at room temperature. This color change is attributed to the formation of a CO adduct of $[Cu(AEP)_2IPAH]^+$ which is characterized by an electronic absorption band at 23 000 cm^{-1} (ϵ = 9300 (Me_2SO), 7900 (acetonitrile)) (Figure 2). The presence of CO causes the disappearance of the absorption band for the free ligand (28 300 cm^{-1}) in acetonitrile solution, apparently favoring the formation of the intact complex as the CO adduct. Removal of CO by vacuum/N_2 cycles at 25 °C restores the system to essentially the initial equilibrium state as shown spectrophotometrically. Attempts to determine the stoichiometry of the adduct in Me_2SO by measuring the extent of adduct formation as a function of CO pressure were unsuccessful owing to the slow disproportionation of $[Cu(AEP)_2IPAH]^+$.

Solid carbon monoxide adducts of both salts of $[Cu(AEP)_2IPAH]^+$ were isolated by exposing a concentrated solution of the complex in acetonitrile to CO. These yellow crystalline adducts were stable only under a CO atmosphere and exhibited a slow loss of CO when stored under N_2. The infrared spectra of the two adducts reveal an intense band at 2075 cm^{-1} characteristic of a terminally bound CO molecule.[23] The remainder of the infrared spectra were essentially identical with those of the respective $[Cu(AEP)_2IPAH]^+$ salts.

The interaction of CO with Cu(I) complexes is well-known,[24] and among the copper(I) carbonyl species with nitrogen-donor ligands recently studied,[24-30] several have possessed sufficient stability to allow X-ray diffraction studies.[24-28] With one exception,[27] the structures of these carbonyl adducts show a pseudotetrahedral geometry about the Cu(I) with a terminally bonded CO. Gagné and coworkers[27] have reported a unique five-coordinate Cu(I) complex with a planar N_4 macrocyclic ligand and an axially bonded CO. The Cu(I)–CO species exhibit values of ν_{CO} over the range 2055–2091 cm^{-1}. The reversibility of the CO adduct formation varies widely with the solid complexes $[Cu(dien)CO]BPh_4$[25,31] and $[Cu_2(hm)_3(CO)_2](BPh_4)_2$[26,31] stable toward loss of CO in vacuo and by heating. In solution, the copper(I)–histamine complexes are reversible CO carriers.[26] Varying degrees of instability toward loss of CO are exhibited by $[Cu(en)CO]Cl$,[29,31] $[Cu(HB(pz)_3)CO]$,[30,31] and the five-coordinate carbonyl adduct of the Cu(I) macrocycle.[27] Hemocyanin reversibly combines with CO and carboxyhemocyanin[32] exhibits ν_{CO} = 2063 cm^{-1}. In view of the crystallographic results for Cu(I)–CO complexes a probable structure for $[Cu(AEP)_2IPAH(CO)]^+$ would have a pseudotetrahedral stereochemistry with the CO adding to a three-coordinate Cu(I) center or displacing a weakly bound pyridine donor from the proposed structure **6**. A five-coordinate adduct seems less likely since the ligand $(AEP)_2IPAH$ does not constrain four-coordination upon the Cu(I) in the same manner as a macrocyclic ligand.

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Registry No. **4**, 73940-71-3; **5**, 73940-72-4; **6a**, 73970-89-5; **6b**, 73970-88-4; $[Cu(AEP)_2IPAH(CO)]BF_4$, 73970-90-8; $[Cu(AEP)_2IPAH(CO)]CuCl_2$, 73953-28-3; IPAH, 7310-95-4; 2-(2-aminoethyl)pyridine, 2706-56-1; benzylamine, 100-46-9; $Cu(CH_3CN)_4BF_4$, 15418-29-8; $[(Cu_2(AEP)_2IPA)OH]Cl_2$, 73970-91-9.

