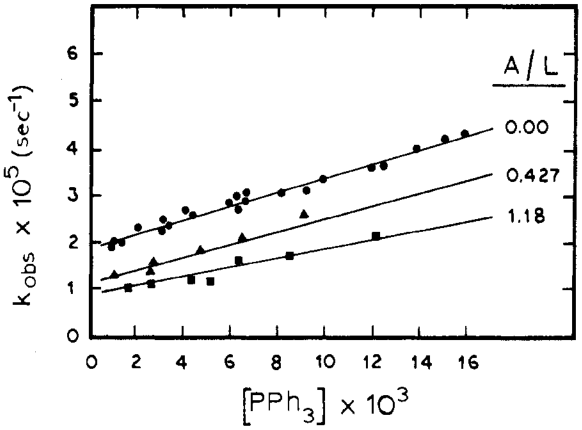

Figure 2. Variation in k_{obsd} as a function of molar ratio for reaction of $Mo(CO)_5(pip)$ with PPh_3 in hexane at 35°, in the presence of added piperidine.

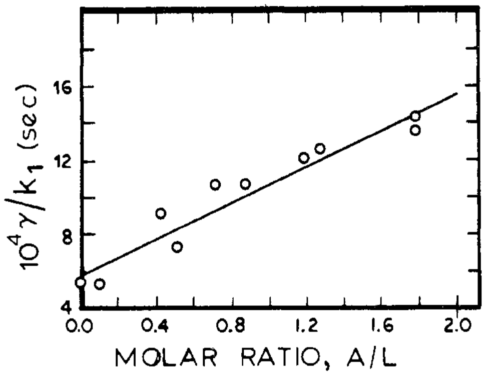

Figure 3. Inverse intercept as a function of molar ratio for reaction of $Mo(CO)_5(pip)$ with PPh_3 in hexane at 35°.

tion ratios and first-order rate constants for all three ligands are presented in Table I.

Experiments with PPh_3-$Mo(CO)_5(pip)$ were also carried out in benzene. The calculated results are included in Table I. In addition to the quantitative results reported in Table I, a series of less accurate experiments was conducted to assess the competition ratio between piperidine and CO. We observed the rate of formation of $Mo(CO)_6$ in a solution of $Mo(CO)_5(pip)$ saturated with CO gas and the effect of added piperidine in repressing the rate of formation of product. The results indicated that the competition ratio for piperidine and CO is also close to unity.

C. Leaving Group Dependence. The compounds cyclohexylamine, quinuclidine, and piperidine were chosen for the variety in their basic and steric character. The aqueous pK_a values[9] increase in the order cyclohexylamine (cha) (10.78) < quinuclidine (quin) (10.95) < piperidine (pip) (11.15). The results of gas-phase basicity studies suggest, however, that the order of gas-phase basicities in this series should follow the expected inductive order, cha < pip < quin.[10] Steric requirement is expected to increase in the same order.

Calculated first- and second-order rate constants for substitution by PPh_3 at zero molar ratio are given in Table II for cyclohexylamine and quinuclidine and in Table III for piperidine.

Table I. Competition Ratios with Piperidine and Calculated First-Order Rates for Reaction of $Mo(CO)_5(pip)$ with L in Various Solvents at 35°

L	Solvent	Competition ratio^a	10^5k_1, sec^{-1}
$P(OCH_3)_3$	Hexane	0.74 ± 0.20	1.89
PPh_3	Hexane	0.85 ± 0.24	1.71
$AsPh_3$	Hexane	1.00 ± 0.60	1.70
PPh_3	Benzene	0.48 ± 0.24	0.69

^{a} 99% confidence limits.

