here is exactly what one expects for exchange of CH_3CN between bulk solvent and two paramagnetic species with significantly different exchange rates and/or coupling constants for first-sphere acetonitrile. Thus the nmr line-width and shift data are both consistent with CH_3CN exchange between bulk solvent and two different Ti(III)–CH_3CN species. Hinckley[2] reported no line-width measurements and his shifts, measured at roughly one-tenth our Ti(III) concentration, are too small to show any significant departure from a linear dependence of shift on $1/T$. (His largest shift was less than 2.5 Hz while our maximum shift was 26.7 Hz.)

As mentioned earlier, the dominant species in $TiCl_3$–CH_3CN solutions at room temperature appears to be the electrically neutral species $TiCl_3(CH_3CN)_3$. Conductivity measurements as a function of $TiCl_3$ concentration indicate that a small amount of ionization takes place according to the equation

$$TiCl_3(CH_3CN)_3 + CH_3CN \rightleftharpoons TiCl_2(CH_3CN)_4^+ + Cl^-$$

with an estimated equilibrium constant of 1.39×10^{-4} at room temperature.[5] It thus appears that the two Ti(III)–CH_3CN species required for interpretation of the nmr results could conceivably be either (1) the *cis* and *trans* forms of the neutral $TiCl_3(CH_3CN)_3$ or (2) the ionic species $TiCl_2(CH_3CN)_4^+$ and the neutral species $TiCl_3(CH_3CN)_3$. In the first instance, *cis* and *trans* forms with different exchange rates and/or coupling constants for CH_3CN could account for the nmr observations, either with both forms present over the entire temperature range or with a conversion from one form to the other with change in temperature. With regard to the ionic species $TiCl_2(CH_3CN)_4^+$, it seems unlikely that it could play a significant role at room temperature but since the temperature dependence of the ionization is not known, the possibility that it may become an important species at higher temperatures cannot be entirely ruled out.

In an effort to learn more about the solution species as a function of temperature, we undertook an epr study of $TiCl_3$–CH_3CN solutions. Unfortunately, no epr spectrum was obtained from solution species between the solution freezing point (about −40°) and +80°. This indicates that both Ti(III) species detected by the nmr measurements have short electronic spin–lattice relaxation times.[7] We were able to observe the epr spectrum of the solid compound $TiCl_3(CH_3CN)_3$ prepared by evaporating solutions of $TiCl_3$ in CH_3CN. At room temperature the spectrum of this compound consists of a single line about 250 G wide. However at −140°, the spectrum of solid $TiCl_3(CH_3CN)_3$ is characteristic of that obtained from axially symmetric complexes. The value of $g_\parallel$ is 1.881 and that of $g_\perp$ is 1.919. Thus the epr data indicate that this compound is in the axially symmetric *cis* configuration at least at low temperature. These general conclusions are in agreement with those of Giggenbach and Brubaker[8] but our g values are significantly different from the values which they report. In an acetonitrile glass at −150° prepared by cooling a $TiCl_3$–CH_3CN solution until it solidified, we observed an epr spectrum which strongly indicates that the axial symmetry observed in solid $TiCl_3(CH_3CN)_3$ is beginning to break down, probably due to interaction of the solvent with the $TiCl_3(CH_3CN)_3$ complex.

Though the epr results are of interest in themselves, they do not serve to discriminate between possible solution species. Unless the compositions and relative amounts of all solution species are known at each temperature, one cannot derive reliable rate parameters from the nmr data.

(7) W. B. Lewis and L. O. Morgan, *Transition Metal Chem.*, **4**, 33 (1968).

(8) W. Giggenbach and C. H. Brubaker, Jr., *Inorg. Chem.*, **8**, 1131 (1969).

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Octahedral Metal Carbonyls. XV.[1] Estimates of Ligand–Chromium Bond Strengths from Kinetic Data

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The nature of metal–ligand bonding in octahedral metal carbonyls is incompletely understood. In particular, recent studies have demonstrated a poor correlation between carbonyl stretching frequencies and reactivities of derivatives.[3] Several investigations have attempted more fully to define the nature of metal–ligand bonding. Graziani, Zingales, and Belluco studied the kinetics of replacement of various Lewis bases (L) from $(L)_2M(CO)_4$ complexes (M = Mo, W) by 2,2′-bipyridyl.[4] Since kinetic data indicated the reactions to proceed *via* a dissociative mechanism, relative rates were taken as a rough measure of M–L bond strengths. It was stressed, however, that since the postulated intermediates in these systems are $LM(CO)_4$ species, the effect of the various L on the energy of the activated complexes must be reflected in the M–L bond strength data obtained. Angelici and Ingemanson have studied equilibria between (amine)$W(CO)_5$ and other $LW(CO)_5$ complexes and have obtained comparisons of the relative ground-state energies of the species.[5] However, the derived values of $\Delta H°$ and $\Delta S°$ appear to be anomalously high.

