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LIGAND DISSOCIATION FROM MONO-SUBSTITUTED DERIVATIVES OF HEXACARBONYLCHROMIUM $\text{Cr}(\text{CO})_5\text{L}$, $\text{L} = \text{P}(\text{C}_6\text{H}_5)_3$, $\text{P}(\text{C}_4\text{H}_9)_3$, $\text{P}(\text{OCH}_3)_3$, $\text{P}(\text{OC}_6\text{H}_5)_3$, AND $\text{As}(\text{C}_6\text{H}_5)_3$

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Summary

The rates of dissociation of the unique ligand from $\text{Cr}(\text{CO})_5\text{L}$ have been determined for $\text{L} = \text{P}(\text{C}_6\text{H}_5)_3$, $\text{P}(\text{OC}_6\text{H}_5)_3$, $\text{P}(\text{OCH}_3)_3$, and $\text{As}(\text{C}_6\text{H}_5)_3$ by reaction with CO. The reactions were investigated from 80–140°C and activation parameters were determined. The rate data were fully consistent with rate-determining dissociation of the ligand L. The order of ligand lability is $\text{As}(\text{C}_6\text{H}_5)_3 > \text{P}(\text{C}_6\text{H}_5)_3 > \text{P}(\text{OC}_6\text{H}_5)_3 > \text{P}(\text{OCH}_3)_3$. For $\text{L} = \text{P}(\text{C}_4\text{H}_9)_3$ an equilibrium was observed and the equilibrium constant evaluated at 140 and 170°C. The equilibrium greatly favors $\text{Cr}(\text{CO})_5\text{P}(\text{C}_4\text{H}_9)_3$ as the product. These studies allow the ligand binding to be compared quantitatively for these complexes. An activation of the Cr–P bond by room light has been noted.

Introduction

Ligand dissociation of a two electron ligand from eighteen-electron species leading to sixteen-electron intermediates plays a very important role in reactions of organometallic compounds and in homogeneous catalysis [1,2]. Carbon monoxide dissociation occurs in reactions of $\text{Ni}(\text{CO})_4$ [3], $\text{Mn}(\text{CO})_5\text{Br}$ [4], $\text{Cr}(\text{CO})_6$ [5], $\text{Ru}_3(\text{CO})_{12}$ [6], and $\text{Os}_3(\text{CO})_{12}$ [7], phosphite and phosphine dissociation from NiL_4 [8] and in catalytic reactions of $\text{Rh}(\text{P}(\text{C}_6\text{H}_5)_3)_3\text{Cl}$ [9,10] and $\text{C}_3\text{H}_5\text{Co}(\text{P}(\text{OCH}_3)_3)_3$ [11], and amine dissociation from $\text{Cr}(\text{CO})_5$ -(amine) [12]. Detailed studies of carbon monoxide dissociation have provided information about reactivities of transition metal carbonyl complexes and stabilities of sixteen-electron intermediates [13–15], but there have been relatively few systematic studies of dissociation of different ligands from organometallic complexes.

An early kinetics study of ligand exchange with $\text{Ni}(\text{CO})_2\text{L}_2$ showed first order kinetics, indicating a rate-determining dissociation of L [16]. The rates of disso-

ciation were in the order $\text{PCl}_3 > \text{P}(\text{C}_6\text{H}_5)_3 > \text{P}(\text{C}_4\text{H}_9)_3 > \text{P}(\text{OC}_6\text{H}_5)_3$ [11], which parallels neither σ -donating nor π -accepting capabilities. A study of dissociation of ligands from $\text{Cr}(\text{CO})_3(\text{phen})\text{L}$, phen = *o*-phenanthroline, provided quantitative data on rates of dissociation of $\text{P}(\text{C}_4\text{H}_9)_3$ and $\text{P}(\text{OC}_2\text{H}_5)_3$ and qualitative observations on $\text{P}(\text{C}_6\text{H}_5)_3$ and $\text{P}(\text{OC}_6\text{H}_5)_3$ [17]. The rates of dissociation were not very different, all within a factor of ten, but gave an order of Cr—L bond strengths in $(\text{phen})\text{Cr}(\text{CO})_3\text{L}$ as $\text{P}(\text{C}_4\text{H}_9)_3 > \text{P}(\text{OC}_2\text{H}_5)_3 > \text{CO} > \text{P}(\text{OC}_6\text{H}_5)_3 > \text{P}(\text{C}_6\text{H}_5)_3$. It was suggested from these data that ligand basicity (σ donor ability) was the predominant factor in the binding of these ligands.

The rates of dissociation of a series of amines were obtained from a study of the decomposition of $\text{M}(\text{CO})_5\text{amine}$ compounds [12], where the basicity was found to be the predominant factor although aromatic amines had additional stability. The rate of dissociation from NiL_4 , which has very large steric interactions, has provided a measure of the steric contribution of the ligands as the "cone angle" [8]. It is surprising that the π -bonding ability of these ligands is not important in the dissociative process.

We have studied the dissociation of ligands from $\text{Cr}(\text{CO})_5\text{L}$ ($\text{L} = \text{P}(\text{C}_6\text{H}_5)_3$, $\text{P}(\text{C}_4\text{H}_9)_3$, $\text{P}(\text{OCH}_3)_3$, $\text{P}(\text{OC}_6\text{H}_5)_3$, and $\text{As}(\text{C}_6\text{H}_5)_3$). These complexes can be readily prepared and the rates conveniently studied between 80–140°C (eq. 1).