Table II. First- and Second-Order Rate Constants for Reaction of $Mo(CO)_5$(amine) with PPh_3 at 35° in Various Solvents

Amine	Solvent	10^5k_1,^{a} sec^{-1}	10^3k_2,^{a} M^{-1} sec^{-1}
cha	Hexane	9.92 ± 0.41	3.88 ± 0.63
	Cyclohexane	8.05 ± 0.30	2.90 ± 0.39
	Benzene	3.42 ± 0.49	0.11 ± 0.67
	1,4-Dioxane	10.45 ± 0.24	0.55 ± 1.76
quin	Hexane	0.94 ± 0.07	0.03 ± 0.01
	Cyclohexane	0.80 ± 0.14	0.01 ± 0.03
	Benzene	0.65 ± 0.07	0.00
	1,4-Dioxane	2.68 ± 0.14	0.00

^{a} 99% confidence limits

Table III. Rate Constants for PPh_3-$Mo(CO)_5(pip)$ (Various Solvents, 35°)

Solvent	10^5k_1,^{a} sec^{-1}	10^3k_2,^{a} M^{-1} sec^{-1}	ϵ^b
Hexane	1.84 ± 0.12^b	1.24 ± 0.15	1.9
Cyclohexane	1.37 ± 0.16	0.47 ± 0.03	2.0
Decalin	1.55 ± 0.27	0.37 ± 0.04	2.11^c
1,4-Dioxane	5.87 ± 0.30	0.17 ± 0.69	2.21
Benzene	0.66 ± 0.07	0.16 ± 0.11	2.27
Chlorobenzene	1.86 ± 0.11	0.06 ± 0.02	5.45
Dichloromethane	2.19 ± 0.06	0.05 ± 0.01	8.9
1,2-Dichloroethane	2.70 ± 0.32	0.07 ± 0.05	10.37
Nitromethane	6.07 ± 0.19	0.00	38.57

^{a} 99% confidence limits. ^{b} Dielectric constant at 25°, except where noted. J. A. Riddick and W. B. Bunger in "Techniques of Organic Chemistry," Vol. 2, A. Weissberger, Ed., Wiley–Interscience, New York, N. Y., 1970. ^{c} At 20°.

D. Temperature Dependence. The first- and second-order rate constants for the reaction of PPh_3 with $Mo(CO)_5A$, A = piperidine, cyclohexylamine, and quinuclidine, were observed in cyclohexane as a function of temperature in the range 25–70°. Activation energies, E_a, and preexponential factors, A, were calculated from Arrhenius plots, a typical example of which is presented in Figure 4. Calculated activation parameters are tabulated in Table IV for both the first- and second-order rate processes.

E. Reagent Ligand Dependence. The substitution rate on $Mo(CO)_5$(piperidine) was studied as a function of reagent ligand in hexane at 35°. The ligands chosen were thought to differ widely in their basic and steric character. Calculated first- and second-order rate constants are presented in Table V.

Data in Table V include an estimated second-order rate constant for $P(p\text{-}C_6H_4OCH_3)_3$ (TMP) which is insoluble in hexane. Kinetic data were gathered in 1,2-dichloroethane instead. The first-order rate constant in that solvent of (2.5 ± 0.3) × 10^{-5} sec^{-1} for TMP compares favorably with (2.7 ± 0.3) × 10^{-5} sec^{-1} observed for PPh_3 under similar conditions for reaction with $Mo(CO)_5(pip)$ at 35°. The second-order rate constant of (0.15 ± 0.11) × 10^{-3} M^{-1} sec^{-1} for TMP, however, is twofold larger than the corresponding rate constant of (0.07 ± 0.04) × 10^{-3} M^{-1} sec^{-1} for PPh_3.

An assumption that solvent effects are parallel for all L was made on the basis of a comparison of the rate constants obtained for PPh_3 and $P(OCH_3)_3$ for reaction with $Mo(CO)_5$(cha) in benzene at 35°. The first-order rate constants were

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[9] D. D. Perrin, "Dissociation Constants in Aqueous Solution," Butterworths, London, 1965.

[10] J. I. Brauman, J. M. Riveros, and L. K. Blair, *J. Amer. Chem. Soc.*, 93, 3914 (1971).

