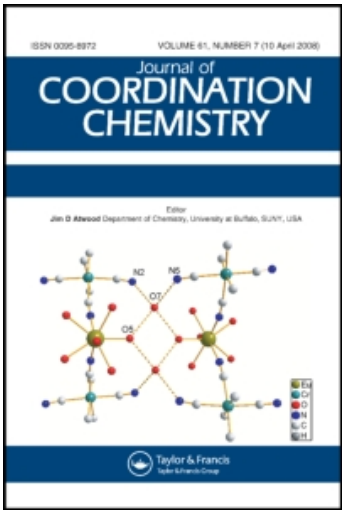

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KINETICS AND MECHANISM OF REACTIONS OF *cis*-(PIPERIDINE)(L)Mo(CO)$_4$ COMPLEXES WITH PHOSPHINES AND PHOSPHITES

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The kinetics and mechanism of ligand-exchange reactions of *cis*-(pip)(L)Mo(CO)$_4$ complexes (pip = piperidine; L = $P(OCH_3)_3$, $P(OC_2H_5)_3$, $P(OCH(CH_3)_2)_3$, $P(OC_6H_5)_3$, $P(C_6H_5)_3$, $P(OCH_2)_3CCH_3$, $P(C_6H_{12}N_3)$; L′ = $P(OCH(CH_3)_2)_3$, and L = $P(OCH(CH_3)_2)_3$; L′ = $P(OCH_3)_3$, $P(OC_2H_5)_3$, $P(OC_6H_5)_3$, $P(C_6H_5)_3$, $P(OCH_2)_3CCH_3$, $P(n\text{-}C_4H_9)_3$,

$$cis\text{-(pip)(L)Mo(CO)}_4 + L' \rightarrow cis,trans\text{-(L)(L')Mo(CO)}_4 + \text{pip} \qquad (2)$$

have been studied. Both the reactants and products (15 complexes) for these reactions have been synthesized and characterized. All reactions cleanly follow a mechanism involving initial Mo–pip hond-breaking, followed by competition between pip and L′ for the resulting five-coordinate [(L)Mo(CO)$_4$] intermediate. These data complete the study of these systems for the series of metals, Cr, Mo, W. The activation parameters for Mo–pip bond-breaking in the reactions of *cis*-(pip)(L)Mo(CO)$_4$ with L′ have been obtained. Where L is a trialkyl phosphite, both the enthalpies and entropies of activation are in very close agreement. These values, when compared to those for complexes where L is a trialkyl phosphine, support intramolecular N–H···O–P– hydrogen bonding in the phosphite complexes, but not in the phosphines. The data are interpreted in terms of a "fundamental" ligand exchange, involving [(L)Mo(CO)$_4$] and L′. The steric outcome of these reactions also is influenced by intramolecular hydrogen bonding. The reliability of the reported activation parameters in these and related systems is discussed. The consistency from complex to complex of the reported activation parameters strongly indicates that they can be accepted with confidence.

Keywords: Kinetics; piperidine; molybdenum; metal carbonyl; enthalpies of activation

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INTRODUCTION

There have been a large number of kinetic studies of ligand-exchange in Group VI metal carbonyls and their substitution products.[1] However, these studies have not necessarily translated into a systematic overview of the field, especially for series of related complexes. As a consequence, a clear picture has yet to emerge of variations of M–L bond-strengths (L = Lewis base) down the series of Group VI metals, M = Cr, Mo, W. This is true both for the hexacarbonyls and in complexes in which the dissociating ligand is other than CO.

Yet such data, enthalpies of activation in particular, have become increasingly important in view of the interest in the determination of M–L bond-strengths through the application of time-resolved photoacoustic calorimetric methods (TRPAC).[2] Moreover, in contrast to "stable" and isolable metal carbonyls and derivatives,[1] there have been comparisons involving the dissociation of weakly binding nucleophiles, heretofore considered as "solvents," alkanes, arenes and their halogenated substitution products, produced after flash photolysis, e.g.,

$$(\eta^2\text{-}C_6H_5R)Cr(CO)_5 + R'CH{=}CH_2 \rightarrow (R'CH{=}CH_2)Cr(CO)_5 + C_6H_5R \quad (1)$$

Such studies[3] have revealed discrepancies between Cr–L bond-strengths determined as activation parameters from kinetic studies and from TRPAC data, which may have a basis in nature rather than in systematic error inherent in the two methods of analysis. Thus, for example, data indicate that ligand exchange involving photogenerated arenes containing alkyl substituents of various chain-lengths (C_6H_5R) and alkenes also containing linear alkanes ($R'CH{=}CH_2$), Eq. (1), takes place through the intermediacy of the chains, perhaps involving retention of "agostic" C–H···Cr···H–C– binding in the transition state.[4,5] This interpretation is consistent both with the stronger arene–Cr bond-strengths inferred from TRPAC vs. enthalpies of activation, and the near-zero entropies of activation observed for the latter.