Carbon monoxide is selected as the entering ligand for several reasons: (1) The product, $\text{Cr}(\text{CO})_6$, is easily distinguished from the starting $\text{Cr}(\text{CO})_5\text{L}$ complexes by infrared spectroscopy. (2) The possibility of nucleophilic attack upon the complex is minimized. (3) The analysis is not complicated by products arising from CO dissociation. The complexes $\text{Cr}(\text{CO})_5\text{L}$ were selected for this study to minimize steric effects on the rate of dissociation. The ligands investigated encompass a range of σ and π bonding capabilities which can be extended further by comparison with $\text{Cr}(\text{CO})_6$ and $\text{Cr}(\text{CO})_5\text{amine}$. The ligands investigated are also often involved in homogeneous catalysts.

Experimental

Materials. Decane was purified before use by stirring with H_2SO_4 , washing with water, passing down an alumina column, and storing over sodium. All other reagents were used as obtained from commercial sources.

$\text{Cr}(\text{CO})_5\text{P}(\text{C}_6\text{H}_5)_3$ was synthesized as previously described [18]. The melting point was 126–127°C (reported 127–128°C) [18]. The infrared spectrum is described in Table 1. Microanalysis showed C, 60.1; H, 3.4 (calcd.: C, 60.8; H, 3.3%).

$\text{Cr}(\text{CO})_5\text{As}(\text{C}_6\text{H}_5)_3$ was synthesized by the procedure of Connor et al. [19]. The melting point was 135–136°C (reported 135–135.5°C) [18]. The infrared spectrum is described in Table 1. Microanalysis showed C, 54.0; H, 3.1. (calcd.: C, 55.4; H, 3.0%).

The procedure of Connor et al. [19] was altered for the synthesis of $\text{Cr}(\text{CO})_5\text{-P}(\text{OC}_6\text{H}_5)_3$. Aluminium trichloride was added to a CH_2Cl_2 solution of $\text{Cr}(\text{CO})_5\text{Cl}^-$ and stirred for 10 minutes. The solution became red-orange. Addition of $\text{P}(\text{OC}_6\text{H}_5)_3$ and rapid removal of solvent minimized production of $\text{Cr}(\text{CO})_4(\text{P}(\text{OC}_6\text{H}_5)_3)_2$. The

TABLE 1
 CARBONYL STRETCHING FREQUENCIES ^a OF Cr(CO)₅L IN DECANE

L	A ₁ (radial) (cm ⁻¹)	E (cm ⁻¹)	A ₁ (axial) (cm ⁻¹)
P(<i>n</i> -C ₄ H ₉) ₃	2061w	1936s	1944m
P(C ₆ H ₅) ₃	2066w	1945s	1945s
As(C ₆ H ₅) ₃	2067w	1946s	1946s
P(OCH ₃) ₃	2075w	1950s	1965m
P(OC ₆ H ₅) ₃	2078w	1960s	1969m

^a s, strong; m, moderate; w, weak.

product was recrystallized from C₂H₅OH/H₂O yielding white crystals. Micro-analysis showed C, 54.9; H, 2.9; Cr, 10.1 (calcd.: C, 55.0; H, 3.0; Cr, 10.3%). The infrared spectrum is reported in Table 1. The complex is extraordinarily soluble in hexane, i.e. 1 g Cr(CO)₅P(OC₆H₅)₃ will dissolve in 2 ml hexane.

The procedure described above was used for synthesis of Cr(CO)₅P(OCH₃)₃. This white material crystallized from hexane solution at -78°C. The hexane was poured off and the solid washed with cold hexane. This material is a liquid at room temperature (reported melting point is 0-5°C) [19]. The infrared spectrum is reported in Table 1.

Cr(CO)₅P(C₄H₉)₃ was prepared by the procedure described for P(OC₆H₅)₃. A green liquid was obtained (reported as a chartreuse liquid) [18]. Attempts to crystallize the green liquid failed. Elution of the liquid with hexane on an alumina column gave a yellow liquid with a green band remaining on the column. The infrared spectrum is described in Table 1.

Kinetics measurements. Infrared spectra were measured on a Perkin-Elmer 521 infrared spectrophotometer in the absorbance mode using 1.0 mm NaCl solution cells. Linear Beer's law plots with hexane as solvent were constructed for Cr(CO)₆, Cr(CO)₅P(C₆H₅)₃, Cr(CO)₅P(OC₆H₅)₃, and Cr(CO)₅As(C₆H₅)₃. Beer's law plots of the species, Cr(CO)₅P(C₄H₉)₃ and Cr(CO)₅P(OCH₃)₃, which are liquids at room temperature, were not attempted. At least five solutions were prepared for each plot and in all cases the line passed through the origin. The slope of this line gives the extinction coefficient; these values for Cr(CO)₆, Cr(CO)₅P(C₆H₅)₃, Cr(CO)₅P(OC₆H₅)₃, and Cr(CO)₅As(C₆H₅)₃ are 4.40×10^4 , 2.13×10^3 , 1.37×10^3 , and 2.24×10^3 M⁻¹, respectively. All kinetic studies were carried out in a foil-wrapped 100 ml 2-necked jacketed reaction flask equipped with a rubber septum to allow sample removal via syringe. A Haake fs circulator maintained a constant jacket temperature and the solution was constantly stirred with a magnetic stirrer.