Table IV. Activation Parameters for Reaction of $Mo(CO)_5$(amine) with PPh_3 in Cyclohexane

First-Order Process

Amine	E_a,[a] kcal mol^{-1}	A, sec^{-1}	ΔH_1^*,[a] kcal mol^{-1}	ΔS_1^*,[a] eu
Quinuclidine	27.5 ± 2.8	2.9×10^{14}	26.9 ± 3.4	5.5 ± 10.7
Piperidine	26.4 ± 1.4	7.2×10^{13}	25.8 ± 3.7	2.8 ± 11.6
Cyclohexylamine	25.2 ± 2.9	5.5×10^{13}	24.5 ± 2.2	2.2 ± 7.0

Second-Order Process

Amine	E_a,[a] kcal mol^{-1}	A, l. mol^{-1} sec^{-1}	ΔH_2^*,[a] kcal mol^{-1}	ΔS_2^*,[a] eu
Quinuclidine	13.9 ± 5.8	9.2×10^{4}	13.2 ± 6.1	−38.0 ± 19.0
Piperidine	17.2 ± 8.3	7.2×10^{8}	16.5 ± 8.4	−20.1 ± 26.0
Cyclohexylamine	16.5 ± 3.4	1.5×10^{9}	15.9 ± 2.1	−18.6 ± 6.8

[a] 99% confidence limits.

Table V. Rate Constants for Reaction of $Mo(CO)_5$(pip) with Lewis Bases in Hexane at 35°

L	$10^5 k_1$, sec^{-1}	$10^3 k_2$, M^{-1} sec^{-1}
$P(p\text{-}C_6H_4OCH_3)_3$		2.5[a]
$P(OCH_2)_3CC_2H_5$	1.93 ± 0.22	2.07 ± 0.08
$P(OCH_3)_3$	1.92 ± 0.12	1.16 ± 0.10
PPh_3	1.84 ± 0.12	1.25 ± 0.08
$AsPh_3$	1.62 ± 0.20	1.34 ± 0.43
$SbPh_3$	1.43 ± 0.24	$0.38_0 \pm 0.07_8$
$P(OPh)_3$	1.76 ± 0.10	$0.15_2 \pm 0.04_1$

[a] Estimate from data taken in 1,2-dichloroethane solvent.

$(3.4 \pm 0.5) \times 10^{-5}$ and $(3.1 \pm 0.2) \times 10^{-5}$ sec^{-1}, respectively; the second-order rate constants were $(0.11 \pm 0.67) \times 10^{-3}$ and $(0.10 \pm 0.16) \times 10^{-3}$ M^{-1} sec^{-1}, respectively. Corresponding rates are equal within experimental error, just as they were found to be in hexane (Table V). Therefore, it was presumed that transfer to a different solvent does not affect the *relative* rates for the reagent ligands. Accordingly, the twofold difference found in the second-order rates for TMP and PPh_3 in 1,2-dichlorobenzene was assumed to apply in other solvents.

F. Solvent Effect. The reaction of $Mo(CO)_5$(pip) with PPh_3 was observed in various solvents at 35°. Observed first- and second-order rate constants are listed in Table III, along with solvent dielectric constants. There are two trends in the data. First-order rates increase, while second-order rates decrease, with increasing solvent dielectric constant.

Discussion

Few attempts have been made to measure the selectivity of the coordinatively unsaturated intermediate produced by dissociation of CO or other ligand from a metal carbonyl or substituted metal carbonyl. Day, Basolo, and Pearson reported[11] that the presumed $Ni(CO)_3$ intermediate reacts about 5 times faster with PPh_3 than with CO in a competitive situation. Cardaci and Narciso recently measured the competition between CO and various olefins $CH_2{=}CHX$ for the $Fe(CO)_4$ intermediate[12] and found that reaction with CO is faster by factors ranging from about 2 to perhaps 5. Hyde and Darensbourg[13] recently evaluated the selectivity of a substituted species $Mo(CO)_4PPh_3$ toward amine, phosphine, and CO and found competition ratios between 0.7 and 3. In the present work we have made an accurate evaluation of the relative rates of recombination of ligands with $Mo(CO)_5$, taking full account of the presence of a concurrent second-order process. The results, listed in Table I, represent the rates of recombination of each of the ligands listed with $Mo(CO)_5$, *as compared with piperidine.*

