

shows no change in its ultraviolet spectrum after >50 hr. at 80° in cyclohexane or cyclohexene. Thus R-S-S· apparently does not add to the double bond or abstract hydrogen under these mild conditions.⁴¹ In contrast, disulfides are known to be chain-transfer agents. Thus RS· fragments add to active double bonds quite readily and reinitiate polymerization at 60–80°.⁴² However, e.s.r. investigations,^{30,43} while inconclusive, have given no indication of delocalization of the odd electron in polythiyl radicals.

Bergson, in some semiempirical molecular orbital cal-

(41) It is possible in the cyclohexene case that a small amount of addition takes place. If species such as RS₂R, etc., are also formed, however, no change in the ultraviolet spectrum would be anticipated. Further studies are planned to elucidate this problem.

(42) W. A. Pryor and T. L. Pickering, *J. Am. Chem. Soc.*, **84**, 2705 (1962).

(43) A. G. Pinkus and L. H. Piette, *J. Phys. Chem.*, **63**, 2086 (1959).

culations,⁴⁴ has found that there should be an increase in stability of species such as R-S_n· with *n*. He attributes this stability to the fact that the odd electron can occupy an antibonding π orbital formed from 3pπ orbitals. He estimates that this stabilization should be worth about 30 kcal./mole in a trisulfide compared to a disulfide. This is the same order of magnitude as we find for a tetrasulfide. Investigations on methyl trisulfide are under way to see if its dissociation energy is intermediate between that of disulfides and tetrasulfides.

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Kinetic Studies of Group VI Metal Carbonyl Complexes. I. Substitution Reactions of Dipyridyl Complexes of Chromium Hexacarbonyl¹

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The reaction of Cr(CO)₄(X-X) (where X-X = dipyridyl or 4,4'-dimethyldipyridyl) with phosphites, L (where L = P(OC₂H₅)₃, P(OCH₂)₃CCH₃, and PO₃C₆H₅), to yield cis-Cr(CO)₃(L)(dipy) proceeds according to a first-order rate law at temperatures of 35 to 60° in various organic solvents. The 4,4'-dimethyldipyridyl complex reacts faster than does that of dipyridyl. In contrast to the very slow rates of reaction of Cr(CO)₆ and its phosphine derivatives, these dipyridyl complexes are relatively labile, and the labilizing abilities of these and other ligands are discussed in terms of "hard" and "soft" bases. Activation parameters and solvent effects for the reactions have also been evaluated.

The kinetic inertness of Cr(CO)₆ has been demonstrated by the following observations: it shows no exchange with ¹⁴CO in toluene in 3 weeks at 30°,^{2a} and phosphines are able to replace CO groups from it only at relatively high temperatures.^{2b} Replacement of two CO groups in Cr(CO)₆ by a dipyridyl ligand to form Cr(CO)₄(dipy) would presumably increase chromium π bonding to the remaining four CO groups rendering them more inert than those in Cr(CO)₆.³ However, there was some indication that the CO groups in Cr(CO)₄(dipy) would not be as inert as expected since Mo(CO)₄(dipy) is known to react with ligands, L (where L = pyridine, triphenylphosphine, and diphenyl

sulfide), to form cis-Mo(CO)₃(L)(dipy) at temperatures of 120–160° in the absence of a solvent.⁴ Despite the rather rigorous conditions, it was a surprising result since the CO groups of Mo(CO)₆ can be substituted by phosphines only at rather high temperatures.⁵

In order to determine whether the CO groups in Cr(CO)₄(dipy) are indeed more labile than in Cr(CO)₆, a kinetic investigation of the reactions of Cr(CO)₄(dipy) with phosphites was undertaken.