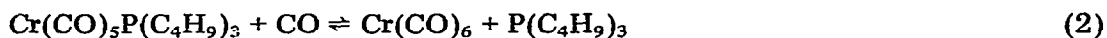
Typically, 25 ml decane and approximately 5×10^{-3} g sample were put into the reaction flask which was then connected to a carbon monoxide Schlenk manifold. After evacuation, the flask was filled with a carbon monoxide atmosphere which was maintained throughout the experiment. At appropriate time intervals, a 0.5 ml portion of sample was removed and the IR spectrum was immediately recorded. By observing the disappearance of the most intense carbonyl stretching frequency (E mode) over the course of the experiment, rate constants, for each reaction were determined. It was noted that Cr(CO)₆,

the product in each reaction, sublimed out of solution and deposited onto the walls of the reaction flask. This made it impossible to follow the kinetics by observing the appearance of $\text{Cr}(\text{CO})_6$. Linear plots of $\ln(A_t - A_\infty)$ vs. time were constructed, where A_t is the absorbance at time t , A_∞ is the absorbance at infinite time, and the slope of the line corresponds to the first-order rate constant. Calculations were performed on a Hewlett-Packard 97 calculator programmed with a modified curve fitting program.

Equilibrium measurements. A rate constant for dissociation of $\text{P}(\text{C}_4\text{H}_9)_3$ was not determined because of an equilibrium between reactants and products. This equilibrium was confirmed by the following experiment. Approximately 10^{-4} g of $\text{Cr}(\text{CO})_5\text{P}(\text{C}_4\text{H}_9)_3$ was dissolved in 10 ml decane and put into a glass tube with a tapered end to permit sealing. The tube was evacuated and then filled with a carbon monoxide atmosphere. It was then dipped into liquid nitrogen until the solvent had solidified. After sealing of the tube, it was placed in an oven set at 170°C for 10 days. From the IR spectrum an equilibrium was clearly present since only a small percentage of the starting material was converted to $\text{Cr}(\text{CO})_6$. The equilibrium constant was also evaluated at 140°C for 21 days in the same manner.

Results

The reaction of each complex with carbon monoxide was investigated at three different temperatures. The first order rate constants for each complex are reported in Table 2. It proved impossible to evaluate a rate for the reaction of $\text{Cr}(\text{CO})_5\text{P}(\text{C}_4\text{H}_9)_3$ with CO. The reaction did not progress at 140°C . Evaluation of an equilibrium constant for reaction 2 was accomplished at 170°C . An estimate



of the equilibrium constant was calculated by the following considerations. At equilibrium, $[\text{Cr}(\text{CO})_6] = [\text{P}(\text{C}_4\text{H}_9)_3]$. The concentration of $\text{Cr}(\text{CO})_6$ was calculated by dividing the absorbance by the extinction coefficient. Because of the large intensity of the E mode for $\text{Cr}(\text{CO})_5\text{P}(\text{C}_4\text{H}_9)_3$, an estimate of $[\text{Cr}(\text{CO})_5\text{P}(\text{C}_4\text{H}_9)_3]$ was calculated. The relation between the A_1 mode intensity and the E mode

TABLE 2
FIRST-ORDER RATE CONSTANTS FOR LIGAND DISSOCIATION FROM $\text{Cr}(\text{CO})_5\text{L}$

L	Temp ($^\circ\text{C}$)	$10^6 k$ (sec^{-1})
$\text{As}(\text{C}_6\text{H}_5)_3$	80	16.7 \pm 0.7
	90	70.7 \pm 3.5
	95	144 \pm 9
$\text{P}(\text{C}_6\text{H}_5)_3$	110	8.91 \pm 0.42
	120	29.1 \pm 1.2
	130	99.7 \pm 6.1
$\text{P}(\text{OC}_6\text{H}_5)_3$	120	5.69 \pm 0.56
	130	15.6 \pm 0.8
	140	43.1 \pm 3.1
$\text{P}(\text{OCH}_3)_3$	130	0.548 \pm 0.038

TABLE 3
ACTIVATION PARAMETERS ^a

L	ΔH^\ddagger (kcal mol ⁻¹)	ΔS^\ddagger (cal mol ⁻¹ deg ⁻¹)	ΔG^\ddagger (kcal mol ⁻¹)
As(C ₆ H ₅) ₃	36.3 ± 0.4	22.2 ± 1.2	27.4 ± 0.5
P(C ₆ H ₅) ₃	36.3 ± 1.9	12.5 ± 4.8	31.3 ± 2
P(OC ₆ H ₅) ₃	31.9 ± 1.1	-2.0 ± 2.6	32.7 ± 1.1
CO ^b	40.2 ± 0.6	22.6 ± 1.5	31.2 ± 0.7
Pyridine ^c	25.4 ± 1.1	3.1 ± 3.5	24.1 ± 1.3

^a Error limits represents 95% confidence limits. ^b Ref. 5. ^c Ref. 12.

intensity is approximately $E = 3.88 A + 0.11$ where E is the E mode intensity and A is the A_1 mode intensity. The extinction coefficient for $\text{Cr}(\text{CO})_5\text{P}(\text{C}_6\text{H}_5)_3$ is estimated to be 2×10^3 which, when divided into the absorbance gives $[\text{Cr}(\text{CO})_5\text{P}(\text{C}_6\text{H}_5)_3]^*$. The CO concentration at 170°C was estimated to be $1 \times 10^{-3} M$ by plotting $\ln([\text{CO}])$ vs. temperature using the CO solubility data of Cetini et al. [20]. From an average of three runs, the K_{eq} is estimated to be $1.3 \pm 0.2 \times 10^{-4}$ at 170°C. Evaluation at 140°C for 21 days gave a value of $5.3 \pm 1 \times 10^{-5}$ for K_{eq} .