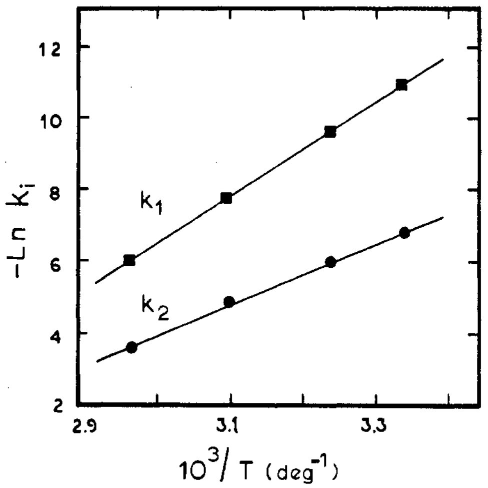

Figure 4. Arrhenius plot for reaction of $Mo(CO)_5$(cha) with PPh_3 in cyclohexane.

The ligands involved represent a fairly wide range of nucleophilicity in terms of kinetic stability once bonded to $Mo(CO)_5$ and differ significantly in steric requirements. Unfortunately, it is not feasible to obtain calorimetric data for the reaction $Mo(CO)_5 + L \rightarrow Mo(CO)_5L$, which would provide some indication of the relative strengths of the metal-ligand bonds for various L. It is known, however, that ligands such as phosphites and phosphines dissociate very much more slowly from $Mo(CO)_5L$ than do amines. Indeed, L in these systems is kinetically more stable than CO. Attempts to measure the equilibrium constant for the reaction

$$Mo(CO)_5L + \text{amine} \rightleftarrows Mo(CO)_5(\text{amine}) + L$$

failed. Solutions with amine/L ratios of up to 10^3 showed only $Mo(CO)_5L$ after standing for several days. It thus appears reasonable to assume that the enthalpy content associated with the metal-saturated amine bond is less than for the P- and As-containing ligands used in the competition studies.

The fact that the intermediate combines with all the ligands at about the same rate suggests that the recombination reaction is an exothermic, associative process with small activation energy. On the basis of arguments analogous to those of Hammond,[14] if the transition state in the recombination of $Mo(CO)_5$ with a ligand involved a considerable amount of bond formation, the transition state would be expected to possess some of the properties of the product molecule. In particular, it would be expected that for different L, with different stabilities for the ground-state $Mo(CO)_5L$ mole-

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(11) J. P. Day, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, 90, 6927 (1968).

(12) G. Cardaci and V. Narciso, *J. Chem. Soc., Chem. Commun.*, 2289 (1972).

(13) C. Hyde and D. J. Darensbourg, *Inorg. Chem.*, 12, 1286 (1973).

(14) G. S. Hammond, *J. Amer. Chem. Soc.*, 77, 334 (1955).

cules, the transition states would possess different free energies, in proportion to the importance of bond making in the transition state. But since the transition states for recombination of different L with $Mo(CO)_5$ differ negligibly in free energy content, relative to separated L and $Mo(CO)_5$, it is reasonable to conclude that $\Delta G^{\ddagger}$ for the reaction $Mo(CO)_5 + L \rightarrow Mo(CO)_5L$ is small. From the principle of microscopic reversibility it follows that the transition state in the dissociative process involving loss of ligand, be it, *e.g.*, CO from $Mo(CO)_6$ or amine from $Mo(CO)_5$(amine), involves essentially complete rupture of the metal–ligand bond.

The dependence of the substitution rate on the nature of the leaving amine group is illustrated by the data in Tables II and III. The first-order constants might be expected to decrease with increasing amine basicity. They do in fact decrease in the order cyclohexylamine > piperidine > quinuclidine, *i.e.*, primary > secondary > tertiary amine. It is noteworthy, however, that k_1 changes over a factor of only 10 in this series. The enthalpies of activation (Table IV) exhibit a small variation in the expected direction which is probably significant, considering that the confidence limits stated are 99%.

