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Ligand Substitution Processes in Tetranuclear Carbonyl Clusters. 6. Steric Contribution to Ligand Dissociation in Multisubstituted $Ir_4(CO)_{12}$ Derivatives

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Abstract: A kinetic investigation of carbon monoxide exchange processes in the series of trisubstituted $Ir_4(CO)_9[PR_3]_3$ derivatives (R = Me, Et, *n*-Bu, Ph, and *i*-Pr) is reported. The rate of dissociation of CO was accelerated as the spatial requirements of the substituted PR_3 ligand increased, with the order of CO-labilizing ability being $PMe_3 < P\text{-}n\text{-}Bu_3 \lesssim PEt_3 < P\text{-}i\text{-}Pr_3 < PPh_3$. A smaller electronic effect of the phosphorus ligand is superimposed on this steric acceleration phenomenon as noted for the PPh_3 case. The overall increase in dissociative CO rates resulting from replacement of three carbon monoxide ligands in the parent $Ir_4(CO)_{12}$ species by PR_3 varied over a factor of 1150–45 100 as the cone angle of the trialkylphosphines increased from 118 to 160 °C while their basicities were essentially unchanged. The activation parameters for CO dissociation in the representative $Ir_4(CO)_9(PEt_3)_3$ species were determined to be $\Delta H^* = 28.4 \pm 2.7$ kcal/mol and $\Delta S^* = 3.52 \pm 6.42$ eu, values consistent with a dissociative process. A similar kinetic lability of the phosphorus ligand in $Ir_4(CO)_8(PR_3)_4$ derivatives was noted for sterically demanding PR_3 ligands. For $Ir_4(CO)_8(PR_3)_4$ derivatives possessing PR_3 ligands of uniform electronic character, R = Me, Et, and *n*-Bu, the rate of phosphine dissociation increased by a factor of 3300 with increasing ligand cone angle. Activation parameters (ΔH^* and ΔS^*) for PEt_3 dissociation in $Ir(CO)_8(PEt_3)_4$ were found to be 33.0 ± 2.7 kcal/mol and 19.1 ± 7.9 eu, respectively. A general discussion of the origin of steric and electronic phosphorus ligand labilizing abilities in metal clusters is provided.

The sizable rate acceleration for CO dissociation observed during the progressive phosphine substitution reaction of $Ir_4(CO)_{12}$ with PPh_3 to eventually afford $Ir_4(CO)_9(PPh_3)_3$ (eq 1)[1,2] is often

$$Ir_4(CO)_{12} \rightarrow Ir_4(CO)_{11}PPh_3 \rightarrow Ir_4(CO)_{10}(PPh_3)_2 \rightarrow Ir_4(CO)_9(PPh_3)_3 \quad (1)$$

regarded as being supportive evidence that electronic interactions can be transmitted from neighboring metal atoms to the active catalytic center in a cluster.[3] The importance to metal cluster chemistry of such a conclusion warrants a more thorough investigation of these ligand substitutional processes in order to examine the generality of this observation as the nature of the phosphorus ligand and metal are varied. This is particularly true in light of the significant structural change accompanying incorporation of the first phosphorus ligand into the parent Ir_4 cluster.[4,5]

Other kinetic data are present in the literature for CO dissociative reactions involving binuclear[6] and cluster[7] metal carbonyls which suggest cooperativity between metal centers. For example, the rate of CO dissociation in $Mn_2(CO)_9L$ is some 50 times faster than that in the parent decacarbonyl species, $Mn_2(CO)_{10}$.[6] Nevertheless, these results can as well be explained by cis labilization[8] or steric induction[9] arguments based on CO dissociation from a previously phosphorus ligand substituted metal center.[10]

Carbon monoxide substitution reactions in group 8 metal carbonyl clusters bear several mechanistic similarities to the corresponding processes involving mononuclear metal carbonyls. That is, in both instances the kinetic behavior is consistent with a two-term rate law (eq 2), where k_1 and k_2 are identified with

$$\text{rate} = k_{\text{obsd}}[M_4(CO)_{12}] = (k_1 + k_2[L])[M_4(CO)_{12}] \quad (2)$$

dissociative and associative or interchange mechanisms, respectively. Dependent on the nature of the entering nucleophile, Co_4 and Ir_4 carbonyl cluster substitution pathways can be dominated by the incoming ligand dependent term.[1,2,11] A feature generally available in these tetranuclear clusters, which is less frequently open to 18-electron mononuclear species,[12] is their ability to accommodate another ligand in the metal's coordination sphere while still maintaining conformity with the 18-electron rule. This is achieved with the simultaneous breaking of metal–metal bonds in the cluster framework, e.g., intermediates of the type shown in Figure 1.[13] The low nucleophilicity of CO, coupled with its limited solubility in organic solvents at moderate pressures, minimizes the $k_2[L]$ term when L equals ^{13}CO. Hence, the measurement of ^{13}CO exchange rates provides a more accurate evaluation of dissociative CO rate parameters, as compared with ligand (L) substitution processes when $k_2[L] >> k_1$.