Angelici and Graham have also reported studies of the reaction of (phen)$Cr(CO)_4$ (phen = *o*-phenanthroline) with L (= $P(OCH_2)_3CCH_3$) to give (phen)Cr-

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(1) The two previous papers in this series: XIII, G. C. Faber and G. R. Dobson, *Inorg. Chim. Acta*, in press; XIV, E. P. Ross and G. R. Dobson, *J. Chem. Soc.*, *D*, 1229 (1969).

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(3) See, *e.g.*, R. J. Angelici, *Organometal. Chem. Rev.*, **3**, 173 (1968).

(4) M. Graziani, F. Zingales, and U. Belluco, *Inorg. Chem.*, **6**, 1582 (1967).

(5) R. J. Angelici and C. M. Ingemanson, *ibid.*, **8**, 83 (1969).

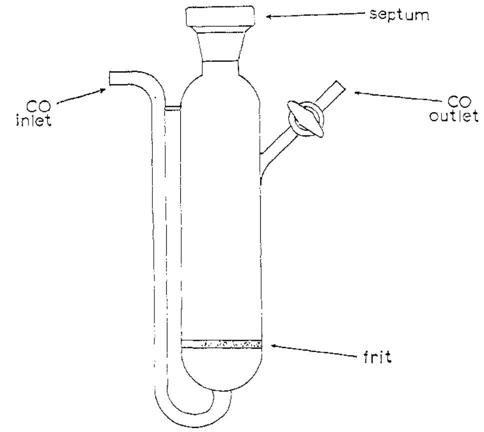
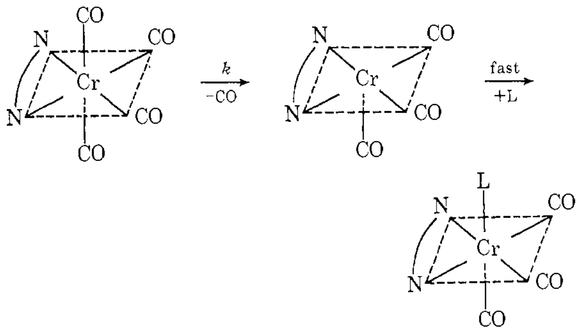


Figure 1.—Reaction vessel.

$(CO)_3L$.[6] This reaction proceeds according to a ligand-independent rate law and is envisioned to involve the rate-determining dissociation of CO



(1)

This reaction is reversible, as shown by

$$(phen)Cr(CO)_3L + CO \underset{k_b}{\overset{k_a}{\rightleftharpoons}} (phen)Cr(CO)_4 + L \qquad (2)$$

The reverse process must, by the principle of microscopic reversibility, involve Cr–L bond fission. In the event Cr–L bond fission is rate determining, more direct estimates of Cr–L bond strengths may be possible, since all such reactions would proceed through a common postulated $(phen)Cr(CO)_3$ activated complex or intermediate. A kinetic investigation of the reactions of various $(phen)Cr(CO)_3L$ with carbon monoxide was therefore undertaken.

Experimental Section

General Information.—Phenylphosphine was prepared after the procedure of Beg and Clark,[7] and $P(OCH_2)_3CCH_3$ was prepared by the method of Verkade, *et al.*[8] Spectrograde 1,2-dichloroethane was the solvent employed for all kinetic runs. Infrared spectra were recorded on a Beckman Model IR-12 infrared spectrophotometer in dichloromethane solvent. The chemical analysis was performed by Midwest Microlab, Inc., Indianapolis, Ind.