Activation parameters were determined for the dissociation of $\text{P}(\text{C}_6\text{H}_5)_3$, $\text{P}(\text{OC}_6\text{H}_5)_3$, and $\text{As}(\text{C}_6\text{H}_5)_3$. These parameters are reported in Table 3.

Discussion

$L = \text{P}(\text{C}_6\text{H}_5)_3, \text{P}(\text{OC}_6\text{H}_5)_3, \text{As}(\text{C}_6\text{H}_5)_3, \text{ and } \text{P}(\text{OCH}_3)_3$. The reaction under consideration is:



Several pieces of evidence indicate a reaction first order in $\text{Cr}(\text{CO})_5\text{L}$ and zero order in CO. The plots of $\ln(A_t - A_\infty)$ versus time are linear for several half lives for each of the complexes. The rates of reactions are independent of the concentration of CO and added ligand. These data are consistent with a rate-determining dissociation of the unique ligand leading to a sixteen-electron intermediate, $\text{Cr}(\text{CO})_5$. The intermediate then rapidly reacts with CO to form $\text{Cr}(\text{CO})_6$. Carbon monoxide dissociation may also occur leading to $\text{Cr}(\text{CO})_4\text{L}$ but this intermediate would add CO to regenerate the complex, $\text{Cr}(\text{CO})_5\text{L}$. This reaction would not interfere with our kinetics study **. We found no evidence for the equilibrium 4 for $L = \text{P}(\text{C}_6\text{H}_5)_3, \text{P}(\text{OC}_6\text{H}_5)_3, \text{P}(\text{OCH}_3)_3, \text{ and } \text{As}(\text{C}_6\text{H}_5)_3$. The complex that dissociates the unique ligand most slowly, $\text{Cr}(\text{CO})_5$ -



$\text{P}(\text{OCH}_3)_3$, was stored under CO atmosphere for 10 days at 170°C. The solution

* The value 2×10^3 was used as the average of the extinction coefficients for the other $\text{Cr}(\text{CO})_5\text{L}$ species. The value was remarkably constant for the ligands $\text{P}(\text{C}_6\text{H}_5)_3, \text{P}(\text{OC}_6\text{H}_5)_3, \text{ and } \text{As}(\text{C}_6\text{H}_5)_3$.

** This could enter into the kinetics if L is readily lost from the $\text{Cr}(\text{CO})_4\text{L}$ intermediate. We consider this unlikely since it would generate a 14-electron species in the presence of nucleophiles.

TABLE 4
KINETIC, ELECTRONIC, SPECTROSCOPIC, AND STRUCTURAL PARAMETERS FOR L

L	$10^6 k^a$	ΔHNP^b	IR (cm^{-1}) ^c	Bond length (Å) ^d	^{31}P shift (ppm) ^e	^{13}C shift (ppm) ^f	Cone angle ^g
P(<i>n</i> -C ₄ H ₉) ₃	131	—	1936	—	—62.5	-221.1	130 ± 4
P(OCH ₃) ₃	0.548	520 ^j	1950	—	-38.6 ^l	-219.1	107 ± 2
P(OC ₆ H ₅) ₃	15.7	875	1960	1.861	—	-218.2	121 ± 10
P(C ₆ H ₅) ₃	99.7	573	1945	1.845	-61.3	-221.2	145 ± 2
CO	130 ^h	—	1985	1.909 ^k	—	-211.3	—
As(C ₆ H ₅) ₃	11600 ⁱ	—	1946	—	—	-222.1	142 ± 5 ^m

^a First-order rate constants at 130°C. ^b The difference in half-neutralization potential between L and N,N'-diphenylguanidine [33]. ^c Infrared carbonyl stretching frequencies of the E mode of Cr(CO)₃L in decane. ^d Cr-C bond lengths of the carbonyl *trans*-L. [26]. ^e Coordination chemical shift, δ complex - δ ligand [28]. ^f ^{13}C NMR chemical shifts [30]. ^g Ref. 8. ^h Ref. 5. ⁱ This value has been determined by extrapolation of the experimental data. ^j This is the value for P(O-*n*-C₄H₉)₃ [32]. ^k Ref. 34. ^l Ref. 29. ^m Ref. 35.

showed no evidence for $\text{Cr}(\text{CO})_5\text{P}(\text{OCH}_3)_3$ after this reaction. The only species present was $\text{Cr}(\text{CO})_6$.

The rates observed for ligand dissociation span a wide range as shown in Table 2. This is in contrast to the previous studies where the rates were within a factor of 10 [17]. For ease of comparison the rate constants for dissociation of L at 130°C are presented in Table 4. The order of lability is $\text{As}(\text{C}_6\text{H}_5)_3 > \text{P}(\text{C}_6\text{H}_5)_3 \sim \text{CO} > \text{P}(\text{OC}_6\text{H}_5)_3 > \text{P}(\text{OCH}_3)_3$. This order is similar to that obtained in previous observations on dissociation of phosphine and phosphite ligands [16,17].

