empirically that other parameters, such as σ^* which is nearly the same for bromine and chlorine,[23] may be more reliable guides to polar effects in quadrupole coupling. Good correlations of σ^* with tin Mossbauer splittings have been claimed.[24]

[23] R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, Chapter 13.

Registry No. $HgCl_2$(diox), 27104-48-9; $HgCl_2(diox)_2$, 39152-02-8; $HgCl_2$(dione), 39152-03-9; $HgBr_2$(diox), 28630-99-1; $HgBr_2(diox)_2$, 39152-05-1; HgI_2(diox), 28631-00-7.

[24] (a) R. V. Parish and R. H. Platt, *Inorg. Chim. Acta*, **4**, 65 (1970); (b) R. V. Parish and R. H. Platt, *J. Chem. Soc. A*, 2145 (1969).

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Kinetic Studies of Thermal Decomposition and Substitution Reactions of *cis*-$Mo(CO)_4[P(C_6H_5)_3]$(amine) Compounds. A Competitive Study of Lewis Bases for the Intermediate $[Mo(CO)_4P(C_6H_5)_3]$

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Kinetic and mechanistic studies of thermal decomposition and substitution reactions of *cis*-$Mo(CO)_4[P(C_6H_5)_3]$(amine) (where amine = NHC_5H_{10} or NC_5H_5) are reported. Substitution reactions have been carried out for a variety of entering ligands (L) to form *cis*-$Mo(CO)_4[P(C_6H_5)_3]L$ compounds. These substitution reactions proceed *via* the rate expression: rate = $k[Mo(CO)_4[P(C_6H_5)_3](amine)]$, at low concentrations of L. When L is a strongly nucleophilic ligand and is employed at high concentrations, a second-order term must be added to give a rate expression of the form: rate = $[k + k'[L]][Mo(CO)_4[P(C_6H_5)_3](amine)]$. Competitive reactions for the intermediate $[Mo(CO)_4P(C_6H_5)_3]$ have been investigated for a number of ligands (L) including carbon monoxide, phosphines, and amines. There are only slight differences in the rate constants for the reactions of the $[Mo(CO)_4P(C_6H_5)_3]$ intermediate with various ligands L. Substitution equilibria are however dependent on the nature of L. Steric factors have been shown to be important in these substitution reactions; *e.g.*, for the sterically bulky ligand L = (*o*-tolyl)$_3$P no substitution product is observed.

Introduction

Previously we have reported upon the kinetics of thermal decomposition and substitution reactions of $M(CO)_5$(amine) compounds of group VIb metals.[2] In order to study the role of electronic and steric factors in these types of reactions we have examined the kinetics and mechanism of thermal decomposition reactions of *cis*-$Mo(CO)_4[P(C_6H_5)_3]$(amine) (where amine = NHC_5H_{10} or NC_5H_5) to form $Mo(CO)_5P(C_6H_5)_3$ and *cis*-$Mo(CO)_4[P(C_6H_5)_3]_2$. This reaction proceeds by a rate-determining step involving dissociation of the amine ligand which is first order in starting complex and produces $Mo(CO)_5P(C_6H_5)_3$, *cis*-$Mo(CO)_4[P(C_6H_5)_3]_2$, and insoluble solids as products.

In the presence of Lewis bases L, such as amines, phosphines, phosphites, arsines, and carbon monoxide, the intermediate $[Mo(CO)_4P(C_6H_5)_3]$ species is trapped in the form of *cis*-$Mo(CO)_4[P(C_6H_5)_3]L$ complexes. This substitution can also proceed by an SN2 mechanism (step 3 in eq 1).

Competitive studies employing a variety of group Va ligands, as well as carbon monoxide, were investigated in order to determine the reactivity of the $[Mo(CO)_4P(C_6H_5)_3]$ species toward the different Lewis bases.

The experimental results indicate that the steric properties of the incoming L group are very important. For example,

$$\begin{tikzcd}
cis\text{-}Mo(CO)_4[P(C_6H_5)_3](NHC_5H_{10}) \arrow[r, shift left, "k_1"] \arrow[d, "L", "k_3"'] & {[Mo(CO)_4P(C_6H_5)_3] + NHC_5H_{10}} \arrow[l, shift left, "k_{-1}"] \arrow[dl, "\text{fast}", "L"', "k_2" near end] \\
cis\text{-}Mo(CO)_4[P(C_6H_5)_3]L &
\end{tikzcd} \qquad (1)$$

no substitution was observed when L = $P(o\text{-}CH_3C_6H_4)_3$, even with a very large excess of the organophosphorus ligand present. In addition the intermediate $[Mo(CO)_4P(C_6H_5)_3]$ appears to have a slightly greater affinity toward a softer nucleophilic reagent.

Experimental Section

Materials. Molybdenum hexacarbonyl was the generous gift of Climax Molybdenum Co. and was used without further purification. The tertiary phosphite 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]-octane was donated by Arapahoe Chemicals, Boulder, Colo., and was sublimed before use. ^{13}CO was purchased from Monsanto Research Corp., Miamisburg, Ohio. Tetrahydrofuran (THF) was distilled over lithium aluminum hydride just before use. Diglyme (bis(2-methoxyethyl) ether) was refluxed over sodium and then distilled. Piperidine was purified by vacuum distillation. Triphenylarsine and triphenylstibene were recrystallized from chloroform-methanol.

Preparation of *cis*-$Mo(CO)_4[P(C_6H_5)_3]$(amine) (amine = NHC_5H_{10} or NC_5H_5). The disubstituted molybdenum tetracarbonyl species were prepared photochemically in THF from $Mo(CO)_5P(C_6H_5)_3$ and the corresponding amines by the procedure previously described.[3] The products were purified by recrystallization from chloroform-methanol.

Spectral and Kinetic Measurements. All spectral measurements were recorded in *n*-hexane solvent. Infrared spectra (2100–1830 cm^{-1}) were obtained employing a Perkin-Elmer 521 grating spectro-

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[2] (a) D. J. Darensbourg, M. Y. Darensbourg, and R. J. Dennenberg, *J. Amer. Chem. Soc.*, **93**, 2807 (1971); (b) R. J. Dennenberg and D. J. Darensbourg, *Inorg. Chem.*, **11**, 72 (1972).