For the hexacarbonyls, several studies have provided data for M–CO bond-breaking, both in solution[6,7] and in the gas phase.[8–11] Discrepancies among the data, which could arise as a consequence of the different experimental methods used to obtain them, are also observed.

To ascertain the extent to which experimental uncertainties influence the data, series of independent but related complexes must be studied.

Where differences among members of the series on rate is small, activation parameters for members of the series are expected to be similar; any observed non-systematic differences thus can be attributed to experimental uncertainties inherent in the method of analysis.

We have chosen the ligand-exchange reactions of *cis*-(pip)(L)M(CO)$_4$ complexes (pip = piperidine),

$$cis\text{-(pip)(L)M(CO)}_4 + \text{L}' \rightarrow cis, trans\text{-(L)(L}')\text{M(CO)}_4 + \text{pip} \qquad (2)$$

as such a series. Examples of these complexes for all three metals are known;[12–17] activation data for several examples with M = Cr, W have already been reported;[15,16] and the steric and electronic influences of L, L′ on rates of pip dissociation are relatively small, and, at least for M = Cr, their influences on the activation parameters appear to be within the experimental uncertainties of the measurements.[16] Moreover, activation parameters can be obtained for M–pip bond-breaking itself, rather than for a complex rate constant (*vide infra*). Thus, these series afford several independent measurements through which it should be possible to obtain reliable estimates of the activation parameters. These in turn can provide an estimate as to how these parameters vary along the series of metals, Cr, Mo, W and offer an interesting series of complexes for study via TRPAC.

EXPERIMENTAL

Reagents

$Mo(CO)_6$ (Climax Molybdenum) was sublimed under vacuum before use. Piperidine (Aldrich) was fractionally distilled from anhydrous KOH under nitrogen. Chlorobenzene (Fisher) was fractionally distilled from P_2O_5 under nitrogen. The ligands trimethylphosphite, tri(*iso*propyl)phosphite, triethylphosphite, triphenylphosphite and tri(*n*-butyl)phosphine (Aldrich) were fractionally distilled from sodium under a nitrogen bleed (0.2 torr). Triphenylphosphine (Fluka) was recrystallized from absolute ethanol and dried under vacuum. The "constrained phosphite," 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane, $P(OCH_2)_3CCH_3$, was prepared through the published procedure,[18] twice sublimed under reduced pressure into a wide-mouthed condenser, and recrystallized under nitrogen from hot *n*-hexane. The "constrained phosphine," 1,3,5-triaza-7-phosphaademantane, $P(C_6H_{12}N_3)$, was prepared and purified according to the literature method.[19]

Synthesis of the Complexes

The synthesis of the *cis*-$(pip)_2Mo(CO)_4$ precursor from $Mo(CO)_6$ employed the procedure of Darensbourg and Kump.[14] The substrates for kinetics, *cis*-(pip)(L)$Mo(CO)_4$ (L = $P(OCH_3)_3$, $P(OC_2H_5)_3$, $P(OCH(CH_3))_3$, $P(OC_6H_5)_3$, $P(C_6H_5)_3$, $P(OCH_2)_3CCH_3$, $P(C_6H_{12}N_3)$), were also prepared by their methods.[14] The precursor, *cis*-di(piperidine)tetracarbonylmolybdenum(0) (3.0 g) and a slight (1.1-fold) excess of L were allowed to react under a nitrogen atmosphere for 5 min in 150 mL of boiling dichloromethane. The solvent was removed completely under reduced pressure, after which the solid was taken up in 45 mL of a 1:2 (v:v) mixture of dichloromethane and methanol. The solution was cooled in a freezer overnight, whereupon the yellow complexes precipitated and were collected by suction filtration. They were recrystallized from 50 mL of a 1:4 v:v chloroform/methanol solution and dried under vacuum. Two of these complexes, for L = $P(OCH_3)_3$[17] and $P(C_6H_5)_3$[20] had previously been prepared by similar methods.