The second-order rate constants are considerably more sensitive to the amine. Despite the large uncertainties, the variation in $\Delta S_2^{\ddagger}$ for the three amines is at least sufficiently large to suggest that this quantity is most negative for the sterically most hindered amine. It follows, not unexpectedly, that the steric requirements of the leaving group are of importance in the second-order process. The $\Delta H_2^{\ddagger}$ values vary over about the same range as for the first-order process, but the $\Delta S_2^{\ddagger}$ variation is considerable. The uncertainties in $\Delta H_2^{\ddagger}$ are too large for the differences between the amines to be of significance. It is evident, however, that $\Delta H_2^{\ddagger}$ is significantly lower than $\Delta H_1^{\ddagger}$. These results are consistent with a second-order process which may be characterized as an interchange. It should be noted that the degree to which the results specify the transition state is considerably greater than is the case in the more common instance of transition metal complexes in coordinating solvents. Since the reaction under study is carried out in hexane, no significant *energetic* role can be assigned to solvent. The implication of the present results is thus that the entering ligand participates in formation of the transition state, *i.e.*, the entering ligand must play a sufficient role in the interchange process to alter the activation parameters considerably. It is still not clear, however, from the energetics alone, how sensitive the interchange process should be to the nature of the entering ligand. The data relevant to this question are given in Table V.

These results show that the rate of the second-order process is not very sensitive at all to the nature of the entering ligand. A comparison of the present results with those obtained by Thorsteinson and Basolo[15] for displacement of CO on $CoNO(CO)_3$ shows remarkable similarities. The second-order rate constants for reactions with PPh_3 are not greatly different (the reactions with $CoNO(CO)_3$ were studied in toluene as solvent). Furthermore, the $\Delta H_2^{\ddagger}$ and $\Delta S_2^{\ddagger}$ values obtained are closely similar. On the other hand, the first-order dissociative process involving loss of CO from $CoNO(CO)_3$ is at least 3 orders of magnitude slower than loss of amine from $Mo(CO)_5$(amine); the $\Delta H_1^{\ddagger}$ are 30 and ~26 kcal/mol, respectively.

Since solvent cannot be considered important in determining the energetics of the interchange process, it follows that the lower value of $\Delta H_2^{\ddagger}$ as compared with $\Delta H_1^{\ddagger}$ is due to the influence of entering ligand. But the difference of about 10 kcal/mol between $\Delta H_1^{\ddagger}$ and $\Delta H_2^{\ddagger}$ may be due in large part to residual bonding between metal and departing ligand. Of course, there are other terms due to steric repulsion, etc. The point, however, is that there need be only about 5 kcal/mol or so of bond formation with entering ligand to produce the observed value of $\Delta H_2^{\ddagger}$. In the $CoNO(CO)_3$ system, in which the difference between $\Delta H_1^{\ddagger}$ and $\Delta H_2^{\ddagger}$ is larger, bond making is undoubtedly more important.

Table VI. Relative Rates of Substitution *via* Bimolecular Pathway for $Mo(CO)_5(pip)^a$ and $CoNO(CO)_3{}^b$

Ligand	k_2[$Mo(CO)_5$(pip)]	k_2[$CoNO(CO)_3$]	Ligand cone angle,[c] deg
$P(C_6H_5)_3$	1.0	1.0	145
$P(p\text{-}C_6H_4OCH_3)_3$	2.0	3.0[d]	145
$P(OCH_2)_3CC_2H_5$	1.7	0.65	101
$P(OCH_3)_3$	0.93	1.8	107
$P(OC_6H_5)_3$	0.12	0.034	121
$As(C_6H_5)_3$	1.1	0.002	
$Sb(C_6H_5)_3$	0.3		

[a] Present work. [b] E. M. Thorsteinson and F. Basolo, *Inorg. Chem.*, 5, 1691 (1966). [c] C. A. Tolman, *J. Amer. Chem. Soc.*, 92, 2956 (1970). [d] Based on rates relative to that of $P(C_6H_5)_3$ in CH_3NO_2.