Table I. Infrared Spectra in the Carbonyl Stretching Region for *cis*-$Mo(CO)_4[P(C_6H_5)_3]L$ Compounds[a]

L	$A_1^{(2)}$	$A_1^{(1)}$	B_1	B_2
NHC_5H_{10}	2016	1908	1895	1865
NC_5H_5	2017	1909	1896	1872
$P(C_6H_5)_3$	2021	1926	1908	1897 sh
$As(C_6H_5)_3$	2022	1927	1910	1897 sh
$Sb(C_6H_5)_3$	2023	1929	1909	1902
$P(n\text{-}C_4H_9)_3$	2017	1915	1899	1889 sh
$P(OCH_2)_3CC_2H_5$	2036	1940	1923	1907
$P(C_6H_{11})_3$	2008	1905	1888	1879 sh

[a] Frequencies are listed in cm^{-1} and were determined in hexane solution; sh = shoulder.

Table II. Carbonyl Stretching Frequency Data for $Mo(CO)_5P(C_6H_5)_3$

Molecule	Vibration	Freq, cm^{-1} Input	Freq, cm^{-1} Calcd	Freq, cm^{-1} Obsd
All ^{12}CO species (C_{4v})	A_1	2073.8	2072.6	2073.8
	B_1	1985.0	1987.4	1985.0
	E	1947.0	1950.4	1947.0
	A_1		1945.4	
Monosubstituted ^{13}CO, equatorially (C_s)	A′	2064.8	2064.6	2064.8
	A′		1980.6	
	A′		1945.7	
	A″		1950.4	
	A′	1918.0	1920.7	1918.0[a]
Monosubstituted ^{13}CO, axially (C_{4v})	A_1		2069.9	
	B_1		1987.4	
	E		1950.4	
	A_1	1907.0	1904.6	1907.0[a] w, sh

[a] These frequencies are accurate to ± 2 cm^{-1} due to broadness and overlap problems; all others are accurate to ± 0.5 cm^{-1}. The average error in the calculated frequencies was 2.0 cm^{-1} or 0.104%.

photometer equipped with a linear absorbance potentiometer and an automatic scan recycle. The instrument was calibrated in the CO stretching region with CO vapor above 2000 cm^{-1} and with H_2O vapor below 2000 cm^{-1}. Sample concentrations were in the range 10^{-3} to 10^{-4} *M*. Linear Beer's law plots were obtained. One-millimeter sodium chloride cells were used. The sample cell was fitted with a Beckman water jacket. The temperature of the jacket was maintained by a water-circulating bath with a constant-temperature control of ±0.1°. Temperature was determined by carefully calibrating the cell's internal temperature with that of the water bath. A copper-constantan thermocouple was used for this purpose. The rates of decomposition and substitution reactions of the *cis*-$Mo(CO)_4[P(C_6H_5)_3]$(amine) complexes were followed by observing the decrease in the absorbance of the B_2 carbonyl stretching mode (lowest energy band) with time. The carbonyl stretching frequencies for reactants and products are shown in Tables I and II. The cis-disubstituted molybdenum tetracarbonyl compounds are ideally of C_{2v} symmetry. As such there are four allowed carbonyl stretching modes. These are assigned to the 2 A_1, B_1, and B_2 symmetry representations. The B_1, B_2, and one A_1 modes overlap to varying degrees depending on the substituted ligands and solvent. For most cases, in a nonpolar solvent such as hexane, the overlap is minimized.

Spectra observed in the visible region were recorded on a Cary 14R spectrophotometer. Matching 1-cm quartz cells were used. The temperature was maintained by means of a close-fitting brass block mounted in the cell compartment through which water was circulated from a constant-temperature bath. The concentration ranges required were between 10^{-4} and 10^{-5} *M*. The rates of decomposition of the *cis*-$Mo(CO)_4[P(C_6H_5)_3]$(amine) complexes were followed by observing the decrease in the absorbance of their respective visible absorption bands with time (amine = NHC_5H_{10}, 4010 Å; amine = NC_5H_5, 3950 Å).

Rate constants were calculated using a linear least-squares computer program for the first-order rate plots of ln $(A_t - A_\infty)$ *vs.* time, where A_t is the absorbance at time *t* and A_∞ is the absorbance at infinite time.

Competition studies for the $[Mo(CO)_4P(C_6H_5)_3]$ intermediate were monitored by the infrared spectral changes in the starting materials *cis*-$Mo(CO)_4[P(C_6H_5)_3]$(amine). Hexane solutions of known concentrations of amine and another Lewis base (L) were prepared where amine = NC_5H_5 or NHC_5H_{10} and L = $P(C_6H_5)_3$, $As(C_6H_5)_3$, $Sb(C_6H_5)_3$, $P(OCH_2)_3CC_2H_5$, $P(n\text{-}C_4H_9)_3$, or $P(C_6H_{11})_3$. The molar ratios of amine to L were changed from values of 0 to 6 with the notable exception of $[NHC_5H_{10}]/[As(C_6H_5)_3]$. For the latter study, a second equilibrium process occurs at molar ratios greater than 0.5. The rates of substitution of $Mo(CO)_4[P(C_6H_5)_3]$(amine) in the presence of the added ligands were determined as described previously. Plots of $1/k_{\text{obsd}}$ *vs.* [amine]/[L] were found to be linear.

Over the concentration range employed in these studies, for L = $P(OCH_2)_3CC_2H_5$ and $P(n\text{-}C_4H_9)_3$, the reaction of $Mo(CO)_4[P(C_6H_5)_3](NHC_5H_{10})$ to form $Mo(CO)_4[P(C_6H_5)_3]L$ may proceed *via* an associative (SN2) route as well as the dissociative pathway (eq 1). Hexane solutions of known concentrations of these L compounds were prepared and the rate of substitution was determined as a function of the L concentration. Plots of k'_{obsd} *vs.* [L] were linear with intercepts of k_1.