Experimental Section

Preparation and Purification of Materials. The complexes Cr(CO)₄(X-X) (where X-X = 2,2'-dipyridyl and 4,4'-dimethyldipyridyl) were prepared from chromium hexacarbonyl and the desired dipyridyl as described in the literature⁶ and identified by their infrared spectra.³ The bicyclic phosphite ligands, 4-methyl-3,6,7-trioxa-1-phosphabicyclo[2.2.2]octane, P(OCH₂)₃CCH₃, and 1-phospha-2,8,9-trioxaadamantane, PO₃C₆H₅, were obtained by refluxing P(OCH₃)₃ with the appropriate triol.⁷ Triethyl phosphite was purchased from Matheson Coleman and Bell and used without further purification. Purification of 1,2-dichloroethane was effected by fractional distillation. Chlorobenzene and nitrobenzene were dried over P₂O₅ and fractionally distilled, while reagent grade acetone was used directly.

Determination of Rates. All rates of reaction were determined by following the disappearance of the high-

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(1) Presented before the Division of Inorganic Chemistry at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965.

(2) (a) F. Basolo and A. Wojcicki, *J. Am. Chem. Soc.*, **83**, 520 (1961); (b) T. A. Magee, C. N. Mathews, T. S. Wang, and J. H. Wotiz, *ibid.*, **83**, 3200 (1961).

(3) C. S. Kraihanzel and F. A. Cotton, *Inorg. Chem.*, **2**, 533 (1963).

est frequency C–O stretching absorption of $\text{Cr}(\text{CO})_4(\text{dipy})$ on a Beckman IR-8 infrared spectrophotometer. As the substitution reaction proceeds, the four characteristic C–O absorptions of $\text{Cr}(\text{CO})_4(\text{dipy})$ at 2012 (m), 1905 (vs), 1880 (s), and 1828 (s) cm^{-1} disappear, and the three absorptions of *cis*- $\text{Cr}(\text{CO})_3(\text{L})(\text{dipy})$, where L is a phosphite, begin to grow at about 1935 (vs), 1840 (s), and 1795 (s) cm^{-1} . Because of the low solubility of $\text{Cr}(\text{CO})_4(\text{dipy})$, solution concentrations were approximately $6 \times 10^{-3} M$, and infrared cells of 1-mm. thickness were required to give satisfactory absorption intensities. Prethermostated solutions of $\text{Cr}(\text{CO})_4(\text{dipy})$ and of the phosphite were injected into a nitrogen filled vessel which was wrapped in aluminum foil and sealed with a serum cap. Samples of the solution were periodically withdrawn with a syringe from the thermostated vessel, and the absorbance of the high-frequency band was measured. Linear plots of $\ln(A - A_\infty)$ vs. time yielded the first-order rate constants. Plots were linear to at least 80% completion, and the average deviation of the rate constants for identical runs was almost always less than 2%. Blank runs containing no ligand showed that $\text{Cr}(\text{CO})_4(\text{dipy})$ decomposed at a rate which was about 10% of that of the substitution reaction. This decomposition was accompanied by the formation of a brown precipitate. During the substitution reactions, however, there was no precipitate formation, and it was therefore assumed that no decomposition was occurring under these conditions. The enthalpies and entropies of activation were determined by a least-squares computer program⁸ which also calculated standard deviations for these quantities. The limits of error shown in Table III are one standard deviation.

Product Identification. Since during the kinetic studies the reaction of $\text{Cr}(\text{CO})_4(\text{dipy})$ with $\text{P}(\text{OCH}_2)_3\text{CCH}_3$ was conducted in the presence of a large excess of the ligand, it was not convenient to isolate the product from the reaction mixture. The C–O stretching absorptions of the product appeared, however, at 1935 (vs), 1840 (s), and 1795 (s) cm^{-1} . This spectrum was very similar to that of *cis*- $\text{Mo}(\text{CO})_3[\text{P}(\text{C}_6\text{H}_5)_3](\text{dipy})$, which was assigned a configuration in which the $\text{P}(\text{C}_6\text{H}_5)_3$ group was *trans* to a CO.⁴ To confirm the indication that the kinetic product was indeed the expected compound, $\text{Cr}(\text{CO})_3[\text{P}(\text{OCH}_2)_3\text{CCH}_3](\text{dipy})$, 0.64 g. of $\text{Cr}(\text{CO})_4(\text{dipy})$ and 0.50 g. of $\text{P}(\text{OCH}_2)_3\text{CCH}_3$ were allowed to react in 10 ml. of refluxing 1,2-dichloroethane under a nitrogen atmosphere for about 1.5 hr. Cooling the 1,2-dichloroethane solution in a Dry Ice-acetone bath resulted in the separation of black product crystals. After rinsing several times with hexane, the crystals were dried under vacuum for several hours.