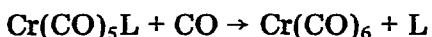
The activation parameters are presented in Table 3. The literature values for L = CO [5] and pyridine [12] are included for comparison. The activation entropies show changes from ligand to ligand which are not consistent with steric size, σ -bonding ability, or π -bonding ability. The entropies of activation are all positive (with the exception of the value for dissociation of $\text{P}(\text{OC}_6\text{H}_5)_3$ which is near zero) and range in value from 22 $\text{cal mol}^{-1} \text{deg}^{-1}$, which clearly indicates a dissociative process to values close to zero, suggestive of a transition state with significant interactions of the dissociating ligand with the $\text{Cr}(\text{CO})_5$ species in the transition state.

$\text{P}(\text{C}_4\text{H}_9)_3$. The complex, $\text{Cr}(\text{CO})_5\text{P}(\text{C}_4\text{H}_9)_3$, was unique among those investigated, in that there was an equilibrium established (eq. 5) greatly favoring

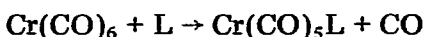


$\text{Cr}(\text{CO})_5\text{P}(\text{C}_4\text{H}_9)_3$ even though the concentration of CO was much greater than that of $\text{P}(\text{C}_4\text{H}_9)_3$. The value of the equilibrium constant, 1.3×10^{-4} , shows the marked preference for $\text{Cr}(\text{CO})_5\text{P}(\text{C}_4\text{H}_9)_3$ as a product. It is clear that $\text{P}(\text{C}_4\text{H}_9)_3$, the strongest σ donor ligand, is strongly bound to the chromium.

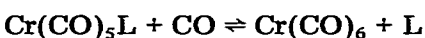
Energy profiles. The reaction which we have studied:



is the reverse of the normal ligand substitution of L for CO [5]:



We may consider these two reactions as an equilibrium:



which can be shifted in either direction depending on the concentrations of L and CO. Application of the principle of microscopic reversibility suggests that the energy profile traversed in the forward direction is the reverse of that for the reaction of $\text{Cr}(\text{CO})_6$ with L [21,22]. Thus, the transition state must be identical for the forward and reverse reactions. The activation parameters for CO dissociation from $\text{Cr}(\text{CO})_6$ are known and we have evaluated the activation parameters for L dissociation from $\text{Cr}(\text{CO})_5\text{L}$. As shown in Fig. 2 the difference in free energies of activation provides the quantitative difference in ground state free energies, thus the free energy change for the reaction, ΔG_{rxn} . By carrying through the analysis for each ligand one can generate a quantitative ordering of ground state free energies. Similarly one can calculate the enthalpy change for the reaction, ΔH_{rxn} , and the entropy change for the reaction, ΔS_{rxn} . These

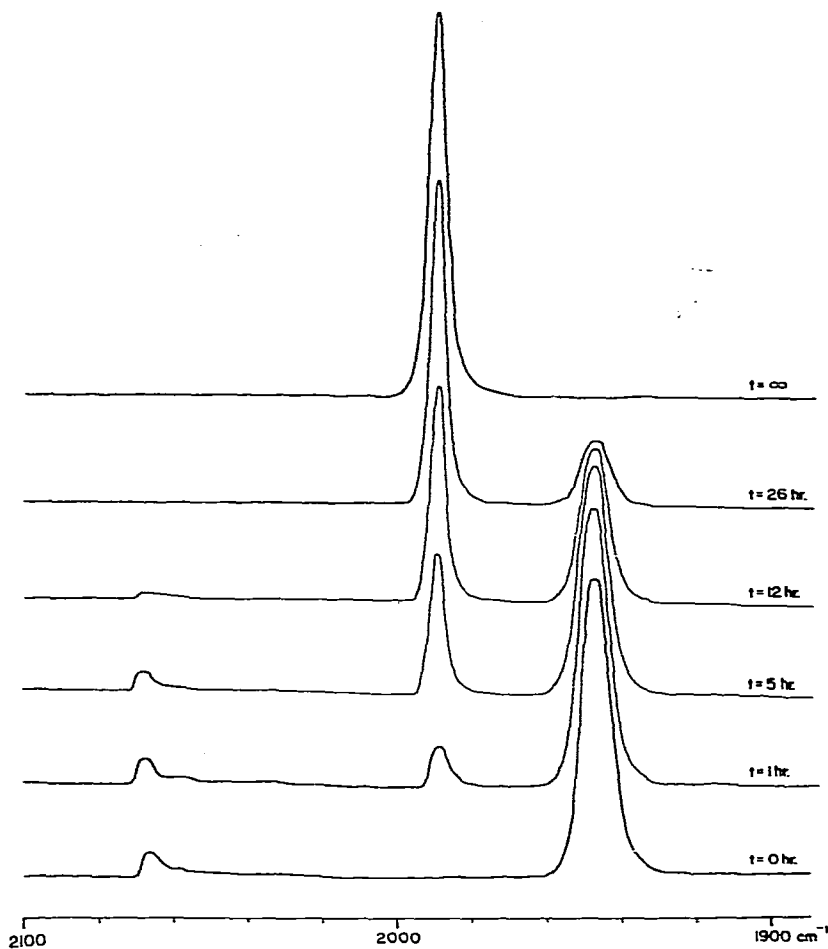


Fig. 1. Infrared spectra for the reaction of $\text{Cr}(\text{CO})_5\text{As}(\text{C}_6\text{H}_5)_3$ with CO at various times.

values for the different ligands are given in Table 5. The differences in free energy for the reaction, ΔG_{rxn} , exactly parallel the rates of dissociation and suggest that kinetic studies provide an accurate measure of the energy of reaction of this type of complex. A linear-free-energy relationship was found between ΔG^\ddagger and G_{rxn} as shown in Figure 3. This relationship (slope = 1) for the series of different ligands implies that there is no binding of the ligand L in the transition state. Our experiment provides no information on the energy difference between the transition state and the five-coordinate intermediate. If the energy difference is significant then the ΔG^\ddagger correlation with ΔG_{rxn} allows us to distinguish between the energy profiles in Fig. 2. The lack of ligand interaction in the transition state would only be consistent with profile c. In the case of very small stabilization of the intermediate with respect to the transition state it would be difficult to distinguish between profiles a, c, and d.