Reactions in the presence of carbon monoxide gas and the competition between NHC_5H_{10} and CO and $P(C_6H_5)_3$ and CO were also investigated. Hexane solutions of known piperidine or triphenylphosphine concentration were prepared and 25-ml aliquots of these solutions were pipetted into a constant-temperature reaction vessel. The reaction vessel was equipped with an internal condenser, rubber adapter for removal of samples during the reaction, and a CO gas inlet. The CO gas was first bubbled through a volume of hexane before going into the reaction solution. Unreacted CO gas was destroyed through oxidation to CO_2 with $KMnO_4$. The temperature was maintained at 28°; CO gas was bubbled into the solution throughout the reaction period and the solution was constantly stirred.

The CO gas was allowed to bubble into the solution of L in hexane for 20–30 min in order to reach saturation prior to the addition of the *cis*-$Mo(CO)_4[P(C_6H_5)_3](NHC_5H_{10})$ complex. Samples were removed periodically and the infrared spectra recorded. The concentration of CO gas was considered to be constant throughout the course of the reaction and was determined by assuming ideal gas behavior and saturation of the CO gas at 1 atm total pressure.

The plot of $1/k_{\text{obsd}}$ *vs.* $[NHC_5H_{10}]/[CO]$ was again found to be linear. For the case of added $P(C_6H_5)_3$ and CO, since both products *cis*-$Mo(CO)_4[P(C_6H_5)_3]_2$ and $Mo(CO)_5P(C_6H_5)_3$ are thermodynamically stable at the reaction conditions, only initial and final spectra were necessary to determine the relative competition of $P(C_6H_5)_3$ and CO for the intermediate $[Mo(CO)_4P(C_6H_5)_3]$. This was indeed verified by the observation that the ratio of products at various times during the substitution reaction was a constant. The final concentrations of CO- and $P(C_6H_5)_3$-substituted products were determined from Beer's law plots. The molar concentration ratio $[Mo(CO)_4[P(C_6H_5)_3]_2]/[Mo(CO)_5P(C_6H_5)_3]$ was determined for a series of $[P(C_6H_5)_3]/[CO]$ ratios and a linear plot of $[Mo(CO)_4[P(C_6H_5)_3]_2]/[Mo(CO)_5P(C_6H_5)_3]$ *vs.* $[P(C_6H_5)_3]/[CO]$ was obtained.

Calculations. Machine calculations were performed on a CDC 6400 at the State University of New York at Buffalo Computing Center. The frequencies necessary in assigning the ^{13}CO absorptions were calculated as previously described.[3]

Results and Discussion

The rate of decomposition of *cis*-$Mo(CO)_4[P(C_6H_5)_3]$(amine) complexes follows the first-order rate law

$$\text{rate} = k_1[Mo(CO)_4[P(C_6H_5)_3](\text{amine})] \tag{2}$$

Values of the rate constants k_1, calculated from the first-order rate expression, are given in Table III for several temperatures. The activation parameters for this dissociation process (eq 3) are reported in Table IV.

$$\begin{array}{c} cis\text{-}Mo(CO)_4[P(C_6H_5)_3](\text{amine}) \underset{k_{-1}}{\overset{\text{slow}}{\underset{}{\overset{k_1}{\rightleftarrows}}}} \\ [Mo(CO)_4P(C_6H_5)_3] + \text{amine} \\ \Big\downarrow P(C_6H_5)_3 \text{ or CO} \\ Mo(CO)_5P(C_6H_5)_3 + cis\text{-}Mo(CO)_4[P(C_6H_5)_3]_2 \end{array} \tag{3}$$

The decomposition products, $Mo(CO)_5P(C_6H_5)_3$ and *cis*-$Mo(CO)_4[P(C_6H_5)_3]_2$, result from combination of the reactive species, $[Mo(CO)_4P(C_6H_5)_3]$, with free CO or $P(C_6H_5)_3$ produced in solution by the breakdown of the unstable $[Mo(CO)_4P(C_6H_5)_3]$ moiety. The production of these prod-

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(3) G. Schwenzer, M. Y. Darensbourg, and D. J. Darensbourg, *Inorg. Chem.*, 11, 1967 (1972).

Table III. First-Order Rates Constants for the Dissociation of *cis*-$Mo(CO)_4[P(C_6H_5)_3]$(amine) Complexes in Hexane

Amine = NHC_5H_{10}		Amine = NC_5H_5	
Temp, °C	10^4k_1, sec^{-1}	Temp, °C	10^4k_1, sec^{-1}
26.8	7.9	25.7	5.8
31.3	14.2	36.5[a]	21.5
36.5[a]	30.7	38.6	27.2
40.3	51.4	40.0	41.8

[a] This rate constant was obtained by interpolation of the data.

Table IV. Activation Parameters for the *cis*-$Mo(CO)_4[P(C_6H_5)_3]$-(amine) Dissociative Process in Hexane Solution

Amine	$\Delta H_1{}^*$,[a] kcal/mol	$\Delta S_1{}^*$,[a] eu
NHC_5H_{10}	25.9 ± 1.2	13.6 ± 3.9
NC_5H_5	22.1 ± 2.3	0.58 ± 7.65

[a] These errors represent standard deviations—95% confidence level.

ucts therefore exhibits an initiation period. This reaction results in formation of 39 ± 5% of *cis*-$Mo(CO)_4[P(C_6H_5)_3]_2$ and 18 ± 4% of $Mo(CO)_5P(C_6H_5)_3$ in addition to a metal-containing precipitate.

There was some concern that the range over which the concentration of *cis*-$Mo(CO)_4[P(C_6H_5)_3]$(amine) was varied was too narrow. Therefore, the reaction with the piperidine derivative was studied by monitoring the visible spectral changes in which the concentration range could be decreased by a factor of 10 beyond that employed for the infrared measurements. The rate constant (k_1) was observed to be 33.8×10^{-4} sec^{-1} at 37.2° by this technique. This result is in excellent agreement with the value of 34.2×10^{-4} sec^{-1} determined by interpolation of the infrared data.

In the presence of Lewis bases (L), substitution reactions lead to products of the form *cis*-$Mo(CO)_4[P(C_6H_5)_3]L$.