Anal. Calcd. for $\text{Cr}(\text{CO})_3[\text{P}(\text{OCH}_2)_3\text{CCH}_3](\text{dipy})$: C, 49.1; H, 3.86. Found: C, 49.0; H, 3.85.

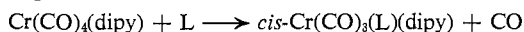
This compound had an infrared spectrum that was identical with those obtained in the kinetic studies and was the only product of the reaction. With the other ligands, $\text{P}(\text{OC}_2\text{H}_5)_3$ and $\text{PO}_3\text{C}_6\text{H}_5$, the product absorptions were virtually identical with those noted above. It was therefore assumed that these ligands formed analogous compounds. The reaction of $\text{Cr}(\text{CO})_4(4,4'\text{-dimethyldipy})$ with $\text{P}(\text{OCH}_2)_3\text{CCH}_3$ also showed the

expected spectrum, which was taken to be positive identification for $\text{Cr}(\text{CO})_3(\text{L})(4,4'\text{-dimethyldipy})$.

Because of the transparency of the solvents in the C–O stretch region of the spectrum, identification of the product was easily noted in 1,2-dichloroethane, acetone, and chloroform; but in chlorobenzene and nitrobenzene, solvent absorptions obscured the product bands, and it was therefore necessary to assume that the same product was also obtained in these solvents. This was supported by the fact that the expected maroon to purple color change also occurred in these solvents during the course of the reaction.

Results

The complex $\text{Cr}(\text{CO})_4(\text{dipy})$ reacted with such ligands as $\text{P}(\text{OC}_2\text{H}_5)_3$, $\text{P}(\text{OCH}_2)_3\text{CCH}_3$, and $\text{PO}_3\text{C}_6\text{H}_5$, according to the equation



The only product was *cis*- $\text{Cr}(\text{CO})_3(\text{L})(\text{dipy})$, in which L is *trans* to a CO group. This assignment of isomers is the same as that made by Stiddard⁴ to the analogous molybdenum complexes and is entirely consistent with the three strong C–O absorptions exhibited by the compounds.

The reaction of $\text{Cr}(\text{CO})_4(\text{dipy})$ with L does not go to completion unless a fairly large excess of ligand is used or unless CO is lost from the reaction solution. At low ligand concentrations (one- or twofold excess of ligand) the reaction goes to approximately 50% completion. However, no accurate measurements of equilibrium constants were possible because of the uncertainty of the equilibrium CO concentration and the slow rate of decomposition of the reaction product. The decomposition of the reaction product slowly shifted the equilibrium to the product and made it impossible to ascertain when equilibrium had been reached. The presence of a reaction equilibrium was also demonstrated by taking a 1,2-dichloroethane solution of the product, *cis*- $\text{Cr}(\text{CO})_3(\text{L})(\text{dipy})$, and slowly bubbling in CO gas. After about 20 min. at 48°, the 1,2-dichloroethane solution contained about equal molar amounts of *cis*- $\text{Cr}(\text{CO})_3(\text{L})(\text{dipy})$ and $\text{Cr}(\text{CO})_4(\text{dipy})$. This solution containing a mixture of products could be entirely reconverted to *cis*- $\text{Cr}(\text{CO})_3(\text{L})(\text{dipy})$ by slowly bubbling in nitrogen to remove the CO from the reaction solution.