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Kinetics Studies of Ligand Dissociation from Bis-Substituted Derivatives of Hexacarbonylchromium, *trans*-$Cr(CO)_4L_2$ (L = $P(C_4H_9)_3$, $P(OC_6H_5)_3$, $P(OCH_3)_3$, $P(C_6H_5)_3$, and $As(C_6H_5)_3$)

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The kinetics of ligand replacement on *trans*-$Cr(CO)_4L_2$ for L = $P(OC_6H_5)_3$, $P(C_4H_9)_3$, and $P(OCH_3)_3$ by CO have been studied between 100 and 140 °C in decane solution. The reactions proceed by rate-determining dissociation of the ligand L. Qualitative data are also reported for $Cr(CO)_4(P(C_6H_5)_3)_2$ and $Cr(CO)_4(As(C_6H_5)_3)_2$. The ordering of dissociation rates $As(C_6H_5)_3 > P(C_6H_5)_3 > P(C_4H_9)_3 > P(OC_6H_5)_3 > CO > P(OCH_3)_3$ is consistent with a very strong dependence of the π-bonding capability of the ligand, in contrast to dissociations from $Cr(CO)_5L$. Activation parameters are presented for dissociations of $P(OC_6H_5)_3$, $P(C_4H_9)_3$, and $P(OCH_3)_3$.

Introduction

Ligand dissociation to open a coordination site on an organometallic center is a very important step in reactions of organometallic compounds. Our recent study of dissociations of different ligands from $Cr(CO)_5L$ (L = $P(C_6H_5)_3$, $P(C_4H_9)_3$, $P(OC_6H_5)_3$, $P(OCH_3)_3$, and $As(C_6H_5)_3$) has shown the rates to be very dependent on the nature of the ligand dissociating; the range of dissociation rates spans five orders of magnitude.[1] The rates could not be correlated with steric size, σ-bonding ability or π-bonding ability; however, the strongly binding

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Table I. Infrared Spectra of *trans*-$Cr(CO)_4L_2$ Complexes

L	freq, cm^{-1}		
$P(OC_6H_5)_3$	2037 (w)	1978 (w)	1935 (s)
$P(OCH_3)_3$		1965 (w)	1916 (s)
$P(C_4H_9)_3$			1873 (s)
$P(C_6H_5)_3$			1884 (s)
$As(C_6H_5)_3$			1910 (s)

ligands ($P(C_4H_9)_3$, $P(OCH_3)_3$, and $P(OC_6H_5)_3$) dissociated much more slowly than the weaker ligands ($P(C_6H_5)_3$ and $As(C_6H_5)_3$).

There have been a few studies of ligand dissociation from more highly substituted complexes. An early study of dissociations from $Ni(CO)_2L_2$ showed the rates of dissociation in the order $PCl_3 > P(C_6H_5)_3 > P(C_4H_9)_3 > P(OC_6H_5)_3$.[2] A study of NiL_4 complexes showed that rates of dissociation correlated nicely with the steric size of the ligands.[3] Several studies have been reported on dissociation of ligands from *cis*-$Mo(CO)_4L_2$. Zingales and co-workers studied dissociations for a variety of ligands and found the order $PCl_3 \gg py > C_8H_{12} \sim As(C_6H_5)_3 > P(C_6H_5)_3 > PCl_2(C_6H_5) > Sb(C_6H_5)_3 \gg CO$ which cannot be explained by any one of the normal properties, i.e. σ- or π-bonding ability or steric size.[4,5] From Darensbourg's recent study of dissociation of L from *cis*-$Mo(CO)_4L_2$ where L is a phosphorus-based ligand, he suggested that steric factors were most important.[6] The ordering of ligand dissociation rates, $P(C_6H_5)(c\text{-}Hx)_2 > P(C_6H_5)_3 > P(O\text{-}o\text{-}tolyl)_3 > P(CH_3)(C_6H_5)_2 > P(OC_6H_5)_3 > P(OCH_3)_2(C_2H_5) \sim PN_3(CH_2)_6 \sim P(CH_3)_2(C_6H_5)$, shows a steric effect on the rate, but electronic factors must also be involved since phosphites dissociated more slowly than phosphines of similar steric size.[6] A number of studies of dissociation of bidentate ligands from $M(CO)_4(L\text{–}L)$ complexes have been reported, primarily by Dobson.[7-17] The rates of replacement were $\widehat{NN} > \widehat{SS} > \widehat{PP}$, an order that is quite similar to that for replacement of cis monodentate ligands. The ease of replacement of nitrogen ligands in comparison to phosphorus was shown by reaction of $(CO)_4M(\widehat{PN})$ with CO which reacted exclusively to form the phosphorus-substituted complex $(CO)_5M\widehat{PN}$.[16,17] Dissociation of trans-substituted complexes has been studied kinetically only for $Mo(CO)_4(P(C_6H_5)_3)_2$ where $P(C_6H_5)_3$ dissociated considerably slower than from the cis analogue which would indicate an influence of steric effects in the cis complex.[6]