The following rate law summarizes the scheme shown in eq 1

$$\text{rate} = [k_1 + k_3[\text{L}]][\text{Mo(CO)}_4[\text{P(C}_6\text{H}_5)_3](\text{amine})] \qquad (4)$$

In the concentration ranges studied, only the ligands $P(OCH_2)_3CC_2H_5$ and $P(n\text{-}C_4H_9)_3$ showed a k_3 term resulting from the SN2 (associative) reaction. For the other ligands (L), 100% formation of the *cis*-$Mo(CO)_4[P(C_6H_5)_3]L$ complexes resulted with observable rate constants having identical values of k_1.[4] The plot of k_{obsd} *vs.* [L] for large excesses of L is shown in Figure 1. The second-order rate constants for these processes were found to be 2.5×10^{-2} and 7.0×10^{-2} M^{-1} sec^{-1} at 36.5° for L = $P(OCH_2)_3CC_2H_5$ and $P(n\text{-}C_4H_9)_3$, respectively.[5] As shown in Figure 1 the intercepts observed from the plots of k_{obsd} *vs.* [L] are very similar to the value of k_1 observed in the absence of added ligands (L). As is generally observed for reactions of this type the tri-*n*-butylphosphine ligand is found to be a better nucleophile than the $P(OCH_2)_3CC_2H_5$ ligand.[6]

It possible to employ a large excess of amine and other ligands (L) simultaneously in order to observe competitive reactions for the intermediate species $[Mo(CO)_4P(C_6H_5)_3]$. A steady-state solution to eq 1 when $k_3 = 0$ yields the rate equation

$$\text{rate} = k_1[\text{Mo(CO)}_4[\text{P(C}_6\text{H}_5)_3](\text{amine})] \times \frac{k_2[\text{L}]}{k_{-1}[\text{amine}] + k_2[\text{L}]} \qquad (5)$$

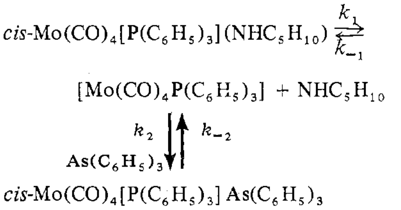
The rate becomes first order in $Mo(CO)_4[P(C_6H_5)_3]$(amine) when [amine] is small compared to [L]. The rate of disappearance of $Mo(CO)_4[P(C_6H_5)_3]$(amine) should be inhibited at high amine concentrations. This is exactly what is observed and thus the dissociative pathway of these reactions is indicated.

Employing large excesses of [L] and [amine] it is possible to observe a pseudo-first-order rate constant (k_{obsd}) for the disappearance of the starting complex. The observed rate constant (k_{obsd}) is then measured as a function of [L] and [amine]

$$\frac{1}{k_{obsd}} = \frac{1}{k_1} + \frac{k_{-1}[\text{amine}]}{k_1k_2[\text{L}]} \qquad (6)$$

These data determined at 36.5° are listed in Table V and are shown graphically in Figure 2.[7] The ratio k_{-1}/k_2, as determined from the slope of the plot of $1/k_{obsd}$ *vs.* [amine]/[L] and the respective values of k_1 (0.00307 sec^{-1} for amine = NHC_5H_{10} and 0.00215 sec^{-1} for amine = NC_5H_5), represents the competition of the amine and the added Lewis base (L) for the intermediate $[Mo(CO)_4P(C_6H_5)_3]$. The values for k_{-1}/k_2 are listed in Table VI.[8]

For the substitution process in the presence of added piperidine and $As(C_6H_5)_3$, two equilibrium processes occur for added molar concentration ratios of $[NHC_5H_{10}]/[As(C_6H_5)_3]$ greater than 0.5 (eq 7)



$$\begin{tikzcd}[column sep=small] \textit{cis}\text{-Mo(CO)}_4[\text{P(C}_6\text{H}_5)_3](\text{NHC}_5\text{H}_{10}) \arrow[r, shift left, "k_1"] & \arrow[l, shift left, "k_{-1}"] \\ {[\text{Mo(CO)}_4\text{P(C}_6\text{H}_5)_3] + \text{NHC}_5\text{H}_{10}} \arrow[d, shift right, "k_2"', "\text{As(C}_6\text{H}_5)_3"'] & \\ \textit{cis}\text{-Mo(CO)}_4[\text{P(C}_6\text{H}_5)_3]\,\text{As(C}_6\text{H}_5)_3 \arrow[u, shift right, "k_{-2}"'] & \end{tikzcd} \qquad (7)$$

The equilibrium constant (K_{eq}) for the overall process may be expressed by

$$K_{eq} = \frac{k_1k_2}{k_{-1}k_{-2}} = \frac{[\text{Mo(CO)}_4[\text{P(C}_6\text{H}_5)_3]\text{As(C}_6\text{H}_5)_3][\text{NHC}_5\text{H}_{10}]}{[\text{Mo(CO)}_4[\text{P(C}_6\text{H}_5)_3]\text{NHC}_5\text{H}_{10}][\text{As(C}_6\text{H}_5)_3]} \qquad (8)$$

The value of K_{eq} was determined to be 1.90 at 36.5°. From K_{eq} and the measured values of k_{-1}/k_2 and k_1, the calculated rate constant k_{-2} was found to be 0.00083 sec^{-1}. Therefore, the rate of dissociation of the molybdenum-arsine bond is considerably less than that of the molybdenum-amine bond. This is an expected result based on the greater thermodynamic

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(4) The concentration ranges of the ligands (L) were as follows: $P(C_6H_5)_3$, 0.0116-0.0419 *M*; $As(C_6H_5)_3$, 0.0117-0.0169 *M*; $Sb(C_6H_5)_3$, 0.0148-0.0172 *M*; CO, 0.0116 *M*.

(5) *cis*-$Mo(CO)_4[P(C_6H_5)_3]NHC_5H_{10}$ should be less susceptible to a nucleophilic attack than $Mo(CO)_6$ since it is sterically more demanding and the metal is more electron rich. It therefore follows that a greater percentage of the substitution reactions of the *cis*-$Mo(CO)_4[P(C_6H_5)_3]NHC_5H_{10}$ species should occur by the dissociative mechanism. If the ratios of k_3/k_1 for $Mo(CO)_6$ (234)[6a] and *cis*-$Mo(CO)_4[P(C_6H_5)_3]NHC_5H_{10}$ (23) are compared for the reaction with $(n\text{-}C_4H_9)_3P$, this is indeed seen to be the case.