The reactions were also studied as a function of the incoming nucleophile, L′ for L = $P(OCH(CH_3)_2)_3$, and their products, *cis*-(L)(L′)$Mo(CO)_4$ (L′ = $P(OCH_3)_3$, $P(OC_2H_5)_3$, $P(OCH(CH_3)_2)_3$, $P(OC_6H_5)_3$, $P(C_6H_5)_3$, $P(OCH_2)_3CCH_3$, $P(C_6H_{12}N_3)$ and $P(n\text{-}C_4H_9)_3$) were also characterized. Thus, *cis*-(pip)$(P(OCH)CH_3)_2)_3Mo(CO)_4$ (0.5 g) and a two-fold excess of L′ were allowed to react in chlorobenzene under nitrogen at 40°C for 12 h, during which time the solution changed from yellow to colorless. The solvent was removed under reduced pressure and the reaction product(s) precipitated upon addition of 20 mL of cold *n*-hexane. They were collected by suction filtration and recrystallized from $CHCl_3/CH_3OH$ (1:4 v:v) and dried under vacuum. Alternatively, the complexes can be prepared photochemically (15 min irradiation, Hanovia 450 W Hg lamp, quartz immersion reactor), and purified by the same methods. The carbonyl stretching spectra for all the complexes (Perkin Elmer 621, 1710 FT-IR, or Nicolet 20-SXB FTIR spectrophotometers), together with elemental analyses (Midwest Microlab, Indianapolis, IN), are given in Tables I and II.

Kinetic Studies

Rates of conversion of *cis*-(pip)(L)$Mo(CO)_4$ to *cis*- or *cis, trans*-(L)(L′) $Mo(CO)_4$ (Eq. (2)) were followed at 430 nm, at which wavelength the reactants absorb but the products do not, by employing Beckman DU-2 or Perkin Elmer 124 UV/visible spectrophotometers. Preparation of the solutions for analysis and sampling techniques, which involved manual removal of

TABLE I Carbonyl stretching spectra for the complexes (cyclohexane solution)

L, L'	*A'*	*A'*	*A''*	*A''*
cis-(pip)(L)Mo(CO)$_4$				
$P(OCH_3)_3$	2025 (m)[a]	1927 (s)	1905 (vs)	1876 (s)
	2024[b]	1928	1906	1877
$P(OC_2H_5)_3$	2023 (m)	1923 (s)	1902 (vs)	1873 (s)
$P(OCH(CH_3)_2)_3$	2022 (m)	1921 (s)	1900 (vs)	1870 (s)
$P(C_6H_5)_3$	2016 (m)	1911 (s)	1899 (vs)	1868 (vs)
	2016[c]	1908	1896	1872
$P(OCH_2)_3CCH_3$	2031 (m)[d]	1913 (s)	1909 (vs)	1868 (s)
$P(C_6H_{12}N_3)$	2016 (m)[d]	1905 (s)	1894 (vs)	1853 (s)
$P(OC_6H_5)_3$	2014 (m)	1936 (s)	1922 (vs)	1886 (s)
$P(O(CH(CH_3)_2)_3(L')(CO)_4$				
$P(OCH_3)_3$	2034 (m)	1940 (s)	—	1920 (vs)
$P(OC_2H_5)_3$	2033 (m)	1936 (s)	—	1918 (vs)
$P(OCH(CH_3)_2)_3$	2032 (m)[a]	1932 (s)	—	1912 (vs)
$P(C_6H_5)_3$	2026 (m)[d]	1936 (s)	1914 (vs)	1898 (vs)
$P(OCH_2)_3CCH_3$	2043 (m)	—	—	1930 (sh)
$P(O(CH(CH_3)_2)_3(L')(CO)_4$				
$P(C_6H_{12}N_3)$	2022 (m)[a,d]	1926 (s)	1907 (vs)	1890 (vs)
$P(OC_6H_5)_3$	2040 (m)[a]	—	—	1928 (vs)
$P(n\text{-}C_4H_9)_3$	2021 (m)[a]	1926 (s)	1907 (vs)	1894 (s)

[a]accidentally degenerate absorption for both *trans* and *cis* isomers.
[b]Ref. [17].
[c]Ref. [20].
[d]Chlorobenzene solution

TABLE II Elemental analyses

Complex, L, L'	*Calculated* (%)		*Found* (%)	
	C	*H*	*C*	*H*
cis-(pip)(L)Mo(CO)$_4$				
$P(OC_2H_5)_3$	39.23	4.83	38.93	5.05
$P(OCH(CH_3)_2)_3$	43.13	6.44	43.13	6.64
$P(OCH_2)_3CCH_3$	38.18	4.57	38.45	4.80
$P(C_6H_{12}N_3)$	40.01	5.15	39.96	4.91
$P(OC_6H_5)_3$	53.75	4.34	53.93	4.43
$(P(OCH(CH_3)_2)_3)(L')Mo(CO)_4$				
$P(OCH_3)_3$	35.57	5.60	35.62	5.68
$P(OC_2H_5)_3$	39.19	6.23	39.40	6.32
$P(O(CH(CH_3)_2)_3$	42.32	6.78	42.18	6.66
$P(C_6H_5)_3$	54.88	5.35	55.73	5.34
$C(OCH_2)_3CCH_3$	38.31	5.36	38.47	5.37
$P(C_6H_{12}N_3)$	39.88	5.80	39.62	5.85
$(P(OCH(CH_3)_2)_3)(L')Mo(CO)_4$				
$P(OC_6H_5)_3$	51.25	4.99	51.13	5.12
$P(n\text{-}C_4H_9)_3$	48.55	7.82	48.80	7.90