To further expand our understanding of dissociations of ligands, we have investigated the kinetics of replacement of L by CO in *trans*-$Cr(CO)_4L_2$ for L = $P(C_4H_9)_3$, $P(OCH_3)_3$, $P(OC_6H_5)_3$, $P(C_6H_5)_3$, and $As(C_6H_5)_3$. The trans disposition of the ligands minimizes steric interactions and maximizes the electronic effects because of the shared orbitals of trans ligands.

Experimental Section

Materials. Decane was purified as previously described.[1] All other reagents were used as obtained from commercial sources.

Table II. First-Order Rate Constants for Ligand Dissociation from $Cr(CO)_4L_2$

L	temp, °C	k, s^{-1}
$P(OC_6H_5)_3$	110	$(3.26 \pm 0.09) \times 10^{-5}$
	120	$(1.21 \pm 0.04) \times 10^{-4}$
	130	$(3.97 \pm 0.19) \times 10^{-4}$
$P(C_4H_9)_3$	100	$(1.84 \pm 0.09) \times 10^{-5}$
	110	$(7.39 \pm 0.63) \times 10^{-5}$
	120	$(3.42 \pm 0.09) \times 10^{-4}$
	130	$(1.38 \pm 0.07) \times 10^{-3}$
$P(OCH_3)_3$	120	$(2.23 \pm 0.09) \times 10^{-6}$
	130	$(9.22 \pm 0.23) \times 10^{-6}$
	140	$(3.44 \pm 0.26) \times 10^{-5}$

Table III. Activation Enthalpies and Entropies for Dissociation of L from $Cr(CO)_4L_2$

L	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
$P(OC_6H_5)_3$	37.6 ± 1.0	18.6 ± 2.6
$P(C_4H_9)_3$	42.5 ± 1.8	33.2 ± 4.7
$P(OCH_3)_3$	43.4 ± 0.6	25.5 ± 1.6
CO[20]	40.2	22.6

$Cr(CO)_4(P(OC_6H_5)_3)_2$ was prepared and purified by the literature procedure.[18] The melting point observed was 148–150 °C (reported 148–149 °C). Anal. Calcd: Cr, 6.6; P, 7.9; C, 61.2; H, 3.9. Found: Cr, 6.6; P, 7.4; C, 60.1; H, 4.0. The infrared spectrum was in agreement with that previously reported, and the frequencies are listed in Table I.[18]

The reported synthesis for $Cr(CO)_4(P(OCH_3)_3)_2$ was followed, yielding white crystals with a melting point of 79–81 °C (reported 76–78 °C[19]). Anal. Calcd: Cr, 12.6; P, 15.0; C, 29.1; H, 4.4. Found: Cr, 13.0; P, 14.8; C, 29.4; H, 4.5. The infrared frequencies are listed in Table I.

The previously unreported bis(tri-*n*-butylphosphine) complex, $Cr(CO)_4(P(C_4H_9)_3)_2$, was prepared by reacting a diglyme solution of $Cr(CO)_6$ and 2 equiv of $P(C_4H_9)_3$ at 120 °C for 2 days under an argon atmosphere. The diglyme was removed under vacuum, and the oily solid product was dissolved in a minimum of hexane, yielding a yellow-green solution which was chromatographed on an alumina column with hexane as solvent. A yellow solution resulted which produced yellow needles after hexane removal and recrystallization from $CHCl_3/C_2H_5OH$. The crystals melted at 38–39 °C. Anal. Calcd: Cr, 9.1; P, 10.8; C, 59.1; H, 9.6. Found: Cr, 9.5; P, 10.9; C, 58.7; H, 9.2. The CO stretching frequencies listed in Table I and shown in Figure 1 are consistent with a trans configuration for the $P(C_4H_9)_3$ ligands.