The ^{13}CO exchange technique has been employed in obtaining the relative order of reactivity for dissociative CO substitutional processes in $Co_4(CO)_{12}$ with progressive substitution of $P(OMe)_3$ (eq 3).[9,14] These data dramatically illustrate the absence of an

$$Co_4(CO)_{12} \xrightarrow{1.00} Co_4(CO)_{11}P(OMe)_3 \xrightarrow{0.62} Co_4(CO)_{10}[P(OMe)_3]_2 \xrightarrow{1.46} Co_4(CO)_9[P(OMe)_3]_3 \quad (3)$$

effect on the rate parameters for CO loss in the Co_4 cluster with successive replacement of CO by the *small*, good π-acceptor $P(OMe)_3$ ligand.

We have for some time maintained a keen interest in steric effects on the rates of ligand substitution processes in mononuclear metal carbonyl derivatives.[15,16] For example, our investigations involving *cis*-$Mo(CO)_4L_2$ derivatives, where X-ray structural data indicate significant steric crowding when L is a bulky phosphorus ligand,[17] reveal steric interactions to be of paramount importance

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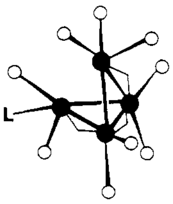

Figure 1. $M_4(CO)_{12}L$ intermediate.

in determining rates of phosphorus ligand dissociation. Similarly, comparative kinetic studies of either *cis*-CO labilization or phosphine dissociation in $W(CO)_5PMe_3$ and $W(CO)_5P$-*t*-Bu_3 derivatives demonstrate both processes to be greatly enhanced in the sterically demanding P-*t*-Bu_3 species,[18] observations consistent with the solid-state structures of these complexes.[19,20] There is no reason to anticipate a lessening of steric acceleration of dissociative ligand displacement in metal cluster species. For certain, the solid-state geometries of several $M_4(CO)_{12-n}L_n$ derivatives appear to be dictated by the steric bulk of the ligand, L. For instance, in $Co_4(CO)_{10}[P(OMe)_3]_2$ both of the small $P(OMe)_3$ ligands are axial,[21] whereas in $M_4(CO)_{10}(PPh_3)_2$ (M = Rh, Ir)[22,23] the bulky PPh_3 ligands orient themselves in equatorial and axial sites. Interligand repulsions also account for the significant Ir–Ir bond lengthening (2.794 (1) Å vs. 2.720 (1) Å) noted in $Ir_4(CO)_8(PMe_3)_4$ between iridium atoms bearing axial PMe_3 ligands.[24] More pertinent to the tenor of this report, kinetic data for ligand dissociation reaction in this $Ir_4(CO)_8(PMe_3)_4$ species[24] and in related $Co_4(CO)_{12-n}L_n$ systems[9] are consistent with sterically induced processes.

In this paper we wish to examine dissociative loss of both phosphine and carbon monoxide ligands in substituted $Ir_4(CO)_{12}$ clusters with emphasis being placed on variations in rates as a function of the spatial requirements of the substituents.

Experimental Section

Compound Preparations. (a) $Ir_4(CO)_9(PMe_3)_3$. This complex, as well as the others described below, was prepared in much the same manner as that previously reported by Drakesmith and Whyman.[25] A 0.5-g sample of KOH was dissolved in 20 mL of methanol which had been purged with nitrogen. Under a nitrogen atmosphere, 0.2 g of $Ir_4(CO)_{12}$ (0.38 mmol) was added and the solution heated to 50 °C. After 10 min, 1.2 mmol of PMe_3 was added to the clear orange solution. For the volatile trimethylphosphine ligand, the reaction flask was fitted with a Dewar condenser which was cooled with an acetone/dry ice slush. Product precipitated slowly during 2 h of stirring; the solid was filtered from the hot solution. Purification of $Ir_4(CO)_9(PMe_3)_3$ was accomplished by recrystallization from hot ethanol.