aliquots of the reacting solutions for analysis, have been described previously.[21] Initial substrate concentrations of *ca.* 1×10^{-3} M were employed. The temperature of the reacting solutions was maintained within ± 0.05°C by employing Haake ED or Forma-Temp Jr. 2095 bath circulators. Kinetic data were taken both for pip/L′ and L′ solutions; in all cases at least 20-fold excesses of [pip] and [L′] *vs.* [$Mo(CO)_6$] were employed so as to maintain pseudo first-order reaction conditions. Plots of $\ln(A_t - A_{bl})$ vs. time (A_t and A_{bl} are the absorbances of the reaction solutions at time t and of a solvent/pip/L′ blank, respectively) were linear to three or more half lives, and the correlation coefficients for most plots were 0.999 or better. Data were rejected at the 90% confidence limit (1.65 standard deviations). Limits of error, given in parentheses as the uncertainties of the last digit(s) of the cited value, are one standard deviation.

RESULTS

Reactions Studied

From the synthetic results it is clear that the ligand-substitution reactions are described by Eq. (2). Infrared data show that mixtures of *cis*- and *trans*-($P(OCH(CH_3)_2)_3$)(L′)$Mo(CO)_4$ products are produced for all L′ but P(*n*-$C_4H_9)_3$, where only the *cis* product is observed. These conclusions are based on a comparison of the relative intensities of the highest energy carbonyl stretching bands to those at ca. 1900 cm^{-1}, assigned as the E_u modes for the *trans* isomers, for a $Mo(CO)_4$ moiety of D_{4h} local symmetry.

Mechanism

Kinetic data were taken as a function of L, the coordinated ligand, in *cis*-(L)(L′)$Mo(CO)_4$, where L = $P(OCH_3)_3$, $P(OC_2H_5)_3$, $P(OCH(CH_3)_2)_3$, $P(OC_6H_5)_3$, $P(C_6H_5)_3$, $P(OCH_2)_3CCH_3$, $P(C_6H_{12}N_3)$ and L′, the incoming nucleophile, is $P(OCH(CH_3)_2)_3$, and as a function of L′ (= $P(OCH_3)_3$, $P(OC_2H_5)_3$, $P(OCH(CH_3)_2)_3$, $P(OC_6H_5)_3$, $P(C_6H_5)_3$, $P(OCH_2)_3CCH_3$ and P(*n*-$C_4H_9)_3$), where L = $P(OCH(CH_3)_2)_3$. At 31.1°C for varying ratios of [L′]/[pip], all plots of k_{obsd} vs. [L′]/[pip] were observed to be severely concave downward, (Figure 1) suggestive of the previously observed[13] mechanism involving competition between pip and L′ for an [(L)$Mo(CO)_4$] intermediate produced after initial pip–Mo bond-breaking,

$$cis\text{-(L)(pip)Mo(CO)}_4 \underset{k_{-1}[\text{pip}]}{\overset{k_1}{\rightleftharpoons}} [\text{(L)M(CO)}_4] \xrightarrow{k_2[\text{L}']} \text{(L)(L')Mo(CO)}_4 \qquad (3)$$

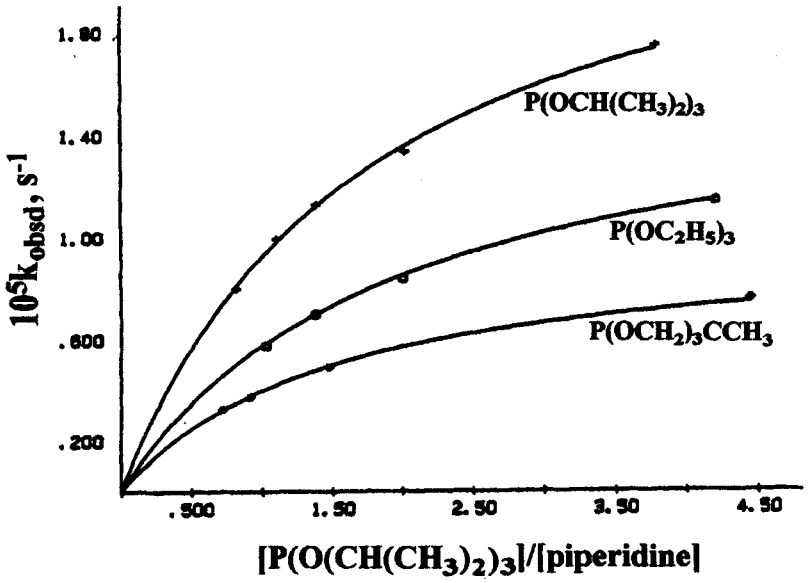

FIGURE 1 Plots of k_{obsd} vs. $[P(OCH(CH_3)_2)_3]/[piperidine]$ for selected reactions of *cis*-(piperidine)(L)Mo(CO)$_4$ complexes with $P(OCH(CH_3)_2)_3$ in chlorobenzene at 31.1°C.