(6) (a) J. R. Graham and R. J. Angelici, *Inorg. Chem.*, 6, 992 (1967). The rate constants were extrapolated to 36.5° from the activation parameters given in this reference. (b) J. R. Graham and R. J. Angelici, *ibid.*, 6, 2082 (1967).

(7) From these data it is possible to conclude that the reverse reactions with amine (k_{-1}) and the forward reaction with ligand (k_2) are first-order in amine and ligand (L) concentrations, respectively.

(8) T. L. Brown and W. Covey (University of Illinois, Urbana, Ill.) have obtained similar data for the $Mo(CO)_5$(amine) species, whereas, R. J. Angelici and B. Knebel (Iowa State University, Ames, Iowa) have recently studied similar reactions for the bidentate complex $Mo(CO)_4PN$ (where PN = $(C_6H_5)_2PCH_2CH_2NC_2H_5$).

Table V. Competition Studies of Amines *vs.* Lewis Bases (L) for the Intermediate $[Mo(CO)_5P(C_6H_5)_3]^a$–k_{obsd} as a Function of [Amine]/[L]

Amine added	Lewis base added	[Amine][b]	[L][b]	k_{obsd}, sec^{-1}
NHC_5H_{10}	$P(C_6H_5)_3$	0.0077	0.0419	25.7
		0.0077	0.0335	25.5
		0.0039	0.0150	23.5
		0.0077	0.0231	26.5
		0.0077	0.0210	31.2
		0.0077	0.0185	28.2
		0.0077	0.0168	25.8
		0.0079	0.0150	21.5
		0.0077	0.0116	20.8
		0.0131	0.0150	18.5
		0.0227	0.0150	14.7
		0.0315	0.0150	11.5
		0.0630	0.0150	8.2
		0.0788	0.0150	6.8
NHC_5H_{10}	$As(C_6H_5)_3$	0.0002	0.0117	26.2
		0.0004	0.0117	23.8
		0.0005	0.0117	28.9
		0.0010	0.0143	25.0
		0.0012	0.0143	24.5
		0.0010	0.0117	23.5
		0.0018	0.0150	21.8
		0.0025	0.0169	21.8
		0.0024	0.0143	19.6
		0.0035	0.0150	19.2
		0.0049	0.0169	19.7
		0.0044	0.0150	15.9
		0.0048	0.0143	17.2
NHC_5H_{10}	$Sb(C_6H_5)_3$	0.0041	0.0172	20.8
		0.0102	0.0172	17.7
		0.0204	0.0172	13.1
		0.0273	0.0148	13.7
		0.0341	0.0148	10.6
		0.0510	0.0172	8.7
		0.0546	0.0148	7.4
		0.0682	0.0148	5.4
		0.1021	0.0172	4.8
NHC_5H_{10}	$P(n\text{-}C_4H_9)_3$	0.0016	0.0152	32.3
		0.0123	0.0152	16.7
		0.0160	0.0152	11.0
		0.0200	0.0152	10.9
		0.0246	0.0152	11.2
		0.0321	0.0152	7.5
NHC_5H_{10}	$P(OCH_2)_3CC_2H_5$	0.0026	0.0162	33.8
		0.0026	0.0162	39.7
		0.0033	0.0162	32.3
		0.0033	0.0162	34.9
		0.0066	0.0162	35.0
		0.0132	0.0162	26.3
		0.0331	0.0162	19.1
		0.0397	0.0162	16.8
		0.0662	0.0162	12.3
NHC_5H_{10}	CO[c]	0.000	0.0116	7.4
		0.0102	0.0116	1.75
		0.0204	0.0116	1.32
		0.0640	0.0116	0.47
		0.1255	0.0116	0.24
NC_5H_5	$P(C_6H_5)_3$	0.0020	0.0129	18.8
		0.0040	0.0129	16.0
		0.0048	0.0129	17.4
		0.0120	0.0129	11.7

[a] This intermediate is produced from the starting material *cis*-$Mo(CO)_4[P(C_6H_5)_3]NHC_5H_{10}$ in all cases except the last case where it is produced from *cis*-$Mo(CO)_4[P(C_6H_5)_3]NC_5H_5$. [b] These concentrations are in units of moles per liter. [c] In this particular case the reaction was run at 28.0° as opposed to the 36.5° temperature for the other competitive studies.

stability of metal-arsine or -phosphine bonds as compared with metal-amine bonds.

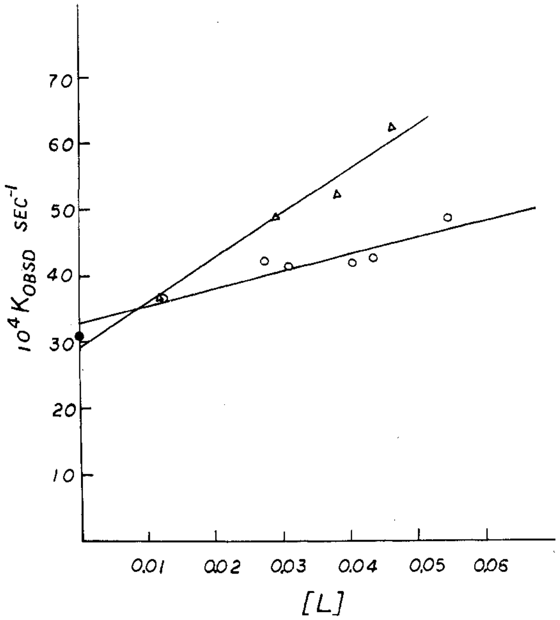

Figure 1. Kinetics of the reaction of *cis*-$Mo(CO)_4[P(C_6H_5)_3]$-NHC_5H_{10} with (△) $(n\text{-}C_4H_9)_3P$ and (○) $P(OCH_2)_3CC_2H_5$, both at 36.5°. Predicted intercept at ●.