It is of interest to compare the relative rates of the bimolecular process for a series of ligands reacting with $Mo(CO)_5$(amine) as compared with $CoNO(CO)_3$. This is done in Table VI, in which the rates under roughly comparable conditions are compared. In each case the relative rates are listed, with the rate for PPh_3 set at 1. It is evident that the cobalt system is more sensitive to the nature of the entering ligand than $Mo(CO)_5$(pip). It is rather surprising that the steric requirements of the entering ligand, as measured, for example, by the "cone angle,"[16] appear to play such a minor role in determining the relative reactivities of the ligands toward the six-coordinate complex. A similar lack of sensitivity was noted by Ingemanson and Angelici[4] in the bimolecular process for substitution at $W(CO)_5$(amine) complexes.

The results just discussed suggest that bond making does indeed play a minor role in the second-order process for $Mo(CO)_5$(amine) compounds and that most of the difference in $\Delta H_1^{\ddagger}$ and $\Delta H_2^{\ddagger}$ is due to differing degrees of bond breaking in the bond to the departing ligand. This conclusion is supported to some degree by the solvent effect data in Table III, which shows the effect of solvent change on the rates of both the dissociative and interchange processes.[17] Increasing solvent polarity causes a slight increase in the rate of the dissociative process, but appears effectively to quench the bimolecular path. If the interchange mechanism is to operate, the entering ligand must be in position to replace the departing ligand. It may be that with increasing solvent polarity, solvation of the individual reactant species is sufficient to diminish substantially the occurrence of reactants within the same solvent cage.

We conclude that the observed kinetics for amine substitution in $Mo(CO)_5$(amine) are best accounted for in terms of concurrent dissociative (D) and dissociative interchange (I_d) mechanistic pathways. Furthermore, we believe that the conclusion is probably applicable as well to all instances of substitution at metal carbonyl centers in which there is a dis-

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(15) E. M. Thorsteinson and F. Basolo, *Inorg. Chem.*, 5, 1691 (1966).

(16) C. A. Tolman, *J. Amer. Chem. Soc.*, 92, 2956 (1970).

(17) Both the k_1 and k_2 results for dioxane are subject to considerable uncertainty, because the solvent itself, which is a relatively much stronger base than any of the other solvents employed, is capable of reacting with starting material to produce a product which could persist for some time before itself undergoing substitution by PPh_3.

tribution of 18 valence electrons about the metal, where the reaction center may be properly thought to be the metal itself and where ligand rearrangements leading to a decrease in the effective valence electron number at the metal are absent.[18,19]

Experimental Section

Starting materials and spectral grade solvents were obtained from commercial sources. Each was purified by chemical or physical means, or both, according to procedures given in the standard literature. Solvents were stored in amber bottles over appropriate drying agents after deaeration by boiling and saturation with nitrogen.

Monosubstituted molybdenum carbonyl complexes were prepared from $Mo(CO)_6$ and the appropriate ligand, L, by either a thermal or a photochemical method.[3]

The thermal reactions were carried out in a 50-ml, 1-necked, round-bottom Bantam-ware flask equipped with an 8-in. coil condenser. The flask was flushed with nitrogen before addition of reactants and solvent (usually 1,4-dioxane, rendered peroxide free by distillation from tin(II) chloride); otherwise no particular precautions were taken to exclude oxygen. The reaction mixtures were heated to solvent reflux temperatures and stirred. Overhead fluorescent light was excluded by wrapping the apparatus with opaque paper or aluminum foil. Reaction times were 1–4 hr, determined by the appearance of turbidity in the reaction mixture.

The work-up procedures were identical for both synthetic methods. Reaction mixtures were allowed to cool to ambient temperature, if necessary. Solvent was then removed under vacuum in a rotary flash evaporator. Unreacted hexacarbonyl was removed by vacuum sublimation. Crude solid products were purified by recrystallization from either hexane or an equal mixture of ethanol and trichloromethane at Dry Ice–acetone slush temperature. Recrystallized material was finally dried under vacuum overnight.