The determination of reproducible rate constants using low ligand concentrations was made difficult because of a falling off of the reaction rate as the reaction approached equilibrium. Attempts were made to determine initial rate constants by following the first 10% of the reaction, but the average deviation of rate constants for identical runs was quite high, about 7%. To avoid these equilibrium difficulties, the rate constant study was carried out using ligand concentrations of 15-fold excess and greater.

As shown in Tables I and II, the rate of the above reaction follows a simple first-order rate law, rate = $k[\text{Cr}(\text{CO})_4(\text{dipy})]$, and is independent of the concentration and only slightly dependent on the nature of the entering ligand. Recorded in Table III are the activation parameters calculated from the rate data given in Tables I and II. The slight dependence of the reaction rates and the activation parameters on the nature of the incoming ligand could be explained by an association of

(8) R. H. Moore, based on a report from Los Alamos Scientific Laboratory, LA2367 and Addenda.

Table I. Rates of Reaction of $\text{Cr}(\text{CO})_4(\text{dipy})$ with Phosphites in 1,2-Dichloroethane

Phosphite L	[L], moles/l.	Temp., °C.	$10^3 k_{\text{obsd.}}$ sec. ⁻¹	
$\text{P}(\text{OC}_2\text{H}_5)_3$	0.111	37.8	13.4	
	1.00	37.8	13.5	
	1.30	37.8	13.5	
	0.0089	47.9	43.1	
	0.0297	47.9	44.8	
	0.0322	47.9	45.4	
	0.0594	47.9	49.3	
	0.111	47.9	51.6	
	0.550	47.9	51.2	
	0.779	47.9	51.5	
	0.403	58.1	158	
	0.574	58.1	163	
	0.725	58.1	159	
	$\text{P}(\text{OCH}_2)_3\text{CCH}_3$	0.156	37.8	13.4
		0.656	37.8	13.6
1.41		37.8	14.0	
0.0056		47.9	43.7	
0.0224		47.9	47.8	
0.0625		47.9	45.8	
0.0625		47.9	49.1	
0.365		47.9	46.8	
0.658		47.9	46.5	
1.09		47.9	46.7	
0.156		58.1	149	
1.09		58.1	147	
1.41		58.1	148	
$\text{PO}_3\text{C}_6\text{H}_5$		0.0873	37.8	10.8
		0.271	37.8	11.2
	0.677	37.8	11.4	
	0.0045	47.9	42.9	
	0.0239	47.9	45.8	
	0.0559	47.9	46.6	
	0.0873	47.9	43.7	
	0.338	47.9	43.8	
	0.773	47.9	43.9	
	0.0873	58.1	146	
	0.338	58.1	148	
	0.676	58.1	149	

Table II. Rates of Reaction of $\text{Cr}(\text{CO})_4(\text{dipy})$ with Phosphites in Chlorobenzene

Phosphite L	[L], moles/l.	Temp., °C.	$10^3 k_{\text{obsd.}}$ sec. ⁻¹
$\text{P}(\text{OC}_2\text{H}_5)_3$	0.114	37.8	5.57
	0.798	37.8	5.57
	0.114	47.9	18.3
	0.798	47.9	17.9
	0.114	58.1	55.8
	0.798	58.1	55.8
$\text{P}(\text{OCH}_2)_3\text{CCH}_3$	0.106	37.8	4.88
	1.69	37.8	4.92
	0.365	47.9	21.4
	1.09	47.9	21.3
	0.156	58.1	89.4
	1.27	58.1	89.7
$\text{PO}_3\text{C}_6\text{H}_5$	0.150	37.8	6.20
	0.451	37.8	6.17
	0.0178	47.9	18.4
	0.137	47.9	18.4
	0.150	58.1	75.2
	0.451	58.1	75.1

the reacting complex with the ligand. In an attempt to obtain some independent evidence for this interaction, the solubility of $\text{Cr}(\text{CO})_4(\text{dipy})$ in pure 1,2-dichloroethane and 1,2-dichloroethane containing varying amounts of ligand was determined spectrophotometrically in the C–O stretching region of the infrared spectrum. A standard curve for $\text{Cr}(\text{CO})_4(\text{dipy})$ was determined by plotting absorbance vs. the concentration