$Cr(CO)_4(P(C_6H_5)_3)_2$ was prepared by the literature procedure.[18] The melting point of 254 °C agrees with that previously reported (250–252 °C). The CO stretching frequencies in methylene chloride are reported in Table I.

The reaction of $Cr(CO)_6$ and $As(C_6H_5)_3$ (fivefold excess) in refluxing diglyme for 5 h led to a yellow solution with an infrared absorption at 1910 cm^{-1} which cannot be assigned to $Cr(CO)_5As(C_6H_5)_3$. Attempts to pass this material down an alumina column resulted in decomposition to $Cr(CO)_6$ and $Cr(CO)_5As(C_6H_5)_3$. We were unable to purify this species ($Cr(CO)_4(As(C_6H_5)_3)_2$) and believe that $As(C_6H_5)_3$ must be present in solution to avoid dissociative loss of $As(C_6H_5)_3$ from $Cr(CO)_4(As(C_6H_5)_3)_2$ leading to decomposition.

Kinetics Measurements. The previously reported experimental procedure was followed, except as noted below.[1] Infrared spectra were recorded on a Beckman 4240 infrared spectrophotometer in the absorbance mode using 1.0-mm NaCl solution cells. All quantitative data were obtained on the most intense infrared stretching frequency (E mode). Beer's law plots (hexane solution) were constructed for $Cr(CO)_4(P(OC_6H_5)_3)_2$, $Cr(CO)_4(P(OCH_3)_3)_2$, and $Cr(CO)_4(P(C_4H_9)_3)_2$ with extinction coefficients of 9.05×10^2, 1.47×10^3, and 2.47×10^3 M^{-1}, respectively. For $Cr(CO)_4(P(OC_6H_5)_3)_2$ and $Cr(CO)_4(P(OCH_3)_3)_2$ linear Beer's law plots were found throughout the concentration range which can be studied by infrared ($(1\text{–}6) \times 10^{-4}$ M). However for the bis(tributylphosphine) compound $Cr(CO)_4(P(C_4H_9)_3)_2$, significant deviations occurred for absorbances greater

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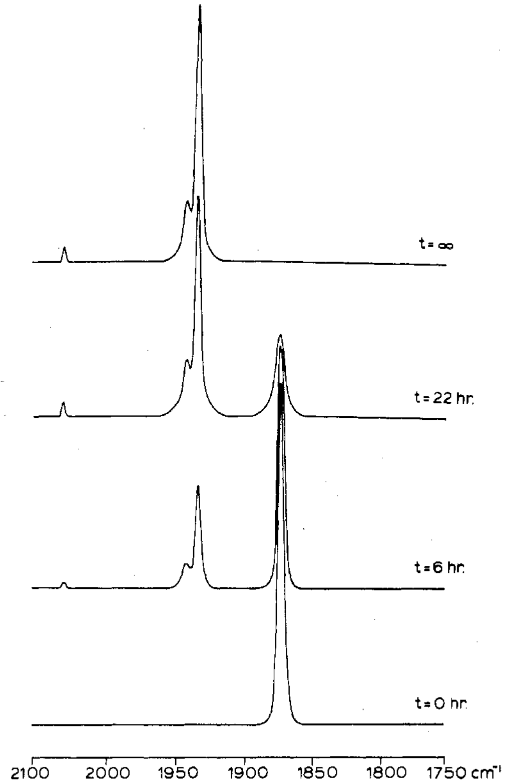

Figure 1. Infrared spectra in the CO stretching region obtained on addition of CO to $Cr(CO)_4(P(C_4H_9)_3)_2$.

than 0.70 (2.8×10^{-4} M^{-1}). Data for this complex were collected only at absorbances below 0.70, and we made no effort to ascertain the reasons for the deviations.

Results

The first-order rate constants evaluated for substitution of L by CO on *trans*-$Cr(CO)_4L_2$ are reported in Table II. For L = $P(OC_6H_5)_3$, $P(OCH_3)_3$, and $P(C_4H_9)_3$ the reactions were studied for at least three temperatures, and the activation parameters are reported in Table III. The reactions yielded only $Cr(CO)_5L$ as product; $Cr(CO)_6$ was not observed.