The amine complexes are somewhat air sensitive and thermally unstable and were therefore stored in a desiccator at low temperature. The identity and purity of the complexes were mainly established from elemental analyses and ir spectra in the carbonyl stretching region, 1900–2000 cm^{-1}. The amine complexes were bright yellow crystals. The complexes with group V ligands were white crystalline powders.

A. Compounds Prepared *via* Thermal Reaction. *Anal.* Calcd for $Mo(CO)_5$(pip), $C_{10}H_{11}O_5NMo$: C, 37.45; H, 3.46; N, 4.37. Found: C, 37.60; H, 3.43; N, 4.44. Ir bands (hexane): 2073, 1944, 1923 cm^{-1}. Lit.[20] (hexane): 2075, 1941, 1922 cm^{-1}.

Anal. Calcd for $Mo(CO)_5$(cha), $C_{11}H_{13}O_5NMo$: C, 39.41; H, 3.95. Found: C, 39.42; H, 3.95. Ir bands (hexane): 2075, 1939, 1919 cm^{-1}. Lit.[3] (hexane): 2075, 1940, 1920 cm^{-1}.

Anal. Calcd for $Mo(CO)_5(PPh_3)$, $C_{23}H_{15}O_5PMo$: C, 55.48; H, 3.08. Found: C, 55.83; H, 3.07. Ir bands (hexane): 2075, 1989, 1950 (b) cm^{-1}. Lit.[20] (hexane): 2075, 1989, 1952, 1945 cm^{-1}.

Anal. Calcd for $Mo(CO)_5(AsPh_3)$, $C_{23}H_{15}O_5AsMo$: C, 50.98; H, 2.80. Found: C, 50.48; H, 2.72. Ir bands (hexane): 2075, 1989, 1950 (b) cm^{-1}. Lit.[20] (hexane): 2076, 1989, 1952, 1945 cm^{-1}.

Anal. Calcd for $Mo(CO)_5(SbPh_3)$, $C_{23}H_{15}O_5SbMo$: C, 46.90; H, 2.57. Found: C, 45.99; H, 2.44. Ir bands (hexane): 2075, 1955 cm^{-1}. Lit.[20] (hexane): 2075, 1955 cm^{-1}.

Anal. Calcd for $Mo(CO)_5$(1-ethyl-3,5,8-trioxa-4-phosphabicyclo[2.2.2]octane), $C_{11}H_{11}O_8PMo$: C, 33.18; H, 2.79. Found: C, 32.31; H, 2.78. Ir bands (hexane): 2086, 1972 (sh), 1966 cm^{-1}. Lit.[21] (hexane): 2081, 1972, 1966 cm^{-1}.

Anal. Calcd for $Mo(CO)_5P(OPh)_3$, $C_{23}H_{15}O_8PMo$: C, 50.56; H, 2.77. Found: C, 50.67; H, 3.18. Ir bands (hexane): 2094, 2001, 1966 (b) cm^{-1}. Lit.[22] (hexane): 2095, 2000, 1972, 1967 cm^{-1}.

Anal. Calcd for $Mo(CO)_5(P(p\text{-}C_6H_4OCH_3)_3)$, $C_{26}H_{21}O_8PMo$: C, 53.15; H, 3.50. Found: C, 53.35; H, 3.79. Ir bands (hexane): 2071, 1986, 1948, 1943 (sh) cm^{-1}.

B. Compounds Prepared Photolytically: $Mo(CO)_5$(pip) has the values as mentioned above.

Anal. Calcd for $Mo(CO)_5$(quin), $C_{12}H_{13}O_5NMo$: C, 41.51; H, 3.78; N, 4.04. Found: C, 41.91; H, 3.84; N, 4.10. Ir bands (hexane): 2072, 1937, 1919 cm^{-1}. Lit.[23] (cyclohexane): 2067, 1925, 1901 cm^{-1}.