Table III. Enthalpies and Entropies of Activation for the Reaction of $\text{Cr}(\text{CO})_4(\text{dipy})$ with Phosphites in 1,2-Dichloroethane and Chlorobenzene

Phosphite L	ΔH^* , kcal./mole	ΔS^* , e.u.
In 1,2-Dichloroethane		
$\text{P}(\text{OC}_2\text{H}_5)_3$	24.3 ± 0.3^a	1.9 ± 0.9
$\text{P}(\text{OCH}_2)_3\text{CCH}_3$	23.4 ± 0.1	-1.1 ± 0.3
$\text{PO}_3\text{C}_6\text{H}_5$	25.4 ± 0.2	5.1 ± 0.6
In Chlorobenzene		
$\text{P}(\text{OC}_2\text{H}_5)_3$	22.6 ± 0.1	-5.4 ± 0.2
$\text{P}(\text{OCH}_2)_3\text{CCH}_3$	28.6 ± 0.1	13.6 ± 0.3
$\text{PO}_3\text{C}_6\text{H}_5$	24.4 ± 1.0	0.5 ± 3.0

^a One standard deviation error limits.

of $\text{Cr}(\text{CO})_4(\text{dipy})$. This curve yielded a molar extinction coefficient of 1080 l./mole cm. for $\text{Cr}(\text{CO})_4(\text{dipy})$ which was found to be unaffected by the ligand concentrations used in the solubility study. $\text{Cr}(\text{CO})_4(\text{dipy})$ has a solubility of 0.0110 mole/l. at 25° in pure 1,2-dichloroethane. This solubility increases for ligand concentrations of 0.008 to 0.200 M by about 1% for $\text{P}(\text{OC}_2\text{H}_5)_3$, 4% for $\text{P}(\text{OCH}_2)_3\text{CCH}_3$, and 10–14% for $\text{PO}_3\text{C}_6\text{H}_5$. The relative independence of the solubility of $\text{Cr}(\text{CO})_4(\text{dipy})$ in a ligand solution of concentration greater than 0.008 M on the ligand concentration indicates that there is virtually no association between the complex and ligand at 25°.

It might also be expected that any association would alter the position of the C–O absorptions in $\text{Cr}(\text{CO})_4(\text{dipy})$. In an experiment to detect the slightest shift in absorption, a solution of $\text{Cr}(\text{CO})_4(\text{dipy})$ in 1,2-dichloroethane was placed in the reference cell of the double beam spectrophotometer, and a solution of the same complex concentration but containing added $\text{P}(\text{OCH}_2)_3\text{CCH}_3$ was placed in the sample beam. This differential spectrum showed absolutely no difference between the two solutions.

If some associated species were a reactive form of the complex, an equilibrium between the free complex and this species would result in a ligand dependence of the rate constants at low ligand concentrations. Because the reaction being measured came to equilibrium at these concentrations, initial rates were determined. As the ligand concentrations were decreased, these rates appeared to decrease slightly at 47.9° in 1,2-dichloroethane. While a decrease would suggest complex–ligand association, the observed decrease is so small and almost within experimental error even for $\text{P}(\text{OC}_2\text{H}_5)_3$, which exhibited the largest apparent change in rate, that it is not possible to say that the kinetic data definitely indicate association.

Since the solubility and infrared studies strongly suggest that there is no association between the complex and ligand, and the kinetic studies are inconclusive, it appears that the slight variation in rates and activation parameters is due to some other interaction than complex–ligand association before reaction. It is not clear at what point the ligand exerts its effect.