We confirmed the previous observations that $P(C_6H_5)_3$ dissociates quite readily from $Cr(CO)_4(P(C_6H_5)_3)_2$ at 40 °C but did not study the reaction quantitatively.[21] We attempted the preparation of $Cr(CO)_4(As(C_6H_5)_3)_2$ but were unsuccessful in isolating the complex. From the infrared spectrum we believe it was present in solution but decomposed when the excess ligand was removed from solution. Apparently $As(C_6H_5)_3$ dissociation is extremely rapid from $Cr(CO)_4(As(C_6H_5)_3)_2$ at room temperature.

Discussion

We have investigated the kinetics of the reaction

$$Cr(CO)_4L_2 + CO \rightarrow Cr(CO)_5L + L \qquad (1)$$

of $Cr(CO)_4L_2$ with CO in decane solution between 100–140 °C. The reactions proceed cleanly with complete consumption of $Cr(CO)_4L_2$ leading to only $Cr(CO)_5L$ as product. In no reaction was there evidence for $Cr(CO)_6$ as a product nor was there any evidence for the reverse of reaction 1. The reaction was first order in $Cr(CO)_4L_2$. The activation parameters indicate a rate-determining dissociation of L from $Cr(CO)_4L_2$ leading to the 16-electron intermediate $Cr(CO)_4L$. Thus the rate of dissociation provides information on the binding of the ligand to the chromium.[1] Our previous work showed that the rate of dissociation can provide quite accurate information on the bond strength. The rates of dissociation from *trans*-$Cr(CO)_4L_2$ span greater than 10 orders of magnitude as shown in Table IV where we have collected the rate constants for 130 °C. The ordering of rates of dissociation is $P(OCH_3)_3 < CO < P(OC_6H_5)_3 < P(C_4H_9)_3 < P(C_6H_5)_3 < As(C_6H_5)_3$, which is similar to the ordering for $Cr(CO)_5L$ with the exception of $P(C_4H_9)_3$ which will be discussed later. The ordering of the ligands shows that phosphites dissociate much more slowly than the phosphine ligands. Triphenylarsine dissociates most rapidly.

Table IV. Rate Constants for Dissociation of L from $Cr(CO)_4L_2$ and $Cr(CO)_5L$ at 130 °C

L	10^6k bis	10^6k mono	$k(bis)/k(mono)^c$
$P(OCH_3)_3$	9.22	0.548	8.4
$P(OC_6H_5)_3$	397	15.7	12.7
$P(C_6H_5)_3$	$9.9 \times 10^{7\,a}$	99.7	5×10^5
$P(C_4H_9)_3$	1380	0.0065^b	1×10^5
$As(C_6H_5)_3$	very fast	11 600	
CO^{20}	130	130	1

[a] Calculated from the data in ref 21 by assuming a $\Delta H^\ddagger$ of 38 kcal/mol. [b] Calculated from the equilibrium constant and the rate constant for the reverse reaction. [c] Corrected for the statistical factor of two ligands for the bis-substituted complex.

Comparison with the dissociation rates for monosubstituted complexes, given in Table IV, is quite informative.[1] In all cases the ligand dissociates more rapidly from *trans*-$Cr(CO)_4L_2$ than from $Cr(CO)_5L$. The rates of dissociation for $P(OCH_3)_3$ and $P(OC_6H_5)_3$ are a factor of 10 greater for the bis complex compared to the monosubstituted complex, while for the phosphines, $P(C_4H_9)_3$ and $P(C_6H_5)_3$, dissociation from the bis-substituted complex occurs $\sim 10^5$ times more readily than from the monosubstituted. In examining kinetic effects of this type, one must look at both transition-state and ground-state effects. For L dissociation from $Cr(CO)_5L$ the transition state corresponds to complete removal of L and probably closely resembles the $Cr(CO)_5$ intermediate. Activation parameters for dissociation of L from $Cr(CO)_4L_2$ indicate that the transition state for this reaction also corresponds to complete removal of L. This transition state is probably very similar to the five-coordinate intermediate $Cr(CO)_4L$, in which L occupies the axial position of a square pyramid. Lichtenberger and Brown have shown this five-coordinate intermediate to be higher in energy than the intermediate with L in the basal position.[26] There is probably a second step in the energy profile which allows rearrangement of the axially substituted $Cr(CO)_4L$ species to the basal. The energy of this intermediate depends on the ligand L, with a stabilization observed for weaker π-bonding ligands (i.e., $Cr(CO)_4P(C_6H_5)_3$ would be lower in energy than $Cr(CO)_5$).[22-26] The maximum stabilization of a transition state similar to the intermediate $Cr(CO)_4L$ with L in a basal position for the ligands $P(C_4H_9)_3$, $P(C_6H_5)_3$, $P(OC_6H_5)_3$, and $P(OCH_3)_3$ would lead to an acceleration in rate of ~ 50 times.[23] With the assumption of similar stabilization of the transition state with axial L, the largest rate effect from transition-state stabilization would be $\sim 10^2$. For the ligands $P(OCH_3)_3$ and $P(OC_6H_5)_3$ the amount of increase from monosubstituted to bis-substituted is small enough[9] that transition-state arguments could be offered; however no data are available on whether $Cr(CO)_4P(OR)_3$ would indeed be lower in energy than $Cr(CO)_5$. It is perhaps