(b) $Ir_4(CO)_9(PPh_3)_3$. Preparation was accomplished as for $Ir_4(CO)_9(PMe_3)_3$, using 1.2 mmol of PPh_3 and a carbon monoxide atmosphere.

(c) $Ir_4(CO)_9$(P-*i*-$Pr_3)_3$. A 0.5-g sample of $Ir_4(CO)_{12}$ was combined with 0.5 mL of P-*i*-Pr_3 in 60 mL of toluene. The mixture was stirred under reflux under a carbon monoxide atmosphere for 4 h. The solution was cooled and then filtered, and the solvent was removed from the filtrate by vacuum distillation. The residue was chromatographed on a silica gel column with a 50:50 mixture of toluene and hexane. The first orange band was collected and the solvent removed, yielding a residue of pure product.

(d) $Ir_4(CO)_9(PR_3)_3$ (R = Et, *n*-Bu). To a suspension of 0.2 g of $Ir_4(CO)_{12}$ (0.38 mmol) in 70 mL of toluene was added 1.2 mmol of P-*n*-Bu_3 or 1.2 mmol of redistilled PEt_3. When volatile PEt_3 was involved, the reaction flask was fitted with a Dewar condenser which was cooled with an acetone/dry ice slush. The mixture was refluxed under an atmosphere of CO for 2 h. Solvent was removed by vacuum distillation and 10 mL of ethanol added. The yellow product was filtered and recrystallized from hot heptane.

Table I. Elemental Analysis of $Ir_4(CO)_{12-n}[PR_3]_n$ (n = 3, 4) Derivatives

	% C		% H	
derivative	calcd	found	calcd	found
$Ir_4(CO)_9(PEt_3)_3$	23.57	23.71	3.27	3.43
$Ir_4(CO)_9$(P-*n*-$Bu_3)_3$	33.20	32.91	5.02	5.02
$Ir_4(CO)_9(PPh_3)_3$	40.89	39.99	2.51	2.62
$Ir_4(CO)_8(PMe_3)_4$	18.51	18.26	2.78	2.81
$Ir_4(CO)_8(PEt_3)_4$	26.20	25.98	4.09	4.10
$Ir_4(CO)_8$(P-*n*-$Bu_3)_4$	37.32	36.94	6.04	6.14
$Ir_4(CO)_8[P(OPh)_3]_4$	43.01	43.48	2.71	3.06
$Ir_4(CO)_8[P(OMe)_3]_4$	16.13	16.18	2.44	2.38

Table II. Infrared Spectra in ν(CO) Region (cm^{-1}) in C_2Cl_4 for $Ir_4(CO)_{12-n}L_n$ (n = 3, 4)

$Ir_4(CO)_9L_3$, L =				
PMe_3	PEt_3	P-*n*-Bu_3	P-*i*-Pr_3	PPh_3
2030	2030	2029	2033	2040
2008	2006	2006	2004	2002
1992	1990	1988	1996	1996
1988	1984	1982	1986	1982 (sh)
1976	1962	1960	1965	1965
1783	1784	1784	1780	1797, 1788

$Ir_4(CO)_8L_4$, L =					
PMe_3	PEt_3	P-*n*-Bu_3	PPh_2Me	$P(OMe)_3$	$P(OPh)_3$
1993	1990	1988	2004	2015	2033
1973	1978 (sh)	1975 (sh)	1987	1995 (sh)	2015
1958	1959	1956	1972	1987	2005
1929	1926	1924	1939		1982
1777	1775	1773	1773	1794	1813

(e) $Ir_4(CO)_8(PR_3)_4$ (PR_3 = PMe_3, PEt_3, P-*n*-Bu_3, $P(OMe)_3$, $P(OPh)_3$, PPh_2Me). A mixture of 10 mL of toluene, 0.37 g of $Ir_4(CO)_{12}$ (0.7 mmol), and 3.5 mmol of PR_3 was refluxed under carbon monoxide for 2 h. When a volatile phosphine was used (R = Me, Et), the reaction flask was fitted with a Dewar condenser which was cooled with a dry ice/acetone slush. The solvent was removed and 10 mL of ethanol added. Product was filtered from ethanol solution and dried in vacuo. Purification of $Ir_4(CO)_8[P(OPh)_3]_4$ was accomplished by recrystallization from cold (−2 °C) octane, overnight. All other products were recrystallized from hot ethanol.