The analogous complex with 4,4'-dimethyl-2,2'-dipyridyl, $\text{Cr}(\text{CO})_4(4,4'\text{-dimethyldipy})$, also reacted with $\text{P}(\text{OCH}_2)_3\text{CCH}_3$ to yield only *cis*- $\text{Cr}(\text{CO})_3[\text{P}(\text{OCH}_2)_3\text{CCH}_3](4,4'\text{-dimethyldipy})$. In 1,2-dichloroethane at 47.9° with ligand concentrations of 0.121, 0.509, and 1.09 M $\text{P}(\text{OCH}_2)_3\text{CCH}_3$, the reaction proceeded

Table IV. Rates of Reaction of $\text{Cr}(\text{CO})_4(\text{dipy})$ with $\text{P}(\text{OCH}_2)_3\text{CCH}_3$ in Various Solvents at 37.8°

Solvent	$\text{P}(\text{OCH}_2)_3\text{CCH}_3$, moles/l.	10^3k , sec.^{-1}
Chlorobenzene (5.6) ^a		4.90
1,2-Dichloroethane (10.4)		13.7
Acetone (20.7)	0.258	17.5
Acetone	0.734	17.7
Acetone	1.57	17.5
Nitrobenzene (34.8)	0.096	13.2
Nitrobenzene	0.373	15.6
Nitrobenzene	0.373	15.5

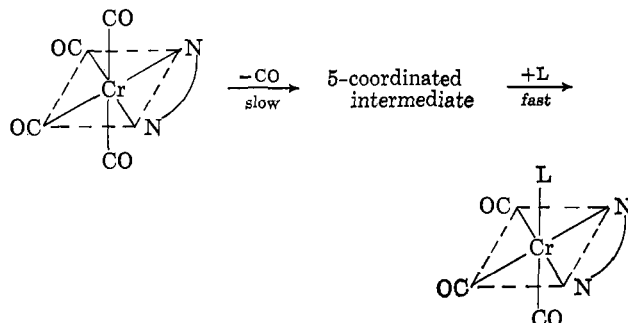
^a The number in parentheses is the dielectric constant of the solvent at 25° .

with first-order rate constants of 9.52×10^{-4} , 9.58×10^{-4} , and $9.61 \times 10^{-4} \text{ sec.}^{-1}$, respectively. Since the rate constant for the reaction of $\text{Cr}(\text{CO})_4(\text{dipy})$ with $\text{P}(\text{OCH}_2)_3\text{CCH}_3$ under identical conditions was $4.67 \times 10^{-4} \text{ sec.}^{-1}$, it is clear that $\text{Cr}(\text{CO})_4(4,4'-dimethyldipy) reacts with $\text{P}(\text{OCH}_2)_3\text{CCH}_3$ about twice as fast as does $\text{Cr}(\text{CO})_4(\text{dipy})$.$

First-order rate constants for the reaction of $\text{Cr}(\text{CO})_4(\text{dipy})$ with $\text{P}(\text{OCH}_2)_3\text{CCH}_3$ in several different solvents are given in Table IV.

Discussion

Rate and Mechanism of Reaction. The first-order rate law and the product of the reaction of $\text{Cr}(\text{CO})_4(\text{dipy})$ with $\text{P}(\text{OC}_2\text{H}_5)_3$, $\text{P}(\text{OCH}_2)_3\text{CCH}_3$, or $\text{PO}_3\text{C}_6\text{H}_5$ suggest a dissociative mechanism for the transformation.



It is likely that the rate-determining step is one in which one of the two CO groups *trans* to each other dissociates. The reasons for implicating the two CO groups *trans* to each other are that the product is *cis*- $\text{Cr}(\text{CO})_3(\text{L})(\text{dipy})$ and that C–O vibrational assignments³ indicate that the CO groups *trans* to the dipyridyl group are more tightly bonded to Cr than are the CO groups *trans* to each other. That the reaction follows a dissociative mechanism is not surprising since octahedral complexes are usually found to proceed by such a path.

Compared to the inertness of $\text{Cr}(\text{CO})_6$, $\text{Cr}(\text{CO})_4(\text{dipy})$ is a relatively labile complex. It was reasoned that if the replacement of two weakly basic groups in $\text{Cr}(\text{CO})_6$ by a relatively strong base such as dipyridyl ($\text{p}K_a = 4.50$) resulted in the labilization of at least two of the remaining CO groups, then the introduction of an even stronger base such as 4,4'-dimethyldipyridyl ($\text{p}K_a = 5.45$) would even further increase the lability of these CO groups. This was indeed found to be the case.