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significant that the Cr–P bond length in $Cr(CO)_5P(OC_6H_5)_3$ is 2.309 Å[27] while the Cr–P bond length for *trans*-$Cr(CO)_4(P(OC_6H_5)_3)_2$ is 2.252 Å.[28] These data suggest that the triphenyl phosphite is more strongly bonded in $Cr(CO)_4(P(OC_6H_5)_3)_2$ than in $Cr(CO)_5P(OC_6H_5)_3$ and that the increased rate of dissociation arises from transition-state effects. For $Cr(CO)_4(P(C_6H_5)_3)_2$ and $Cr(CO)_4(P(C_4H_9)_3)_2$ the increased rate of dissociation over the monosubstituted analogues is too large to be accounted for by the transition-state effects as described by Brown and co-workers;[26] ground-state effects must contribute most of the observed acceleration. $P(C_6H_5)_3$ and $P(C_4H_9)_3$ are much poorer π acceptors than the phosphite ligands. Through σ donation the phosphines create a net buildup of electron density along the P–Cr–P axis which cannot be dissipated. In the monosubstituted compounds the ligand trans to phosphine is a CO, which effectively removes electron density through π-acceptor action and creates a stronger Cr–P bond. Thus the second substitution of a phosphine ($P(C_6H_5)_3$ or $P(C_4H_9)_3$) for CO causes a weakening of the trans Cr–P bond and a much greater dissociation rate for the phosphine.

The activation parameters as shown in Table III are consistent with the dissociative nature of the reaction. The large positive entropies of activation indicate a more disordered transition state as expected for ligand dissociation. The enthalpy of activation in a dissociative process is sometimes related to the bond strength of the bond which is breaking. For the complexes $Cr(CO)_5P(OC_6H_5)_3$ and $Cr(CO)_4(P(OC_6H_5)_3)_2$, for which crystal structures are known, the comparison of $\Delta H^{\ddagger}$ with bond length can be made.[27,28] The $Cr(CO)_4(P(OC_6H_5)_3)_2$ complex which has the shorter Cr–P bond length (2.252 Å) has a larger $\Delta H^{\ddagger}$ (37.6 kcal). The values for $Cr(CO)_5P(OC_6H_5)_3$ are Cr–P (2.309 Å) and $\Delta H^{\ddagger}$ (31.9 kcal). Both shorter bond length and large $\Delta H^{\ddagger}$ could indicate a strengthening of the Cr–P bond in the ground state of $Cr(CO)_4(P(OC_6H_5)_3)_2$ over $Cr(CO)_5P(OC_6H_5)_3$.

Our data provide no direct information of the nature of the intermediate; however, Darensbourg and Graves' recent work on the reaction of *trans*-$Mo(CO)_4(P(C_6H_5)_3)_2$ with ^{13}CO is similar enough to allow speculation.[6] They observed that *cis*-$Mo(CO)_4(^{13}CO)P(C_6H_5)_3$ is the only product of this reaction.[6] While they offered no explanation for the cis stereochemistry, it would seem that a direct application of the principle of microscopic reversibility would require cis incorporation since $M(CO)_5L$ complexes have been shown to selectively dissociate CO from the cis position.[24] Thus the intermediate generated by ligand loss from $M(CO)_4L_2$ must rearrange and incorporate CO along the preferred low-energy path which would give cis addition.