A quantitative relative ordering of the ground state free energies of the compounds $\text{Cr}(\text{CO})_6$, $\text{Cr}(\text{CO})_5\text{P}(\text{C}_6\text{H}_5)_3$, $\text{Cr}(\text{CO})_5\text{P}(\text{OC}_6\text{H}_5)_3$, $\text{Cr}(\text{CO})_5\text{As}(\text{C}_6\text{H}_5)_3$, and $\text{Cr}(\text{CO})_5\text{py}$ is shown in Fig. 4. Since the $\text{Cr}(\text{CO})_5$ unit is very little changed

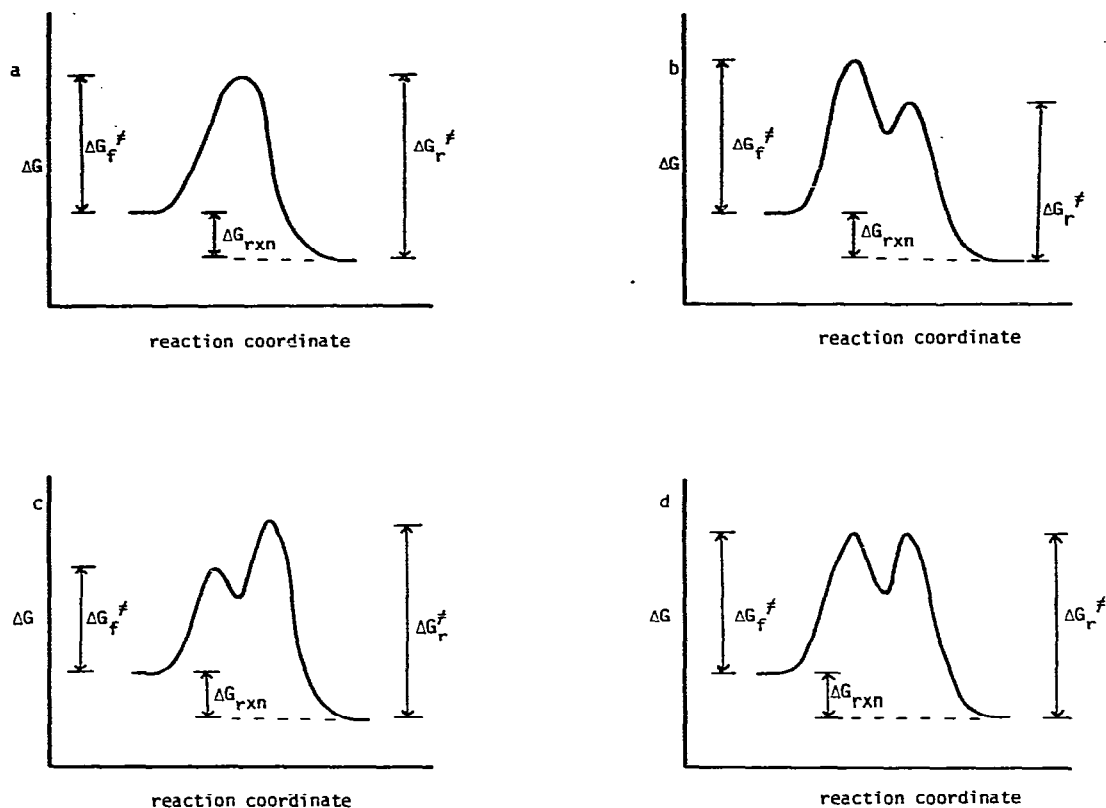


Fig. 2. Possible energy profiles for the reaction of $\text{Cr}(\text{CO})_5\text{L}$ with CO : (a) shows a transition state with no energy lowering for the intermediate $\text{Cr}(\text{CO})_5$; (b) shows a transition state before formation of the intermediate probably with a $\text{Cr}\cdots\text{L}$ interaction; (c) shows a transition state after the formation of $\text{Cr}(\text{CO})_5$ which has a $\text{Cr}\cdots\text{CO}$ interaction; (d) shows a profile with the reaction of the intermediate proceeding with equal facility in either direction.

by the different ligands, these free energies may be used as a measure of the $\text{Cr}-\text{L}$ binding strengths. It is interesting that $\text{P}(\text{C}_6\text{H}_5)_3$ binds to the Cr with nearly the same energy as CO despite the rather marked difference in σ and π bonding ability and steric size. There is considerable literature precedent which

TABLE 5
ENERGY CHANGES FOR THE REACTION $\text{Cr}(\text{CO})_5\text{L} + \text{CO} \rightarrow \text{Cr}(\text{CO})_6 + \text{L}$ AT 130°C ^a

L	ΔG_{rxn} (kcal/mol ⁻¹)	ΔH_{rxn} (kcal/mol ⁻¹)	ΔS_{rxn} (eu)	K_{eq}
$\text{As}(\text{C}_6\text{H}_5)_3$	-3.8	-3.9	-0.4	120
$\text{P}(\text{C}_6\text{H}_5)_3$	0.1	-3.9	-10.1	0.88
$\text{P}(\text{OC}_6\text{H}_5)_3$	1.5	-8.3	-24.6	0.15
$\text{P}(\text{C}_4\text{H}_9)_3$	8.1			4.2×10^{-5}
CO ^b	0.0	0.0	0.0	1.0
Py ^c	-7.1	-14.8	-19.5	7.1×10^3

^a Error limits represent 95% confidence limits. ^b Ref. 5. ^c Ref. 12.