Table VI. *cis*-$Mo(CO)_4[P(C_6H_5)_3]$(amine) Rates of Reaction and Competition Ratios for Selected Lewis Bases in Hexane Solution at 36.5°

L	$10^4 k_{intercept}$, sec^{-1}	k_{-1}/k_2
	Amine = NHC_5H_{10}	
$P(C_6H_5)_3$[a]	31.1	0.68 ± 0.13
$As(C_6H_5)_3$[b]	27.6	2.13 ± 0.09
$Sb(C_6H_5)_3$[a]	29.2	0.90 ± 0.30
CO[c]	6.6	3.24 ± 0.56
$P(OCH_2)CC_2H_5$[d]	38.9	0.42 ± 0.05
$P(n\text{-}C_4H_9)_3$[d]	37.4	1.47 ± 0.30
	Amine = NC_5H_5	
$P(C_6H_5)_3$[e]	21.6	0.93 ± 0.07

[a] For the concentrations of these ligands employed the predicted $k_{intercept}$ is 0.00307 sec^{-1}. [b] For ratios of $[NHC_5H_{10}]/[As(C_6H_5)_3]$ less than 0.5; again $k_{intercept}$ is predicted to be 0.00307 sec^{-1}. [c] Determined at 28°; $k_{intercept}$ predicted to be 0.00088 sec^{-1}. [d] For the concentration of these ligands employed the predicted values of $k_{intercept}$ are 0.00376 and 0.00393 sec^{-1}, respectively. [e] The predicted value of $k_{intercept}$ for this reaction is 0.00215 sec^{-1}.

Angelici and Ingemanson[9] have reported an equilibrium constant defined for the related reaction

$$(\text{amine})W(CO)_5 + L \overset{K_{eq}}{\rightleftarrows} (L)W(CO)_5 + \text{amine}$$

These reactions were studied under conditions of excess quantities of amine relative to ligand (L). It is most likely that the equilibrium process studied under these conditions is really the more complex equilibria described in eq 7. If so, the K_{eq} reported by these workers would be a product of two equilibrium constants, K_1K_2.

The rather small value of the equilibrium constant (K_{eq}) for $As(C_6H_5)_3$ as compared with the presumably much larger values for the $P(C_6H_5)_3$ and $Sb(C_6H_5)_3$ analogs can probably be attributed to steric effects. That steric effects are important in these reactions is seen in the effect of increasing the bulkiness of the phosphine ligand without significantly changing the electronic character of the phosphine. No substitution product was observed when excessive quantities of the ligand, $P(o\text{-}CH_3C_6H_4)_3$, were employed. This phosphine has the largest cone angle[10] thus far deter-

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[9] R. J. Angelici and C. M. Ingermanson, *Inorg. Chem.*, 8, 83 (1969).