These observations are directly opposed to current π bonding arguments which suggest that the replacement

of a CO group in a metal carbonyl by a stronger base, or a more poorly π -bonding ligand, allows more metal-to-CO π bonding which increases the metal-carbonyl bond strength. Although the introduction of a dipyridyl group into chromium hexacarbonyl labilizes at least two of the remaining CO groups, we have found that the introduction of $\text{P}(\text{OCH}_2)_3\text{CCH}_3$ into chromium hexacarbonyl has no such labilizing effect. Others^{2b} have also noted that the thermal replacement of CO groups from $\text{Cr}(\text{CO})_5\text{L}$ or $\text{Cr}(\text{CO})_4\text{L}_2$, where L = phosphine or phosphite, occurs only under drastic conditions. Therefore, the presence of dipyridyl in the coordination sphere has an effect on the remaining CO groups which is quite different from that of phosphines or phosphites.

The only striking difference between dipyridyl and the phosphines seems to be in the relative "hardness" of these two bases.⁹ Relatively "soft" bases such as CO, phosphines, and phosphites appear to have no labilizing effect, while significantly "harder" bases such as dipyridyl do increase the lability of the remaining CO groups. The increased lability of the 4,4'-dimethyldipyridyl complex further suggests that the "harder" the base the more labile the CO groups become.

The introduction of "hard" and "soft," or labilizing and nonlabilizing, bases into the isoelectronic Mn(I) carbonyls also appears to yield similar trends. Like $\text{Cr}(\text{CO})_6$, $[\text{Mn}(\text{CO})_6]^+$ is very inert and shows no exchange with ^{14}CO in 15 hr. at 30° .¹⁰ Replacement of a "soft" CO group by a "hard" halide group, X, yields $\text{Mn}(\text{CO})_5\text{X}$, which readily undergoes ^{14}CO exchange¹¹ and reaction with phosphines and phosphites,¹² L, to form *cis*- $\text{Mn}(\text{CO})_4\text{LX}$, at 30° by way of a dissociative mechanism. Moreover, the rate of CO dissociation from $\text{Mn}(\text{CO})_5\text{X}$ increases with X in the following order: $\text{I} < \text{Br} < \text{Cl}$. Not only do the "hard" halides labilize the remaining CO groups but the degree of labilization increases with the "hardness" of the halide.

The complexes, *cis*- $\text{Mn}(\text{CO})_4\text{LBr}$, have been found to undergo further substitution to form *cis*- $\text{Mn}(\text{CO})_3\text{L}_2\text{Br}$, in which the L groups are *cis* to each other and to Br.¹³ The reaction again proceeds by way of a dissociative mechanism, and the rates depend on the nature of L in the complex. When L is a phosphine or phosphite, the rate of reaction is about the same as that for $\text{Mn}(\text{CO})_5\text{Br}$ itself. However, when L is pyridine or aniline,¹³ the reaction occurs instantly and kinetic measurements were not feasible.

Thus the available kinetic data for the Cr(0) and Mn(I) carbonyl complexes can be qualitatively accounted for in terms of the contrasting abilities of "hard" and "soft" bases to labilize CO groups. The reason for this difference may be the significantly stronger π -bonding ability of phosphines as compared to pyridine or the greater polarizability of phosphorus. The basicity of the phosphine or pyridine, however, appears to be unimportant since phosphorus ligands of both higher and lower basicity¹⁴ than pyridine are much the same in their labilizing abilities.