The steady-state rate law for this mechanism is $(d[(L)Mo(CO)_4]/dt \approx 0)$ under pseudo first-order reaction conditions ($[(pip)(L)Mo(CO)_4] \ll [L']$, [pip]), is,

$$k_{obsd} = k_1 k_2 [L']/(k_{-1}[pip] + k_2[L']). \tag{4}$$

The rearrangement of Eq. (4) affords,

$$1/k_{obsd} = 1/k_1 + k_{-1}[pip]/k_1 k_2 [L']; \tag{5}$$

thus plots of $1/k_{obsd}$ vs. [pip]/[L'] are expected to be linear, with positive intercepts ($1/k_1$) and slopes ($k_{-1}/k_1 k_2$). Moreover, where the reaction is run in the absence of pip, Eq. (4) reduces to,

$$k_{obsd} = k_1, \tag{6}$$

and k_1 can be determined directly. Values of k_1 determined by either method are very similar. Typical examples of the "double reciprocal plots," Eq. (5), are illustrated in Figure 2. Since we were largely concerned with the activation parameters for this mechanistic step, data at other temperatures were taken in the absence of added pip. The first-order rate constants for unimolecular pip–Mo bond-breaking, together with the "competition ratios,"

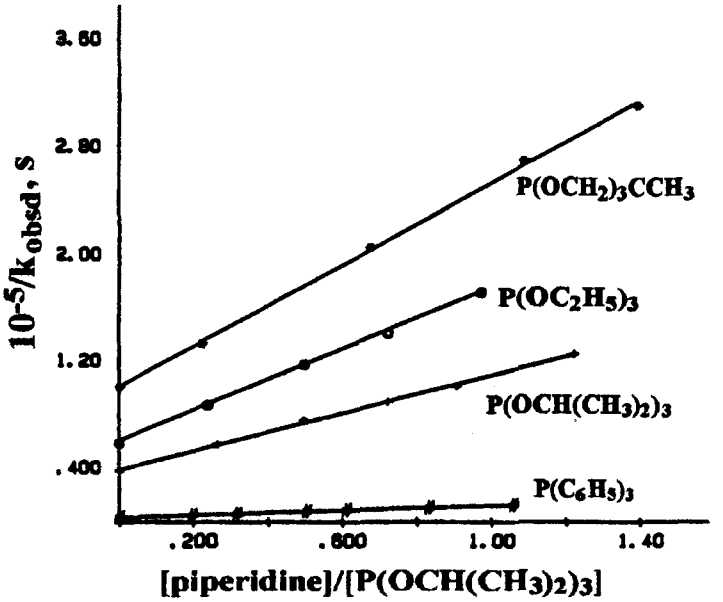

FIGURE 2 Plots of $1/k_{obsd}$ *vs.* [piperidine]/[$P(OCH(CH_3)_2)$] for selected (piperidine)(L)-$Mo(CO)_4$ complexes in chlorobenzene at 31.1°C.

TABLE III Data for thermal reactions of *cis*-(pip)(L)$Mo(CO)_4$ with $P(OCH(CH_3)_2)_3$/pip solutions in chlorobenzene, solvent at 31.1°C