Methods. Elemental analyses on the iridium cluster derivative were performed by Galbraith Laboratories (Table I). All cluster compounds were characterized by infrared spectroscopy in the ν(CO) region (Table II). Infrared spectra were obtained on a Perkin-Elmer 283-B infrared spectrophotometer interfaced with an infrared data station which enabled the accumulation and averaging of spectra. Samples were prepared in tetrachloroethylene and spectra run in matched 1-mm NaCl cells.

The reaction of the tetrakis(phosphine)-substituted complex with carbon monoxide to afford the tris(phosphine)-substituted complex was examined kinetically. A 50-mL Schlenk flask containing 10 mL of $Ir_4(CO)_8(PR_3)_4$, where PR_3 = PMe_3, PEt_3, P-*n*-Bu_3, PPh_2Me, in organic solvent was evacuated and filled with carbon monoxide. The flask was heated in a constant temperature bath, and samples were withdrawn periodically by syringe and subjected to infrared analysis.

The rates of phosphine dissociation were compared via the disappearance of carbonyl infrared bands corresponding to $Ir_4(CO)_8(PR_3)_4$ and concurrent appearance of peaks corresponding to $Ir_4(CO)_9(PR_3)_3$. In particular, the increasing absorbance at ~2030 cm^{-1} of $Ir_4(CO)_9(PR_3)_3$ was monitored. By taking the average of five scans, a very accurate absorbance measurement was possible. The process is first order in metal cluster concentration and independent of carbon monoxide concentration.

The rate of incorporation of carbon-13 carbon monoxide was measured in order to assess the steric effect of phosphines on the rate of carbonyl exchange in the clusters. Infrared spectra were useful in detecting ^{13}C carbonyl exchange, because absorption peaks in the carbonyl stretching region shift to lower frequencies as ^{13}CO is incorporated into the various

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Table III. Rate Constants for CO Dissociation in $Ir_4(CO)_9(PR_3)_3$ Derivatives in Tetrachloroethylene[a]

R	10^3k, s^{-1}	$t_{1/2}$, min	θ,[b] deg
Me	0.173	66.8	118
Et	1.33	8.69	132
n-Bu	1.27	9.06	132
i-Pr	6.76	1.71	160
Ph	7.84	1.47	145

[a] These rate constants were obtained from the k_{obsd} values which were multiplied by 7 (seven positions for a single incoming ^{13}CO ligand to distribute itself among to afford one bridging ^{13}CO group) and divided by 2 (selective dissociation of one of the two axial CO groups). The reaction temperature was 80 °C. [b] Taken from: Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

positions. Ten milliliters of a solution of the $Ir_4(CO)_9(PR_3)_3$ derivative in tetrachloroethylene was placed in a 50-mL Schlenk flask filled with 94% ^{13}CO and fitted with a rubber septum cap. The flask was heated in a constant temperature bath, and samples were withdrawn at intervals with a hypodermic syringe and ice cooled. The rate of carbon-13 carbonyl enrichment was monitored via the decrease in the absorbance of the bridging ^{12}CO carbonyl stretch. Again, average scans provided accurate absorbance intensities and resulted in well-behaved data. The ^{13}CO was present in the reaction vessel in considerable molar excess (>20-fold) over the substrate $Ir_4(CO)_9(PR_3)_3$ species. Hence, during the course of the reaction the ^{13}CO content in the carbon monoxide does not change significantly, decreasing from 94 to about 90% at the end of the reaction period. Therefore, no corrections to the rate constants for these small fractional changes in ^{13}CO abundance were made.

Samples of $Ir_4(CO)_9(PR_3)_3$ (R = Et, *n*-Bu, Ph) enriched in carbon-13 labeled carbon monoxide were prepared by synthesizing the compounds as described previously under an atmosphere of ^{13}CO. Samples of $Ir_4(CO)_8(PR_3)_4$ (R = Me, Et, *n*-Bu) enriched in ^{13}C carbon monoxide were obtained by refluxing the ^{13}C-labeled $Ir_4(CO)_9(PR_3)_3$ with excess phosphine in toluene under an atmosphere of ^{13}CO. Enriched samples were examined by ^{13}C NMR spectroscopy with a JEOL-FX60 Fourier transform NMR spectrometer.