Preparation of Complexes.—Three of the $(phen)Cr(CO)_3L$ complexes, for $L = P(C_6H_5)_3$,[9] $P(OC_2H_5)_3$,[9] and $P(OCH_2)_3CCH_3$,[6] had previously been prepared, and were synthesized by the literature methods and identified through their carbonyl stretching spectra. The other four, for $L = P(n\text{-}C_4H_9)_3$, $PH_2(C_6H_5)$, $P[OCH(CH_3)_2]_3$, and $P(OC_6H_5)_3$, were prepared by refluxing $(phen)Cr(CO)_4$ and a twofold excess of the appropriate ligand for *ca.* 0.5 hr in benzene under nitrogen. After the reaction solutions had cooled, the products were collected by suction filtration, washed with small quantities of *n*-hexane, and dried *in vacuo*. They were identified through their characteristic carbonyl stretching spectra (Table III); the $(phen)Cr(CO)_3[P(OC_6H_5)_3]$ complex was further characterized through elemental analysis. *Anal.* Calcd for $C_{33}H_{23}N_2O_6PCr$: C, 63.26; H, 3.70. Found: C, 63.11; H, 3.73.

Kinetic Studies.—1,2-Dichloroethane (70 ml) was allowed to equilibrate in a reaction vessel (Figure 1) placed in a constant-temperature bath. Carbon monoxide (CP) was passed into the side arm and was dispersed through the frit. The positive pressure of CO gas prevented the solution from entering the gas inlet arm. After constant temperature had been attained and sufficient time (*ca.* 15 min) had been allowed to saturate the 1,2-dichloroethane with CO, 60 mg of the appropriate $(phen)Cr(CO)_3L$ substrate was placed in the reaction vessel. Sufficient time for mixing and reequilibration (~100 sec) was allowed, after which 5-ml samples were syringed from the reaction vessel. Their absorbances were measured employing a NaCl variable-thickness cell of 4-mm path length, since a low initial concentration of $(phen)Cr(CO)_3L$ would minimize the reverse reaction (k_b of reaction 2) as L was released into the reaction solution. The decay of the lowest energy carbonyl stretching fundamental of the substrate was monitored on a Beckman Model IR-12 infrared spectrophotometer. The absorbance of a solvent blank was subtracted from all measurements. Plots of $\ln (A_t - A_{bl})$ *vs.* time were linear to about 1 half-life, after which equilibration resulted in a decrease of the observed rates. The differences observed among the reaction rates for various $(phen)Cr(CO)_3L$ substrates confirmed that ligand dissociation rather than attack of CO on $(phen)Cr(CO)_3$ was rate determining; thus it was unnecessary to know the concentration of CO in the reaction solutions. Carbonyl stretching spectra showed $(phen)Cr(CO)_4$ to be the sole reaction product. For the faster reactions ($L = PH_2(C_6H_5)$, $P(C_6H_5)_3$, and $P(OC_6H_5)_3$) relative rates were qualitatively ordered by visual observation of color changes (from blue to red) of the reaction solutions.

Replicate runs for the slower reactions showed values of k_1 to be reproducible to about ±5%. Least-squares analyses were performed on the linear portions of the $\ln (A_t - A_{bl})$ *vs.* *t* plots; limits of error for the activation parameters were calculated through a standard procedure[10] using one standard deviation error limits on the rate constants.

Results and Discussion

Rate constants are given in Table I. The activation data given in Table II show generally positive entropies of activation, which is consistent with a dissociative mechanism as is inferred from the principle of microscopic reversibility.

The extent to which the enthalpies of activation for the substrates investigated here reflect the Cr–L bond strengths depends upon the degree to which the postulated $(phen)Cr(CO)_3$ intermediate actually resembles the transition states. More positive entropies of activation would suggest more bond breaking in the transition state and thus that the postulated intermediate would more closely resemble the transition state. On the basis of the data in Table II, the systems for which the highest enthalpies of activation are found are also generally seen to have the highest entropies of activation. Where this is true the actual Cr–L bond dissociation energies, which must be $\lesssim \Delta H^{\ddagger}$ values, will differ more than do the determined enthalpies of

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(6) R. J. Angelici and J. R. Graham, *Inorg. Chem.*, **6**, 988 (1967).

(7) M. A. A. Beg and H. C. Clark, *Can. J. Chem.*, **39**, 564 (1961).

(8) J. G. Verkade, T. J. Hutteman, M. K. Fung, and R. W. King, *Inorg. Chem.*, **4**, 85 (1965).

(9) L. W. Houk and G. R. Dobson, *ibid.*, **5**, 2119 (1966).

(10) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p 91.