L, *L'*		θ^a (*L*, *L'*)	ν^a (*L*, *L'*)	$10^5 k_1$ (s^{-1})	k_2/k_{-1}
$P(OCH_2)_3CCH_3$	$P(OCH(CH_3)_2)_3$	101, 114	2087.3, 2075.9	1.00(2)	0.67(2)
$P(C_6H_{12}N_3)$	$P(OCH(CH_3)_2)_3$	102, 114	—, 2075.9	29.2(3)	1.01(1)
$P(OCH_3)_3$	$P(OCH(CH_3)_2)_3$	107, 114	2079.5, 2075.9	1.56(8)	0.65(2)
$P(OC_2H_5)_3$	$P(OCH(CH_3)_2)_3$	109, 114	2076.3, 2075.9	1.66(2)	0.51(1)
$P(OCH(CH_3)_2)_3$	$P(OCH_2)_3CCH_3$	114, 101	2075.9, 2087.3	2.78(6)	0.90(3)
$P(OCH(CH_3)_2)_3$	$P(OCH_3)_3$	114, 107	2075.9, 2079.5	2.76(4)	0.76(2)
$P(OCH(CH_3)_2)_3$	$P(OC_2H_5)_3$	114, 109	2075.9, 2076.3	2.62(4)	0.66(2)
$P(OCH(CH_3)_2)_3$	$P(OCH(CH_3)_2)_3$	114, 114	2075.9, 2075.9	2.61(6)	0.54(2)
$P(OCH(CH_3)_2)_3$	$P(OC_6H_5)_3$	114, 128	2075.9, 2085.3	2.87(7)	0.384(15)
$P(OCH(CH_3)_2)_3$	$P(n\text{-}C_4H_9)_3$	114, 132	2075.9, 2060.3	2.87(6)	0.63(3)
$P(OCH(CH_3)_2)_3$	$P(C_6H_5)_3$	114, 145	2075.9, 2068.9	2.81(9)	0.34(2)
$P(OC_6H_5)_3$	$P(OCH(CH_3)_2)_3$	128, 114	2085.3, 2075.9	7.94(7)	0.89(2)
$P(C_6H_5)_3$	$P(OCH(CH_3)_2)_3$	145, 114	2068.9, 2075.9	30(1)	0.38(2)

k_2/k_{-1}, for attack at the intermediate by L' and pip, respectively, at 31.1°C are given in Table III. Individual values of k_{obsd}, where the reactions were studied in the absence and presence of both pip and L', are given in the supplementary material. All interpretations of the data are in agreement with those originally put forth by Hyde and Darensbourg.[13]

Activation parameters determined from data taken at several temperatures are presented in Table IV.

DISCUSSION

Rates as a Function of L

Table III exhibits first- order rate constants for dissociation of pip from *cis*-(pip)(L)Mo(CO)$_4$ at 31.1°C as a function of L. The systematics of the variation in k_1 as a function of the steric and electronic properties of L were evaluated by employing the relationship,

$$\log(k_1) = a\theta + b\nu + c, \tag{7}$$

where θ and ν are the Tolman steric and electronic parameters.[22] For all L this equation did not fit the data well; however, elimination of the two phosphines, P(C_6H_5)$_3$ and P($C_6H_{12}N_3$), greatly improved the fit and the use of a Tolman cone angle of 114° for P(OCH(CH_3)$_2$)$_3$[22,23] afforded an equation,

$$\log(k_1) = 0.0343\theta + 0.00163\nu - 11.9, \tag{8}$$

for which $R = 0.9993$. The influence of the properties of L on k_1, while small, is predominantly steric.

The poor fit for the two phosphine complexes is evident from the values of k_1 which are greater than are those for the phosphites by more than an order of magnitude. This is attributable to relatively strong pip–phosphite –P–O···H–N–Mo– hydrogen binding in the phosphites, supported by the crystal structure of *cis*-(pip)(P(OCH_3)$_3$)Mo(CO)$_4$ and discussed by Atwood and Darensbourg.[17] What is not clear is why the values for k_1 for L = P($C_6H_{12}N_3$) and P(C_6H_5)$_3$, are nearly identical (Table III), despite the very large differences in θ between them.

There is a much less significant influence of the steric properties of L for Mo than for Cr, expected based on the relative sizes of these atoms; for Cr, a *ca.* 15-fold change in rate constant is observed along the series of alkyl phosphites[16] *vs.* 2.6-fold for the Mo analogues.

Rates as a Function of L′

For reactions of *cis*-(pip)(P(OCH(CH_3)$_2$)$_3$)Mo(CO)$_4$ with various L′ (Table III), values of k_1 for the seven incoming L′ are the same, within ± 5%, as expected for a reaction step which is independent of the identity

TABLE IV Activation parameters in solution for dissociation of L″ in *fac*-(L)(L′)M(CO)$_3$ complexes (M = Cr, Mo, W)[a]