Results and Discussion

Carbon monoxide exchange reactions of the $Ir_4(CO)_9(PR_3)_3$ derivatives (PR_3 = PMe_3, PEt_3, P-*n*-Bu_3, P-*i*-Pr_3, and PPh_3) (eq 4) were measured in tetrachloroethylene at 80 °C. The rate

$$\mathrm{Ir_4(CO)_9(PR_3)_3} + m\,{}^{13}\mathrm{CO} \rightleftharpoons \mathrm{Ir_4(CO)_{9-\mathit{m}}(^{13}CO)_{\mathit{m}}(PR_3)_3} + m\mathrm{CO} \quad (4)$$

constants for CO dissociation were measured by monitoring the decrease in absorptions in the bridging ν(CO) region due to the all ^{12}CO species as described in our previous publication.[9,14] This procedure is based on the fact that vibrational frequencies for terminal and bridging CO ligands are not strongly coupled and intramolecular CO rearrangement is fast relative to the CO dissociation process; i.e., the incoming ^{13}CO ligand is statistically distributed throughout the cluster (vide infra). The rate constants, listed in Table III, were calculated by assuming the stereoselective dissociation of the two axial CO ligands in $Ir_4(CO)_9(PR_3)_3$. No observable variations in the rate of ^{13}CO incorporation were noted for CO pressures ranging from 380 to 1140 torr. The once formed highly ^{13}CO-enriched Ir_4 clusters were subjected to the reverse reaction of eq 4, i.e., using ^{12}CO as the entering ligand. The ν(CO) infrared trace of the resulting reaction solution was identical with that observed for the reaction solution prior to any ^{13}CO incorporation. Thus the CO exchange reaction appears to be quite clean, with no side processes occurring.

The disposition of the phosphorus ligands in $Ir_4(CO)_9(PPh_3)_3$[23] and $Rh_4(CO)_9[P(OPh)_3]_3$[22] determined from X-ray structural studies is one axial and two equatorial. ^{31}P NMR investigations on $Rh_4(CO)_9[P(OPh)_3]_3$ have demonstrated this to be the only isomer present in solution as well.[22] Because of the similarity in the solution ν(CO) infrared spectra of the $Ir_4(CO)_9(PR_3)_3$ derivatives herein reported upon with that for the $Ir_4(CO)_9(PPh_3)_3$ species (Table II), all of these substituted clusters are believed to be isostructural. The ^{13}C NMR spectrum of $Ir_4(CO)_9(PEt_3)_3$ is also consistent with this structural designation (see Figure 2) and bears a close resemblance to the ^{13}C NMR spectrum described for $Ir_4(CO)_9(PPh_2Me)_3$ by Stunz and Shapley.[4] This latter derivative was assigned a structure analogous to that of $Ir_4(CO)_9(PPh_3)_3$. Therefore, variations in the reactivity of these $Ir_4(CO)_9(PR_3)_3$ derivatives may be ascribed only to changes in the electronic and/or steric character of the ligand (L) and not to structural variations in the clusters.

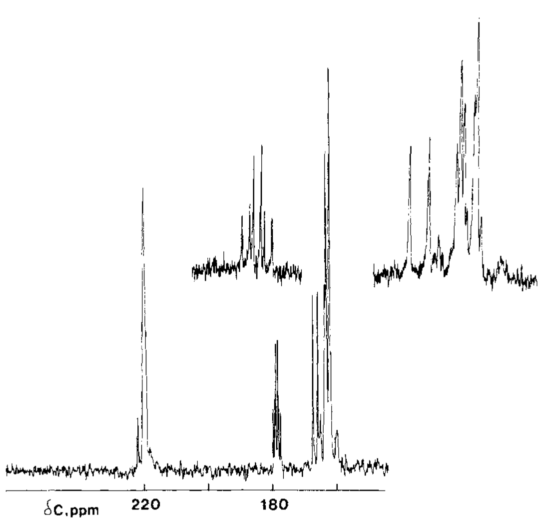

Figure 2. ^{13}C FT NMR spectrum of ^{13}CO-enriched $Ir_4(CO)_9(PEt_3)_3$ in $CDCl_3$ at ambient temperature (same spectrum observed at −33 °C). Sample prepared from $Ir_4(CO)_8(PEt_3)_4$ and ^{13}CO. Peak assignments are analogous to those provided in ref 4. Overlays are expansions of the terminal CO resonances.