TABLE I

RATE DATA FOR REACTION OF (phen)Cr(CO)$_3$(L) COMPLEXES WITH CARBON MONOXIDE IN 1,2-DICHLOROETHANE

Temp, °C	10^5k_1, sec^{-1}	Temp, °C	10^5k_1, sec^{-1}
L = P(n-C_4H_9)$_3$		L = P(OCH_2)$_3$$CCH_3$	
46.3	8.55	40.0	22.1
	8.64		19.0
	8.65		20.6
40.0	3.20	35.0	11.8
	3.49		11.1
	3.32	L = P[OCH(CH_3)$_2$]$_3$	
L = P(OC_2H_5)$_3$		35.0	9.41
40.0	12.6		9.53
	11.3	23.4	[a]
	11.8		
35.0	5.73		
	5.49		

[a] Relative rates: P(OC_6H_5)$_3$ < P(C_6H_5)$_3$ < PH_2(C_6H_5); see Experimental Section.

TABLE II

ACTIVATION PARAMETERS FOR DISSOCIATION OF L FROM (phen)Cr(CO)$_3$(L) IN 1,2-DICHLOROETHANE

L	$\Delta H_1^{\ddagger}$, kcal mol^{-1}	$\Delta S_1^{\ddagger}$, eu
P(n-C_4H_9)$_3$	29.3 ± 1.2	+10.9 ± 3.5
P(OC_2H_5)$_3$	28.2 ± 2.6	+13.4 ± 8.4
CO[a]	26.4 ± 0.8	+7.0 ± 2.6
P(OCH_2)$_3$$CCH_3$	21.9 ± 2.7	−5.6 ± 8.7

[a] Reference 6; limits of error, one standard deviation.

activation. On this basis the qualitative order of bond strengths as given below could be taken with greater confidence. On the other hand, entropies of activation for this dissociative process would be expected to be more positive for bulky ligands, which are more constrained when coordinated to the small Cr atom. This is, within the limits of error, the trend which is observed.

From the observed rates of ligand dissociation the indicated order of Cr–L bond strengths would appear to be P(n-C_4H_9)$_3$ > P(OC_2H_5)$_3$ > CO > P[OCH(CH_3)$_2$]$_3$ $\gtrsim$ P(OCH_2)$_3$$CCH_3$ > P(OC_6H_5)$_3$ > P(C_6H_5)$_3$ > PH_2(C_6H_5). This order is, for similar or identical ligands, the same as the order of W–L bond strengths as determined through the equilibrium studies of Angelici and Ingemanson.[5] The agreement supports the qualitative correctness of the order given.

Inferences as to the relative bond strengths through comparisons of reactivity would appear to be most valid for cases in which the steric nature of the ligands and the entropies of activation for their (phen)Cr(CO)$_3$L complexes are similar. These requirements are best satisfied for (phen)Cr(CO)$_3$[P(n-C_4H_9)$_3$] and (phen)Cr(CO)$_3$[P(OC_2H_5)$_3$]. If it is supposed, as is generally accepted, that P(n-C_4H_9)$_3$ is a stronger Lewis base but a poorer π acid than is P(OC_2H_5)$_3$, it follows from the relative labilities that the change, from one ligand to the other, in bond strength due to σ bonding is greater than is the change in bond strength due to π bonding. Thus in this case changes in σ bonding would appear to exert a dominant influence on Cr–L bond strengths. The dominance of σ bonding is also suggested by the observation that the Cr–L bond strength evidently is greater for L = P(n-C_4H_9)$_3$ than for the strongly π-accepting carbonyl ligands. Finally, as has been noted by Angelici and Ingemanson,[5] the inferred order of M–L bond strengths would appear closely to parallel ligand basicities.

The carbonyl stretching frequencies for the (phen)Cr(CO)$_3$L complexes (Table III) do not parallel reactivities. That this is not surprising is evident from comparison of the data for (phen)Cr(CO)$_3$[P(n-C_4H_9)$_3$] and (phen)Cr(CO)$_3$[P(OC_2H_5)$_3$]: the lower carbonyl stretching frequencies for the former would be expected both on the basis of its stronger σ bonding and its weaker π bonding to the metal.

TABLE III

CARBONYL STRETCHING SPECTRA FOR (phen)Cr(CO)$_3$(L) COMPLEXES IN DICHLOROMETHANE SOLVENT

L	Carbonyl str freq, cm^{-1} (all bands strong)
P(n-C_4H_9)$_3$	1905, 1809, 1783
P(C_6H_5)$_3$	1910, 1822, 1788
P[OCH(CH_3)$_2$]$_3$	1916, 1821, 1787
PH_2(C_6H_5)	1918, 1826, 1792
P(OC_2H_5)$_3$	1919, 1827, 1790
P(OCH_2)$_3$$CCH_3$	1931, 1840, 1801
P(OC_6H_5)$_3$	1935, 1850, 1807

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