L, *L*′, *L*″ (*L*″ dissociates)	*Cr*		*Mo*		*W*		*Ref.*
	ΔH^+ (kcal/mol)	ΔS^+ (cal/K mol)	ΔH^+ (kcal/mol)	ΔS^+ (cal/K mol)	ΔH^+ (kcal/mol)	ΔS^+ (cal/K mol)	
CO, CO, CO[a]	37.6(6)	17.8(16)	30.6(3)	4.6(10)	39.9(7)	15.6(22)	7
CO, CO, CO[a]	38.6(12)	19(3)	28.4(24)	−1.5(46)	38.3(8)	11.2(18)	8
CO, $P(OCH_3)_3$, pip	29.8(2)	17.0(9)	27.9(5)	12(1)	—	—	this work, 16
CO, $P(OC_2H_5)_3$, pip	30.0(2)	19.9(7)	27.78(3)	11.99(9)	33.3(4)	16.4(12)	17, this work, 16
CO, $P(OCH(CH_3)_2)_3$, pip	29.4(4)	20(1)	27.4(4)	12(1)	28.5(1)	8.9(2)	17, this work, 16
CO, $P(OC_6H_5)_3$, pip	29.4(2)	20.0(6)	27.0(2)	12.2(6)	—	—	17, this work
CO, $P(OCH_2)_3CCH_3$, pip	29.8(2)	16.2(8)	27.4(3)	10(1)	28.7(2)	2.3(6)	17, this work, 16
CO, $P(C_6H_{12}N_3)$, pip	25.0(2)	9.3(5)	23.75(3)	3.9(3)	—	—	17, this work
CO, $P(C_6H_5)_3$, pip	—	—	26(2)	10(5)	—	—	this work
$P(C_6H_5)(CH_3)_2$	—	—	—	—	31.6(9)	15.2(13)	16
o-phen,[b] CO	26.0(16)	7(5)	25.1(12)	7.4(24)	32.9(6)	9.3(16)	31
TM-*o*-phen,[b] CO	25.2(1)	5.9(4)	—	—	—	—	31

[a]For consistency, all data were recalculated from experimental values; these data were not given for (*o*-phen)Mo(CO)$_4$.
[b]*o*-Phen = *o*-phenanthroline; TM-*o*-phen = 2,4,7,8-tetramethyl-*o*-phenanthroline.

of the incoming nucleophile. Competition ratios, k_2/k_{-1}, are the ratios of the rate constants for attack by L′ and pip, respectively, at the intermediate. Since values of k_{-1} should be the same for all L′, these ratios should reflect the discriminating abilities of L′ toward the intermediate.

The competition ratios do not differ substantially from unity for the smallest L, L′, in general decrease monotonically with increasing size of L′, and are little influenced by the electronic nature of L′ as reflected in the Tolman ν values.[22] These observations are consistent with what we might call a "fundamental" ligand-exchange mechanism, one in which pip and L′ interact at an intermediate which differs little from [(L)Mo(CO)$_4$] and for which the enthalpy of activation approaches zero. Such a mechanism would be expected to involve little discrimination of the metal carbonyl moiety among incoming nucleophiles since rates of combination of carbonylmetal fragments with L are extremely rapid (ps–fs time-scale).[24] Discrimination can result, however, where steric interactions become significant. Several X-ray structural studies of *cis*-(L)$_2$M(CO)$_4$ complexes (L = P(C$_6$H$_5$)$_{3-n}$(CH$_3$)$_n$, $n = 0, 1, 2$) support the existence of such steric interactions.[25] In contrast, the "fundamental" ligand exchange is not observed in some other systems. For example, in ligand-exchange for (RC$_6$H$_5$)Cr(CO)$_5$ complexes with linear alkenes, competition ratios vary widely and consistently with an exchange mechanism involving the alkyl chains in both RC$_6$H$_5$ and R′CH=CH$_2$.[3]

Isomerization after Ligand-Exchange

Carbonyl stretching data (Table II) indicate that both *cis*- and *trans*-(L)(L′)Mo(CO)$_4$ products are produced for all L′ except where L = P(OCH(CH$_3$)$_2$)$_3$ and L′ = P(*n*-C$_4$H$_9$)$_3$, where no isomerization is observed. The *cis* to *trans* isomerization has been studied by Darensbourg[26] and by Howell[27] and their associates, who have attributed it to a non-dissociative "twist" of three ligands about a C$_3$ axis through a trigonal prismatic transition state. It may be speculated that the accessibility of this isomerization process is hindered by intramolecular –M–P–C–H···O–P–hydrogen bonding, such as is observed in *cis*-(P(C$_6$H$_5$)$_3$)(P(OCH(CH$_3$)$_2$)$_3$)Mo(CO)$_4$.[28] This would account for the failure of *cis*-(P(*n*-C$_4$H$_9$)$_3$)(P(OCH(CH$_3$)$_2$)$_3$)-Mo(CO)$_4$ to undergo isomerization even though the *trans* isomer might be favored on steric grounds.

Activation Parameters

For the five *cis*-(pip)(L)Mo(CO)$_4$ complexes for which L is a phosphite, the activation parameters for M–pip bond-breaking are in close agreement with

one another, with $\Delta H_1^{\ddagger}$ values varying from 27.0(2) to 27.78(3) kcal/mol, with the largest experimental uncertainty of 0.4 kcal/mol. This remarkable consistency is a consequence of the very small influences of the steric and electronic nature of phosphites on reactivity via M–pip bond-breakig. These complexes are very amenable to kinetics study in comparison to the hexacarbonyls: they are non-volatile; their reactions can be studied near ambient temperature; unlike the hexacarbonyls, the concentrations of the leaving group can be fixed with certainty; they are amenable to study in the visible rather than the infrared spectral region; and values of k_1 can be obtained both directly and indirectly. The activation parameters for *cis*-(pip)($P(C_6H_5)_3$)$Mo(CO)_4$ reported by Hyde and Darensbourg[13] (Table IV) are in excellent agreement with the values reported here.