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Another important consideration is whether the CO group is labilized as a result of a weakened metal-carbonyl bond or whether the transition state in the proposed CO dissociation mechanism is stabilized in some manner by the "hard" base. In phosphine-substituted nickel carbonyl complexes, infrared studies clearly indicate that the replacement of a CO by a phosphine increases the Ni-CO bond strength,¹⁵ and studies of the C-O stretching vibrations in Cr(CO)₆ and Cr(CO)₄(dipy) suggest that the Cr-CO bond strength is significantly stronger in the dipyriddy complex than in Cr(CO)₆.³ Since it therefore appears that both phosphine and pyridine bases actually increase the metal-carbonyl bond strength, the labilization of CO must be accounted for in terms of a stabilization of the transition state. While there are a number of possible reasons for a "hard" base stabilization of the transition state, none seems to offer an explanation which is consistent with all the data.

Activation Parameters. Since the data in Tables I and II indicate that the first-order rate constants depend slightly on the phosphite used, the activation parameters (Table III) were evaluated separately for each phosphite. The significant difference in activation parameters with the three phosphites is, as discussed in the Results section, not understood. While any interaction between the complex and ligand might be expected to depend on the basicities of the ligands, there is no correlation of ΔH^* with the basic properties of the phosphites which increase in the order: $P(OC_2H_5)_3 < P(OCH_2)_3CCH_3 < PO_3C_6H_9$.¹⁶

The ΔH^* values are relatively low and considerably lower than what one might have expected on the basis

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of the C-O stretching frequencies of Cr(CO)₄(dipy).¹⁷ They are also significantly lower than the activation energy (39.3 kcal.) obtained for the gas phase ¹⁴CO exchange of Cr(CO)₆ also by way of a dissociative mechanism.¹⁸

The entropies of activation are generally positive or only slightly negative, which tends to support a dissociative mechanism in which the transition state is gaining some degree of freedom. It is also to be noted that ΔS^* decreases as ΔH^* decreases which implies that in the cases where the transition state energy is lowered by solvation there is an accompanying decrease in the over-all ΔS^* as a result of a decrease in the degrees of freedom of the solvating molecules. While these ideas explain the data, it should be added that in most systems ΔS^* usually decreases with ΔH^* .

Solvent Effects. To determine what role the solvent plays, the reaction of Cr(CO)₄(dipy) with P(OCH₂)₃-CCH₃ was studied in those solvents listed in Table IV. The rates were found to be independent of the phosphite and only affected to a small extent by the solvent. Small solvent effects have also been found in other carbonyl substitution reactions¹² and are to be expected for such nonionic reactions; but, while rates of reaction in chlorobenzene and 1,2-dichloroethane are much the same, the activation parameters are much more sensitive to the solvent.

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Kinetic Studies of Group VI Metal Carbonyl Complexes. II. Substitution Reactions of Dipyriddy Complexes of Molybdenum and Tungsten Hexacarbonyls

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The 2,2'-dipyriddy complexes of molybdenum and tungsten hexacarbonyls, M(CO)₆(dipy), have been found under rather mild conditions to undergo substitution reactions with phosphites, L (where L = P(OC₂H₅)₃, P(OCH₂)₃CCH₃, and PO₃C₆H₉), to yield three products: M(CO)₅(L)(dipy), M(CO)₄(L)₂, and M(CO)₃(L)₃. The reactions proceed according to the two-term rate law, rate = $k_1[M(CO)_6(dipy)] + k_2[L][M(CO)_6(dipy)]$. This rate law suggests that the reaction proceeds by two different mechanisms. On the basis of the products and their amounts formed during a particular reaction and with the aid of activation parameters, reaction mechanisms are proposed and discussed.

Introduction

Earlier Cr(CO)₄(dipy) was found to react readily with phosphites, L, under rather mild conditions to form *cis*-Cr(CO)₃(L)(dipy). Such behavior was unexpected in view of the inertness of Cr(CO)₆ under the same conditions. This labilizing effect of the 2,2'-dipyriddy was explained in terms of the greater "hardness" of 2,2'-dipyriddy relative to that of carbon monoxide.¹ The 2,2'-dipyriddy complexes of the other group VI metal carbonyls have now also been found to contain CO groups which have been substantially labilized by the

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