Sonnenberger and Atwood[26] have reported a rate constant for CO dissociation in the parent $Ir_4(CO)_{12}$ cluster in chlorobenzene of $(6.0 \pm 0.5) \times 10^{-5}$ s^{-1} at 109 °C which extrapolates to a value of 1.80×10^{-6} s^{-1} at 80 °C.[27] Correcting this parameter for the number of dissociable CO ligands (12) leads to a rate constant of 1.5×10^{-7} s^{-1} at 80 °C. Hence, the rate parameters for dissociation of CO in the $Ir_4(CO)_9(PR_3)_3$ species listed in Table III all show CO labilization in proceeding from $Ir_4(CO)_{12}$ to $Ir_4(CO)_9(PR_3)_3$, with the relative order of CO labilization being PPh_3 (78 400) > P-*i*-Pr_3 (45 100) > PEt_3 (8870) $\gtrsim$ P-*n*-Bu_3 (8470) > PMe_3 (1150) > CO (1). The overall rate enhancement by a factor of 78 400 for CO dissociation in $Ir_4(CO)_{12-n}(PPh_3)_n$ (n = 0–3) with progressive CO substitution by PPh_3 is in good agreement with that reported by Karel and Norton for n = 0–2 of 41 800, considering the anticipated further rate increase upon added PPh_3 substitution.[1]

The most notable observation to be assimilated from the kinetic data in Table III is that the rate acceleration is attenuated as the spatial requirements for the substituted PR_3 ligands are lessened, while simultaneously holding their basicities constant. This is nicely illustrated in proceeding through the trialkylphosphine series where ΔHNP (half-neutralization potential) varies only slightly (111–131)[28] and the ligand's cone angle spans a wide range from 118 to 160 °C.[29] The overall increase in dissociative CO rates resulting from the replacement of three carbon monoxide ligands in the parent $Ir_4(CO)_{12}$ species by PR_3 varied over a factor of 1150–45 100 as the cone angle of PR_3 increased from 118 to 160 °C. These rate accelerations represent the total increase anticipated in the progressive CO replacement reaction described by eq 5. A smaller electronic effect of the phosphorus ligand is

$$\mathrm{Ir_4(CO)_{12}} \xrightarrow{\mathrm{PR_3}} \mathrm{Ir_4(CO)_{11}PR_3} \xrightarrow{\mathrm{PR_3}} \mathrm{Ir_4(CO)_{10}(PR_3)_2} \xrightarrow{\mathrm{PR_3}} \mathrm{Ir_4(CO)_9(PR_3)_3} \xrightarrow{\mathrm{PR_3}} \mathrm{Ir_4(CO)_8(PR_3)_4} \quad (5)$$

superimposed on this steric acceleration phenomenon as noted for

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Table IV. Temperature-Dependent ^{13}CO Exchange Rate Constants for $Ir_4(CO)_9(PEt_3)_3$ in C_2Cl_4[a]

temp, °C	10^4k, s^{-1}	temp, °C	10^4k, s^{-1}
64.6	2.04 ± 0.05	75.9	9.35 ± 0.32
65.1	1.94 ± 0.25	80.0	13.2 ± 0.67
66.6	2.82 ± 0.07	84.3	17.6 ± 0.67
71.7	5.46 ± 0.33	85.5	28.2 ± 0.74
72.4	4.73 ± 0.21	85.8	26.7 ± 0.56

[a] Obtained from k_{obsd} as described in Table III. Error limits assigned to rate constants reflect 95% confidence limits.

Table V. Rate Data for Phosphine Dissociation in $Ir_4(CO)_8(PR_3)_4$ Derivatives[a]

L (cone angle)[b]	temp, °C	k, s^{-1}
PMe_3 (118°)	85.1	6.35×10^{-7}
PEt_3 (132°)	85.2	2.09×10^{-3}
	70.3	3.86×10^{-4}
P-*n*-Bu_3 (132°)	85.1	1.00×10^{-3}
	70.1	1.45×10^{-4}
PPh_2Me (136°)	70.1	7.22×10^{-4}

[a] Determined in C_2Cl_4 solvent employing CO as the entering ligand. [b] Taken from ref 29.

the PPh_3 case (ΔHNP = 573, θ = 145°). This electronic effect is seen as well in the $P(OPh)_3$ derivatives, where $P(OPh)_3$ is less CO labilizing than trialkylphosphines of comparable steric requirements.[2]