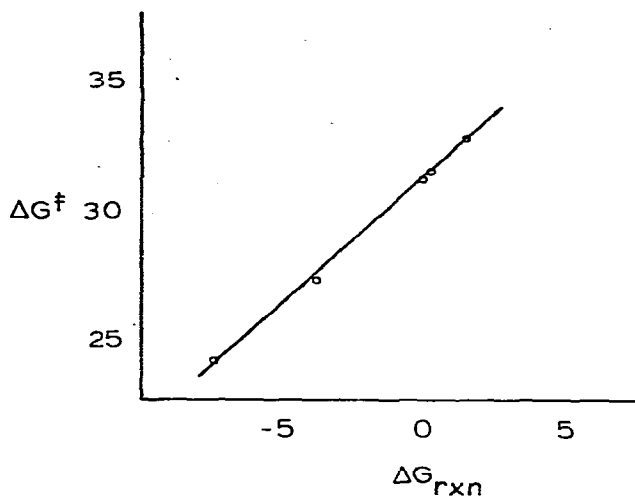


Fig. 3. A linear free energy relationship for $\Delta G_{\text{rxn}}^{\circ}$ and ΔG^{\ddagger} .

suggests that the relative ordering is quite general. It has been noted that complexes which react with phosphines and phosphites often fail to react with $\text{As}(\text{C}_6\text{H}_5)_3$ or pyridine [23]. Dobson reported $\text{W}(\text{CO})_5\text{Sb}(\text{C}_6\text{H}_5)_3$ to be 7.7 kcal lower in enthalpy than $\text{W}(\text{CO})_5(\text{aniline})$ [24]. Comparison of our values for $\text{Cr}(\text{CO})_5\text{As}(\text{C}_6\text{H}_5)_3$ and $\text{Cr}(\text{CO})_5\text{py}$ (10.9 kcal) shows reasonable agreement.

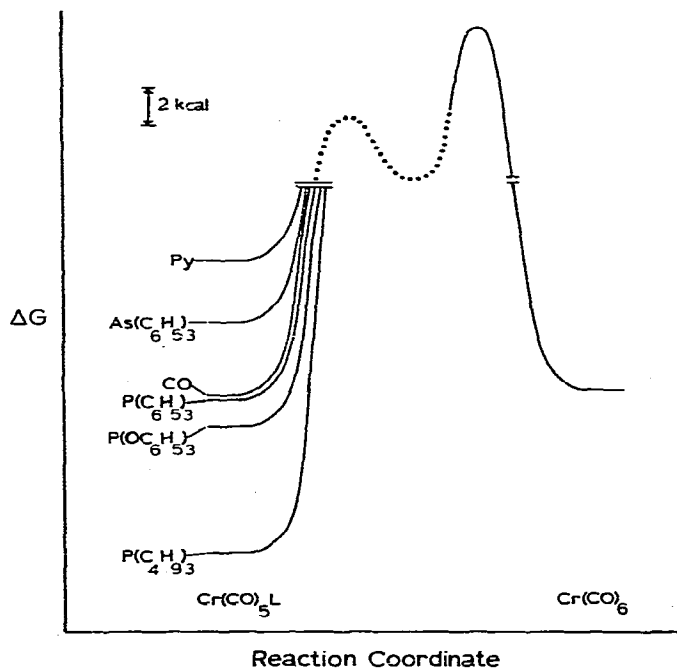


Fig. 4. The quantitative relative ground state energies for the ligands py, $\text{As}(\text{C}_6\text{H}_5)_3$, $\text{P}(\text{C}_6\text{H}_5)_3$, CO, $\text{P}(\text{OC}_6\text{H}_5)_3$, and $\text{P}(\text{C}_4\text{H}_9)_3$. The dotted line indicates an area of uncertainty about the magnitude of the free energy.

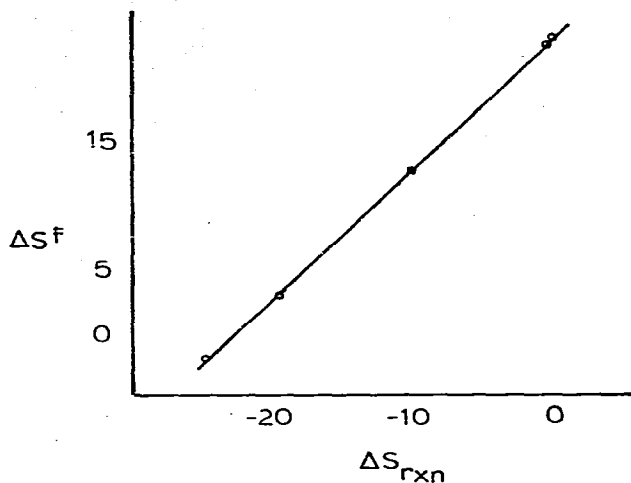


Fig. 5. Correlation of ΔS_{rxn} and ΔS^\ddagger .