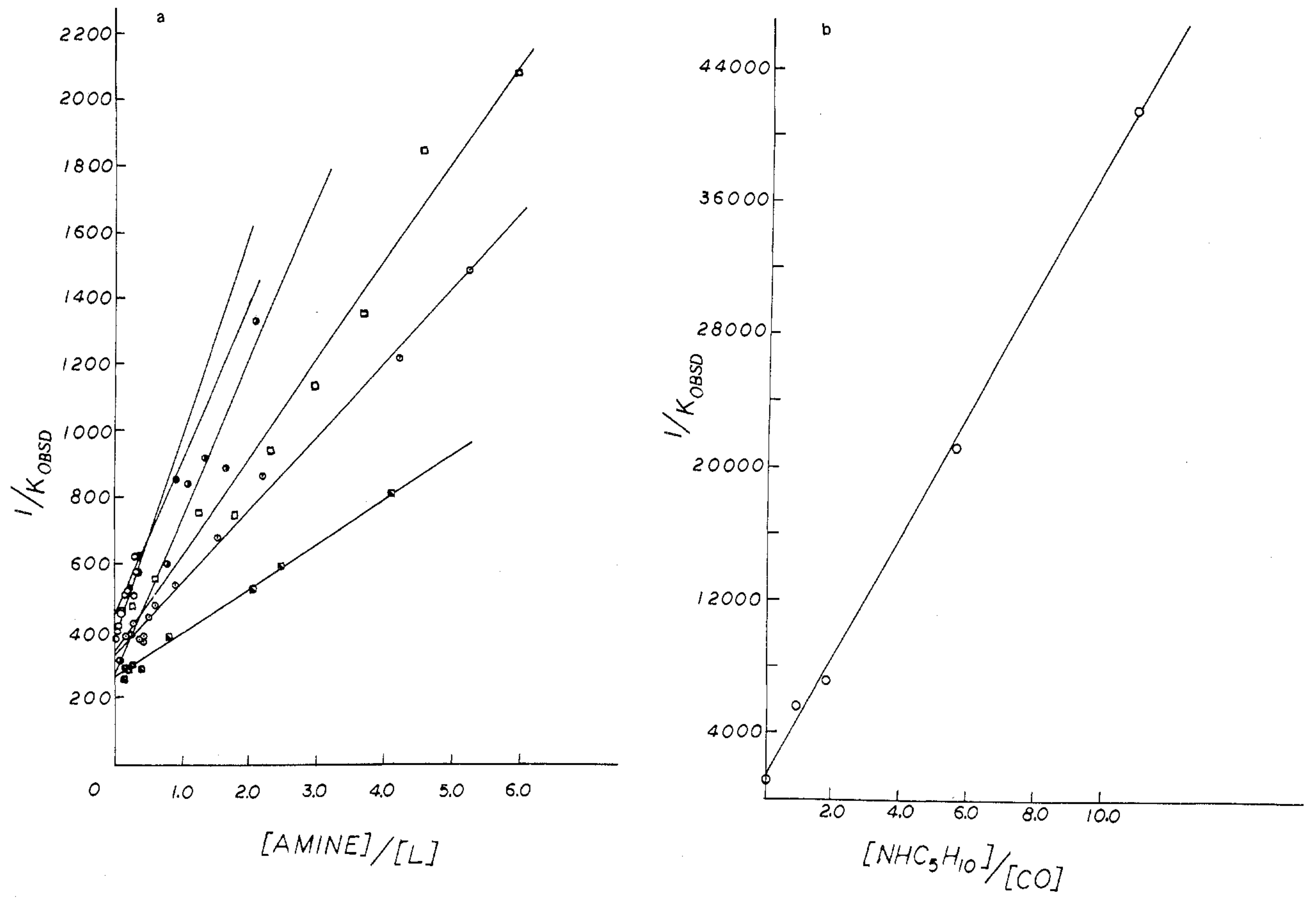

Figure 2. (a) Plot of $1/k_{\text{obsd}}$ *vs.* [amine]/[L] for the reaction of *cis*-$Mo(CO)_4[P(C_6H_5)_3]$(amine) with added amine and ligand (L): ○, $[NHC_5H_{10}]/[As(C_6H_5)_3]$; ◑, $[NHC_5H_{10}]/[P(n\text{-}C_4H_9)_3]$; □, $[NHC_5H_{10}]/[Sb(C_6H_5)_3]$; ⊙, $[NHC_5H_{10}]/[P(C_6H_5)_3]$; ▨, $[NHC_5H_{10}]/[P(OCH_2)_3CC_2H_5]$; ●, $[NC_5H_5]/[P(C_6H_5)_3]$. (b) Plot of $1/k_{\text{obsd}}$ *vs.* $[NHC_5H_{10}]/[CO]$ for reaction of *cis*-$Mo(CO)_4[P(C_6H_5)_3]NHC_5H_{10}$ and CO.

mined, 194 ± 6°, whereas, the $P(C_6H_5)_3$ ligand which has a cone angle of 145 ± 2° and comparable electronic properties readily forms substitution products.

In large excess concentrations, $P(C_6H_{11})_3$ (cone angle 179 ± 10°) will replace the amine group to form *cis*-$Mo(CO)_4[P(C_6H_5)_3]P(C_6H_{11})_3$. This complex is stable in solutions containing large quantities of free tricyclohexylphosphine. Electronically, however, the $(C_6H_{11})_3P$ ligand is much more basic than $P(C_6H_5)_3$; the pK_a values are 9.70 and 2.73[11] for $P(C_6H_{11})_3$ and $P(C_6H_5)_3$, respectively. On the other hand, tributylphosphine (pK_a = 8.43), which is electronically very similar to $P(C_6H_{11})_3$ but with much less stringent steric requirements (cone angle 130 ± 4°], readily yields a cis-substituted product.

Presumably, values of K_{eq} for $P(C_6H_{11})_3$ and $P(o\text{-}CH_3C_6H_4)_3$ are much smaller than the value of 1.9 determined for $As(C_6H_5)_3$.[11a] The high value of k_{-2} for these phosphines precludes measurement of k_{-1}/k_2 under the reaction condition employed. Therefore, although the intermediate $[Mo(CO)_4P(C_6H_5)_3]$ is kinetically fairly insensitive to the nature of the entering ligand L, K_{eq} depends strongly on the nature of L.

The importance of steric factors in these reactions is manifested in the activation parameters (Table IV). The enthalpies of activation for the dissociation of the piperidine ligand in *cis*-$Mo(CO)_4[P(C_6H_5)_3]NHC_5H_{10}$ and $Mo(CO)_5NHC_5H_{10}$[2] are quite similar (25.9 ± 1.2 and 23.1 ± 1.1 kcal/mol) with the former dissociative process being slightly higher; however, the entropy of activation of the sterically more hindered $P(C_6H_5)_3$ derivative is considerably larger than that of the pentacarbonyl derivative (13.6 ± 3.9 *vs.* −3.9 ± 3.5 eu). A similar decrease in $\Delta S^{\ddagger}$ is observed for the amine dissociation in *cis*-$Mo(CO)_4[P(C_6H_5)_3]$(amine) in going from the NHC_5H_{10} derivative to the less bulky NC_5H_5 derivative. Changes in the size of the central metal atom point up this steric effect as well; for example, the $\Delta S^{\ddagger}$ value decreases for the dissociation of piperidine in *cis*-$W(CO)_4[P(C_6H_5)_3]NHC_5H_{10}$ ($\Delta H^{\ddagger}$ = 21.8 and $\Delta S^{\ddagger} = -6.48$) as compared to the molybdenum analog. At the same time the entropy factor is believed responsible for the lack of isolation of the analogous *cis*-$Cr(CO)_4[P(C_6H_5)_3]NHC_5H_{10}$ from $Cr(CO)_5P(C_6H_5)_3$ and NHC_5H_{10}.[3]

It is possible to rank the Lewis bases according to their relative abilities to compete for the five-coordinate intermediate, $[Mo(CO)_4P(C_6H_5)_3]$: $CO < As(C_6H_5)_3 < P(n\text{-}C_4H_9)_3 < NHC_5H_{10} < Sb(C_6H_5)_3 < P(C_6H_5)_3 \sim NC_5H_5 < P(OCH_2)_3CC_2H_5$.

There was some concern that the competition experiments involving carbon monoxide might be quantitatively in error since we did not directly determine the concentration of carbon monoxide in solution. It was assumed that a saturated solution of CO in hexane at 28° and atmospheric pressure has a carbon monoxide concentration of 0.0116 *M*.[12] The absolute concentration of carbon monoxide is, however, not important with respect to a plot such as shown in Figure 2b.

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[10] C. A. Tolman, *J. Amer. Chem. Soc.*, **92**, 2956 (1970).

[11] C. A. Streuli, *Anal. Chem.*, **32**, 985 (1960).

[11a] Note Added in Proof. The value of K_{eq} for $P(o\text{-}CH_3C_6H_4)_3$ was determined at 25° to be <0.089, whereas, K_{eq} for $P(C_6H_5)_3$ at 25° was determined to be ~30.

[12] W. T. Linke, "Solubilities of Inorganic and Metal Organic Compounds," Vol. 1, Van Nostrand, Princeton, N. J., 1958.

The only requirement is that the carbon monoxide concentration be constant throughout the series of experiments. In any case a series of substitution experiments of *cis*-$Mo(CO)_4[P(C_6H_5)_3]$(amine) were carried out involving solutions containing carbon monoxide (assumed concentration value of 0.0116 *M* as described above) and triphenylphosphine (of known concentrations). From the distribution of products, $Mo(CO)_5P(C_6H_5)_3$ and *cis*-$Mo(CO)_4[P(C_6H_5)_3]_2$, and the known ratio of $[CO]/[P(C_6H_5)_3]$ it was possible to arrive at a competition ratio of 6.20 ± 0.53 for $P(C_6H_5)_3$ *vs.* CO for the intermediate $[Mo(CO)_4P(C_6H_5)_3]$ (Figure 3). A competition ratio of 4.76 ± 1.32 is predicted on the basis of the relative competition of CO or $P(C_6H_5)_3$ *vs.* piperidine for $[Mo(CO)_4P(C_6H_5)_3]$, respectively. The excellent agreement of these two different series of experiments is compelling evidence for the accuracy of the assumed carbon monoxide concentration. Day, Basolo, and Pearson[13] have also reported a similar competition ratio of about 5 for $P(C_6H_5)_3$ *vs.* CO toward the intermediate $[Ni(CO)_3]$.