If steric acceleration is of importance in these CO substitution processes, then the coordination site of the CO group which is dissociated must be in rather close proximity to the phosphorus ligand. Crystallographically defined models indicate this to be either the equatorial or axial CO ligands contained in the basal Ir_3 plane. CNDO computations reveal that the axial CO ligands in $Co_4(CO)_{12}$ are the poorest π acceptors of the three types of terminal CO groups,[30] hence these might be expected to be more easily replaced. Indeed this is the assumption we have used in the calculation of the specific CO dissociative rate constants listed in Table III.[31]

The rate of ^{13}CO exchange for a representative $Ir_4(CO)_9(PR_3)_3$ cluster (R = Et) was determined as a function of temperature (Table IV), providing activation parameters of $\Delta H^* = 28.4 \pm 2.7$ kcal/mol and $\Delta S^* = 3.5 \pm 6.4$ eu.[32] for carbon monoxide dissociation. These are similar to the values reported for CO dissociation processes involving $Ir_4(CO)_{11}PR_3$ derivatives.[2]

The kinetic stability towards phosphine dissociation in the reaction products derived from eq 6 were also found to correlate

$$Ir_4(CO)_9(PR_3)_3 + PR_3 \rightleftharpoons Ir_4(CO)_8(PR_3)_4 + CO \qquad (6)$$

well with the size of the PR_3 ligand (see Table V). It was possible to isolate pure samples of $Ir_4(CO)_8L_4$, where L = PMe_3, PEt_3, P-*n*-Bu_3, $P(OMe)_3$, $P(OPh)_3$, and PPh_2Me. An X-ray structural analysis of the $Ir_4(CO)_8(PMe_3)_4$ derivative showed its stereochemistry to be as that depicted in Figure 3,[24] where the geometry of the phosphines about the tetranuclear metal centers is one apical, two axial, and one equatorial. Comparative solution infrared investigations in the ν(CO) region, both with respect to the number of vibrational modes and their intensity patterns, of these tetrasubstituted derivatives (see Table II) indicate all of these species to be isostructural with the possible exception of the $P(OMe)_3$ analogue. This latter species containing the compact $P(OMe)_3$ ligand, displays a somewhat different ν(CO) band pattern and may adopt an all-axial structure analogous to that of $HFeCo_3(CO)_9[P(OMe)_3]_3$.[33,34] That is, in the absence of steric constraints, the coordination sites occupied by the weaker π-acceptor ligands would be the axial sites of the basal Ir_3 moiety. Hence, variations in phosphorus ligand lability in these $Ir_4(CO)_8(PR_3)_4$ derivatives may be ascribed only to changes in the electronic and/or steric character of the ligand (PR_3) and not to structural variations in the clusters, with the possible exclusion of the $P(OMe)_3$ derivative.

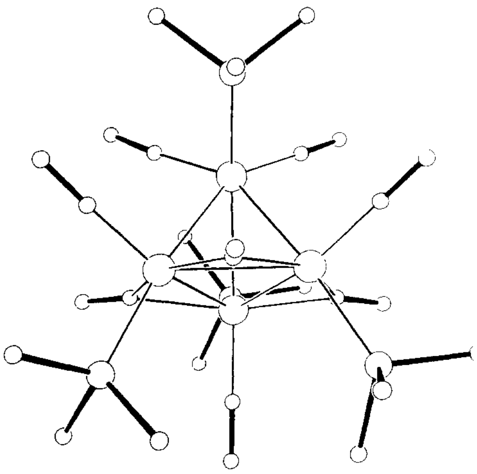

Figure 3. Solid-state structure of $Ir_4(CO)_8(PMe_3)_4$ as determined in ref 24.

Table VI. Kinetic Data for PEt_3 Dissociation in $Ir_4(CO)_8(PEt_3)_4$ in C_2Cl_4[a]

temp, °C	10^5k, s^{-1}	temp, °C	10^5k, s^{-1}
50.1	1.42 ± 0.04	73.5	50.0 ± 3.1
59.9	6.71 ± 0.19	84.0	234 ± 7.0
70.3	38.6 ± 3.0	85.2	209 ± 13.0

[a] Determined employing CO as the entering ligand. Error limits assigned to rate constants reflect 95% confidence limits for a single run.