Disubstituted derivatives of chromium hexacarbonyl dissociate the ligands at widely varying rates depending on the nature and orientation of the ligands. For example *trans*-$Cr(CO)_4(As(C_6H_5)_3)_2$ apparently dissociates $As(C_6H_5)_3$ very rapidly at room temperature while $Cr(CO)_4$(diphos) does not react at 110 °C.[25] Both steric and electronic properties must be important in determining the reactivity. Clearly the trans-disubstituted distribution is the most stable. This is shown by the room-temperature reaction of *cis*-$Cr(CO)_4P(C_6H_5)_3Cl^-$ with $AlCl_3$ and $P(C_6H_5)_3$, leading to *trans*-$Cr(CO)_4P(C_6H_5)_3)_2$, and the substitution of $Cr(CO)_5P(C_6H_5)_3$ with $P(C_6H_5)_3$ which leads to trans substitution even though the cis CO dissociates.[24] Steric effects are probably responsible for the trans distribution. In a study of the cis–trans equilibria in $W(CO)_4LL'$ complexes, Schenk has recently noted the importance of steric interactions in the cis complexes.[29] An interesting series of complexes are *cis*-$Mo(CO)_4(P(C_6H_5)_3)_2$, *trans*-$Mo(CO)_4(P(C_6H_5)_3)_2$ and $Mo(CO)_4$(diphos). The cis isomer dissociates $P(C_6H_5)_3$ at a rate of 3.2×10^{-3} s^{-1} at 70 °C and the trans isomer dissociates $P(C_6H_5)_3$ at a rate of 4.7×10^{-5} s^{-1} at 70 °C while one end of the diphos dissociates at the rate of 4.7×10^{-4} s^{-1} at 110 °C. This suggests in the absence of steric effects (diphos) that cis distribution is more stable kinetically but that steric effects are quite significant in *cis*-$Mo(CO)_4(P(C_6H_5)_3)_2$. The same effect is more dramatic for the smaller chromium center. Thus, *cis*-$Cr(CO)_4(P(C_6H_5)_3)_2$ cannot be formed; *trans*-$Cr(CO)_4(P(C_6H_5)_3)_2$ dissociates $P(C_6H_5)_3$ at a rate of 3.8×10^{-5} at 40 °C, and $Cr(CO)_4$(diphos) gives no evidence of diphos dissociation at 110 °C. We believe these effects are too large to be due solely to a chelate effect; rather they represent electronic preference for the ligands to be cis, whereas steric effects prohibit cis formation. This idea is supported by the observation that smaller ligands such as $P(OCH_3)_3$ or $P(C_2H_5)_3$ form mixtures of *cis*- and *trans*-$Cr(CO)_4L_2$.[30] Further, the recent crystal structure determination of *fac*-$Cr(CO)_3(P(C_2H_5)_3)_3$ shows large steric interactions.[31]

This study has shown that the rate of dissociation of L from *trans*-$Cr(CO)_4L_2$ depends very much on the π-acceptor capabilities of L. This is in contrast to dissociation from $Cr(CO)_5L$ where only the binding strength was important regardless of whether it was a σ donor or π acceptor.

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Registry No. *trans*-$Cr(CO)_4[P(OC_6H_5)_3]_2$, 35039-06-6; *trans*-$Cr(CO)_4[P(OCH_3)_3]_2$, 21370-42-3; *trans*-$Cr(CO)_4[P(C_4H_9)_3]_2$, 20957-93-1; *trans*-$Cr(CO)_4[P(C_6H_5)_3]_2$, 38800-75-8; *trans*-$Cr(CO)_4[As(C_6H_5)_3]_2$, 74034-37-0; $Cr(CO)_5P(OCH_3)_3$, 18461-34-2; $Cr(CO)_5P(OC_6H_5)_3$, 18461-39-7; $Cr(CO)_5P(C_6H_5)_3$, 14917-12-5; $Cr(CO)_5P(C_4H_9)_3$, 18497-59-1; $Cr(CO)_5As(C_6H_5)_3$, 29742-98-1; $Cr(CO)_6$, 13007-92-6.

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