An additional experiment involving the substitution of ^{13}CO for the amine in *cis*-$Mo(CO)_4[P(C_6H_5)_3]$(amine) was carried out (eq 9). As indicated by eq 9 the substitution resulted in a product containing only the equatorially ^{13}CO-

$$\textit{cis}\text{-}Mo(CO)_4[P(C_6H_5)_3](\text{amine}) + {}^{13}CO \rightarrow \textit{cis}\text{-}Mo(CO)_4({}^{13}CO)P(C_6H_5)_3 \qquad (9)$$

substituted $Mo(CO)_5P(C_6H_5)_3$ species.[14] This result is consistent with the cis stereochemistry of the phosphine-substituted products and the lack of fluxionality in the $Mo(CO)_5P(C_6H_5)_3$ species. The more informative and interesting experiment would involve labeling of the starting material, *cis*-$Mo(CO)_4[P(C_6H_5)_3]$(amine), with ^{13}CO stereospecifically and then observing the position(s) of ^{13}CO in the substituted product as was done for the reaction of the $Mo(CO)_5$(amine) species with $As(C_6H_5)_3$.[2a] Labeling of these species is exceedingly difficult; however, attempts are currently being made in our laboratory to prepare these isotopically labeled compounds photochemically. It would indeed be most interesting to study possible rearrangements in $[M(CO)_4L]$ species as a function of the nature of the ligand L.

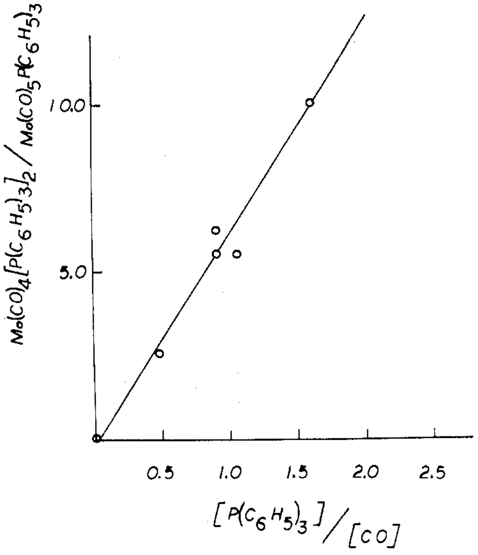

Figure 3. Plot of the product ratio $[Mo(CO)_4[P(C_6H_5)_3]_2]/[cis\text{-}Mo(CO)_5P(C_6H_5)_3]$ *vs.* $[P(C_6H_5)_3]/[CO]$ for the reaction of *cis*-$Mo(CO)_4[(C_6H_5)_3]NHC_5H_{10}$ with $P(C_6H_5)_3$ and CO.

Conclusions

The five-coordinate intermediate, $[Mo(CO)_4P(C_6H_5)_3]$, produced thermally from *cis*-$Mo(CO)_4[P(C_6H_5)_3]$(amine) has been shown to be a very reactive species. It reacts fairly indiscriminantly with a variety of Lewis bases to fill the sixth position of its coordination sphere. There is some slight preference for small, nucleophilic reagents. For example, the smallest phosphine ligand employed in this study, $P(OCH_2)_3CC_2H_5$, which has a cone angle of 101 ± 2° and is at the same time a good nucleophile, reacts with the greatest degree of preference, whereas, carbon monoxide which is sterically more favorable than $P(OCH_2)_3CC_2H_5$ is also a much poorer nucleophile and as a result is less reactive toward the $[Mo(CO)_4P(C_6H_5)_3]$ species. The quantitative order of preference for the substituted ligands (L) for the intermediate, $[Mo(CO)_4P(C_6H_5)_3]$, was found to be as follows: CO (0.31) < $As(C_6H_5)_3$ (0.47) < $P(n\text{-}C_4H_9)_3$ (0.68) < NHC_5H_{10} (1) < $Sb(C_6H_5)_3$ (1.11) < $P(C_6H_5)_3$ (1.47) ~ NC_5H_5 < $P(OCH_2)_3CC_2H_5$ (2.38).

In conclusion, we feel that reactions of the type described in this study will undoubtedly serve as extremely useful systems for the investigation of reactivity and possible geometrical rearrangements in a variety of transient, five-coordinate group VI organometallic species.

Registry No. *cis*-$Mo(CO)_4(PPh_3)(HNC_5H_{10})$, 38780-82-4; *cis*-$Mo(CO)_4(PPh_3)(NC_5H_5)$, 38800-73-6; *cis*-$Mo(CO)_4(PPh_3)_2$, 16742-93-1; *cis*-$Mo(CO)_4(PPh_3)(AsPh_3)$, 38894-68-7; *cis*-$Mo(CO)_4(PPh_3)(SbPh_3)$, 38894-69-8; *cis*-$Mo(CO)_4(PPh_3)(PBu_3)$, 38894-70-1; *cis*-$Mo(CO)_4(PPh_3)[P(OCH_2)_3CEt]$, 38894-59-6; *cis*-$Mo(CO)_4(PPh_3)[P(C_6H_{11})_3]$, 38894-60-9; $Mo(CO)_5(PPh_3)$, 14971-42-7; PPh_3, 603-35-0.

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

[14] This was evidenced from a comparison of the ratios of the highest energy (A′) band in the equatorially monosubstituted ^{13}CO with that of the $A_1^{(2)}$ band in the all-^{12}CO molecule. The relative percentage enrichment was found to be 16.7% for a reaction that had proceeded to approximately 90% completion starting with 20% enriched ^{13}CO and was normalized to the ratio observed in the natural-abundance ^{13}CO species.