Examination of the thermodynamics and activation parameters shows that the entropy change exerts a major influence on the free energy change during the reaction. The entropies of reaction are all negative as expected for a reaction where a gaseous molecule is coordinated and no gases are evolved. We suggest that the differences are a result of more freedom of movement by the ligand when not coordinated. Ligands such as $P(OC_6H_5)_3$ and py would not have as much difference in movement between the coordinated and free ligand as would $P(C_6H_5)_3$ and $As(C_6H_5)_3$ which are much more restricted in the complex such that rotation of the phenyl rings is inhibited. An excellent correlation (slope = 1) was observed between ΔS_{rxn} and ΔS^\ddagger (Fig. 5) for the different ligands again suggesting little ligand interaction in the transition state. The enthalpies of reaction are also negative for all of the ligands, but are small and seem to bear little relationship to the rates of dissociation.

Ligand bonding. Bonding of the ligands studied here involves both steric and electronic considerations. A measure of the steric requirement is given by the cone angle, obtained from molecular models [8]. A listing of the pertinent cone angles is given in Table 4. The cone angle is the best relative measure of steric size available although a recent crystal structure determination has shown that the cone angle measured may be considerably different than that obtained from models [25]. The correlation between rates and cone angles as shown in Table 4 is not good. We believe that the observed rates for dissociation of L from $Cr(CO)_5L$ are not greatly influenced by the steric requirements of the ligand L. Crystal structure determinations have been accomplished on $Cr(CO)_5P(C_6H_5)_3$ and $Cr(CO)_5P(OC_6H_5)_3$ [26]. A steric interaction should be reflected in the angle between the *cis* carbon monoxide and phosphorus. The average angles are very similar for the complexes, 91.6° for $Cr(CO)_5P(C_6H_5)_3$ and 91.7° for $Cr(CO)_5P(OC_6H_5)_3$, although the rates of dissociation are different by a factor of 6. In addition the cone angles for $P(C_6H_5)_3$ and $As(C_6H_5)_3$ are almost identical yet the rates are different by a factor of 100.

There have been a number of methods devised to evaluate the electronic

binding properties of phosphines and phosphites. In Table 4 we have a comparison of the rates of dissociation with the half-neutralization potential (HNP) [5], infrared frequency of the trans carbonyl [27], bond length of the trans carbonyl [26] ^{31}P NMR shift [28,29] and ^{13}C NMR shift of the trans CO [30]. The trans carbonyl was chosen for these comparisons because it should be most affected by the unique ligand. The HNP is a measure of the basicity to a proton, a measure of the σ donating ability of the ligand. There is no correlation between this parameter and the rate of dissociation we have measured. There is possibly an inverse correlation between the rate of dissociation of the unique ligand and the Cr—C bond length for the trans CO. The trans-Cr—C bond should reflect the π -bonding capabilities of the ligand, the weaker π -bonding ligand giving a stronger Cr—C bond in the trans position although sigma bonding could also be involved. Unfortunately there are not sufficient data for a proper correlation with the kinetic data. The ^{31}P NMR chemical shift data are reported to reflect a combination of sigma and π -bonding. The correlation with the rate data is poor. The ^{13}C chemical shift also shows no correlation with the rate constants. Each of the parameters shown in Table 4 reflects a specific aspect of the binding; σ -donation, π -acceptance, or steric size. Any one of these is insufficient to describe the binding of these ligands. The binding is a mix of each of these factors. However, only a kinetics study can properly reflect the overall binding strength of the various ligands studied.

The position of $\text{P}(\text{C}_4\text{H}_9)_3$ is anomalous in the ordering of rates of dissociation. The other tightly bound ligands are excellent π -acceptors with relatively weak sigma-bonding capability while $\text{P}(\text{C}_4\text{H}_9)_3$ is an efficient σ donor with only slight π -bonding abilities yet it is the most strongly bound. Perhaps the ligand which is efficient at either accepting or donating electrons perturbs the metal center and creates a stronger synergistic effect than ligands which are only moderate in donating or acceptance. Of the ligands which dissociate most slowly, $\text{P}(\text{C}_4\text{H}_9)_3$ is a very strong donor ligand, $\text{P}(\text{OCH}_3)_3$ is a strong donor and acceptor, and $\text{P}(\text{OC}_6\text{H}_5)_3$ is a very strong acceptor. Carbon monoxide is a strong π -acceptor, $\text{P}(\text{C}_6\text{H}_5)_3$ is a moderate donor and acceptor, and $\text{As}(\text{C}_6\text{H}_5)_3$ is a weak donor and acceptor. The amines, which dissociate very rapidly, are weak donors with no capability for π -acceptance.

A recent study by Darendbourg has shown that phosphorus—metal bonds are activated by UV light similar to the activation observed for CO dissociation [31]. We have observed that room light activates the Cr—P bond towards dissociation. The activation was most pronounced for phosphites. By contrast the Cr— $\text{As}(\text{C}_6\text{H}_5)_3$ bond shows no activation by room light. That metal—phosphorus bonds are activated towards dissociation by room light suggest that great care should be exercised in mechanistic studies on catalysts containing phosphites and phosphines.

This kinetics study lays a foundation for further studies with more highly substituted complexes which will more closely resemble catalytic systems. We have provided a quantitative ordering of bond strengths in phosphines, phosphites, and arsines, which will be useful in selecting labile ligands. The observation of activation towards dissociation by room light suggests a means of further activating complexes, although careful photochemical studies need to be done in order to select the best wavelength for activation.

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