The activation parameters for the analogous Cr systems (L = phosphite) also are in very close agreement, in the ranges, $\Delta H^{\ddagger} = 29.2(2)$ to 30.0(2) kcal/mole and $\Delta S^{\ddagger} = 16.2(8)$ to 20(1) cal/K mol. At 31.1°C, values of k_1 differ little as a function of the metal and the identity of the phosphite, and are also quite similar to k_1 for L = CO, that is, for dissociation of pip from (pip)$M(CO)_5$ (M = Cr, Mo).[13]

The activation enthalpies for the W complexes[15] are less consistent; two sets, for L = $P(OCH(CH_3)_2)_3$ and $P(OCH_2)_3CCH_3$ are the same, within experimental uncertainty, but two others, for L = $P(OC_2H_5)_3$ and $P(CH_3)_2(C_6H_5)$, differ significantly from these, and fail to show the influence of –N–H···O–P– hydrogen bonding (*vide supra*). However, the free energies of activation vary over a more narrow range, differing by only 2.3(6) kcal/mol.[29] It is also to be noted that values of k_1 are much more sensitive to the identity of L, perhaps suggesting subtle mechanistic differences between W vs. Cr and Mo. Significantly more positive entropies of activation for dissociation of piperidine from Cr than from Mo in the alkyl phosphite complexes, ca. +18 vs. +11 cal/K mol, can be interpreted in terms of greater crowding about the smaller Cr atom and stronger intramolecular –N–H···O–P– binding in *cis*-(pip)(L)$Mo(CO)_4$ complexes, which would afford greater constraint in the ground state.

Table IV presents activation parameters in solution for carbonyl dissociation in systems in which they have been obtained for Cr, Mo and W hexacarbonyls,[6,7] for (*o*-phenanthroline)$M(CO)_4$ complexes[30,31] as well as for the *cis*-(pip)(L)$M(CO)_4$ complexes. A perusal of these values shows, in most instances, that enthalpies of activation along the series Cr, Mo, W do not differ greatly and are significantly smaller than are those for the hexacarbonyls in keeping with "*cis* labilization" of CO by amines.[32] The enthalpies of activation are greater for Cr by about 2 kcal/mol (7 data sets) in the most clearly-defined data, for M = Cr and Mo, for all but the

hexacarbonyls. For $Mo(CO)_6$, however, the data are quite different, with $\Delta H_1^{\neq}$ some 7–10 kcal/mole less for Mo than for Cr.[6,7] Moreover, while the entropies of activation for almost all substituted Cr and Mo complexes are highly positive, for $Mo(CO)_6$ it is about zero.

If data for $Cr(CO)_6$ and $Mo(CO)_6$ were to be comparable with the data for the substituted complexes, one would anticipate both their enthalpies and entropies of activation to be more similar. One cannot rule out a less positive entropy of activation for $Mo(CO)_6$ than for the *cis*-(pip)(L)Mo-$(CO)_4$ systems (L = phosphite) because of the expectation of less release of steric strain in the hexacarbonyls. However, this effect is not observed for Cr in $Cr(CO)_6$, where one would anticipate it to be more important.[7] Note that the enthalpy of activation for CO dissociation from $Mo(CO)_6$ in the gas phase reported by Golden and co-workers, 40.5(30) kcal/mol,[11] is more in line with the *cis*-(pip)(L)$Mo(CO)_4$ results. The presence of intramolecular hydrogen bonding in the (pip)(L)$Mo(CO)_4$ complexes (L = phosphite) means that activation enthalpies obtained for them do not directly reflect Mo–pip bond-strengths.

The preceding discussion suggests that the energetics for CO dissociation from $Mo(CO)_6$ in solution is anomalous when compared to those for other Mo carbonyl systems, or that the enthalpy of activation reported for CO dissociation from $Mo(CO)_6$ may be larger, and the entropy of activation more positive than has been reported;[6,7] those data were taken over a relatively narrow temperature range (13° in each report).[7,8] In any event, where data from which activation parameters are taken are not very extensive, reported activation parameters should be viewed with circumspection. Where enthalpies of activation are to be employed to estimate bond-strengths, the structures of the reacting species and a detailed knowledge of the ligand exchange must be considered. It will be important to re-investigate appropriate previously studied systems.

Supplementary Material

Values of rate constants for the reactions are available from the authors on request.

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