C. Sample Preparation. Solid materials were usually weighed by difference on a precision torque balance (±0.01 mg), No. 5821, Vereenigde Draadfabrieken, Nijmegen, Holland. Samples larger than 10 mg were weighed by difference on an analytical balance (±0.10 mg). Overhead fluorescent light was excluded from sample solution flasks by wrapping them in aluminum foil.

Sample concentrations were generally $10^{-4}\,M$ in carbonyl complex and up to $10^{-2}\,M$ in reagent ligand. Ligand was always present in at least eightfold excess. Spectral measurements were begun as soon as possible after complete dissolution of reactants and after thermal equilibration of the test solutions, usually within 8 min.

D. Instrumentation. Infrared spectral measurements were made on a Beckman IR-7 spectrophotometer, frequency calibrated using water vapor. The spectral width of the instrument was set as an average of 0.7 cm^{-1}. Recording was at a rate of 20 cm^{-1}/min, and 1 cm of paper corresponded to 9.8 cm^{-1} in the 1900–2000-cm^{-1} region. Calibrated 1-mm cells with potassium bromide windows were employed in all measurements.

Ultraviolet–visible spectral measurements were made on a Cary 14 recording spectrophotometer. A matched pair of cylindrical, 1-cm quartz cells (Fisher Supracil, 3.1-ml volume) with Teflon stoppers were used to contain reaction samples and solvent blanks.

Temperature of the sample cell was kept constant by means of a close-fitting brass block mounted in the Cary 14 sample cell compartment. The brass block temperature was maintained by constant flow of thermostated water through internal holes and measured by means of a copper–constantan thermocouple (±0.1°). The block was partially filled with deaerated, deionized water to effect good thermal contact between walls of the brass block and the sample cell. Four minutes was usually allowed for thermal equilibration of each sample.

E. Kinetic Measurements. The substitution reactions were quantitatively followed by observing disappearance of the characteristic band at about 390–400 nm in the visible spectrum. The peak was usually monitored for 32 time intervals of usually 240 sec each or until the absorbance reading was 10% lower than the initially observed value, whichever occurred first.

The λ_{max} of each $Mo(CO)_5$(amine) complex was taken to be the average of at least three tracings over the range 380–410 nm. The absorbance at λ_{max} was continuously monitored as a function of time.

Linear pseudo-first-order plots of $-\ln(A_t - A_\infty)$, where A_t is the absorbance at time t and A_∞ is the absorbance at infinite time, *vs.* time were obtained. Values of A_∞ were taken from Beer's law plots made with synthesized products. At least one sample from each reaction studied was allowed to stand until t_∞ had apparently been reached (usually 8 days) to ensure each reaction was complete, *i.e.*, did not come to a detectable equilibrium state at t_∞. The slopes of the pseudo-first-order plots, k_{obsd}, were calculated and then plotted as a function of added free ligand. The slope of the latter graph is k_2 and the intercept is k_1 of eq 1.

All data were subjected to a least-squares linear fit. Multiple correlation coefficients and 99% confidence limits were also calculated.

Registry No. $Mo(CO)_5$(pip), 19456-57-6; $P(OCH_3)_3$, 121-45-9; PPh_3, 603-35-0; $AsPh_3$, 603-32-7; $Mo(CO)_5$(cha), 21199-57-5; $Mo(CO)_5$(quin), 21615-88-3; $P(p\text{-}C_6H_4OCH_3)_3$, 885-38-9; $P(OCH_2)_3\text{-}CC_2H_5$, 824-11-3; $SbPh_3$, 603-36-1; $P(OPh)_3$, 101-02-0.

Supplementary Material Available. Tables of all rate observations will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-73-2820.

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(18) C. A. Tolman, *Chem. Soc. Rev.*, 1, 337 (1972).

(19) An apparent exception to this rule might occur when there is available to the incoming ligand a virtual orbital in the substrate reactant which lies at exceptionally low energy. This might be the case when one or more ligands possess low-lying virtual orbitals which might serve as a focal point for ligand attack, with subsequent rearrangements leading eventually to substitution.

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