Table VII. Kinetic Data for PEt_3 Dissociation in $Ir_4(CO)_8(PEt_3)_4$ in Heptane[a]

temp, °C	10^5k, s^{-1}	temp, °C	10^5k, s^{-1}
47.0	1.76 ± 0.09	59.8	16.3 ± 1.36
50.0	3.51 ± 0.39	69.9	58.3 ± 3.73
52.7	3.80 ± 0.03	69.9	66.6 ± 4.33
52.7	4.65 ± 0.23	78.3	173 ± 10.1
59.8	14.8 ± 0.48		

[a] Determined employing CO as the entering ligand. Error limits assigned to rate constants reflect 95% confidence limits for a single run.

The rate data for phosphine dissociation in $Ir_4(CO)_8(PR_3)_4$ (reverse of reaction 6) listed in Table V further reflect the effect of phosphorus ligand size on the rate of dissociative ligand substitutional processes in tetranuclear metal carbonyl clusters. That is, although the basicities of the ligands PMe_3, P-*n*-Bu_3, and PEt_3 are essentially identical, the rate of iridium-phosphine bond cleavage increases by a factor of 3300 for these species. The order of phosphorus ligand lability for the cases investigated were PMe_3 < P-*n*-Bu_3 < PEt_3 < PPh_2Me. Again an electronic effect was noted as well in that the $P(OMe)_3$ and $P(OPh)_3$ derivatives showed no phosphite loss under more forcing conditions (90 °C for 44 h) than those of the above reactions.

The origin of the steric crowding is evident in the solid-state structure of $Ir_4(CO)_8(PMe_3)_4$, where interligand repulsions between the two axial PMe_3 ligands is manifested in a significantly elongated Ir–Ir bond.[24] This congestion among phosphorus ligands in the basal Ir_3 plane is relieved in the product of $Ir_4(CO)_8(PR_3)_4$ reaction with CO, $Ir_4(CO)_9(PR_3)_3$, by adopting a configuration

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(30) Freund, H. J.; Hohlneicher, G. *Theor. Chim. Acta* **1979**, *51*, 145.

(31) The conclusions presented here would not be altered significantly if all three basal CO groups are dissociable. The quantitative CO labilizing abilities as reported would be decreased by a factor of 0.667.

(32) Error limits for activation parameters represent 95% confidence limits.

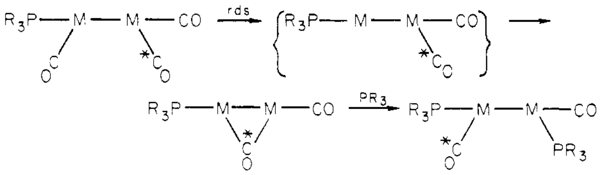
(33) Huie, B. T.; Knobler, C. B.; Kaesz, H. D. *J. Chem. Soc., Chem. Commun.* **1975**, 684.

(34) Teller, R. G.; Wilson, R. D.; McMullan, R. K.; Koetzle, T. F.; Bau, R. *J. Am. Chem. Soc.* **1978**, *100*, 3071.

where only one PR_3 ligand is in an axial coordination site. The experiments carried out in these studies do not answer the question of whether an apical or axial phosphorus ligand is dissociated.[35] In either instance, intramolecular ligand rearrangements would accompany formation of the observed product. For example, the reaction of $Ir_4(CO)_8(PEt_3)_4$ with ^{13}CO did not result in any stereoselectivity of ^{13}CO incorporation in the trisubstituted cluster product (see ^{13}C NMR in Figure 2).

Activation parameters for PEt_3 dissociation in $Ir_4(CO)_8(PEt_3)_4$ were obtained from the temperature-dependent rate data provided in Tables VI and VII. The enthalpy (ΔH^*) and entropy (ΔS^*) of activation for Ir–PEt_3 bond disruption were determined to be 33.0 ± 2.7 kcal/mol and 19.1 ± 7.9 eu in C_2Cl_4.[32] The analogous parameters in the noninteracting heptane solvent were found to be 32.4 ± 2.2 kcal/mol and 18.7 ± 6.8 eu, respectively. Similar activation parameters were derived for P-*n*-Bu_3 dissociation in $Ir_4(CO)_8(P\text{-}n\text{-}Bu_3)_4$. Hence, these activation parameters, coupled with the small dependence of the rate on solvent, are consistent with a phosphine dissociation process.

Concluding Remarks. We have demonstrated that the spatial requirements of the phosphorus ligands render an important role in both phosphine and carbon monoxide ligand substitutional processes involving tetranuclear iridium cluster derivatives. The rate acceleration arising from sterically induced ligand dissociation observed herein in these Ir_4 species resembles that noted previously in mononuclear metal carbonyl phosphine complexes.[16,18] Concomitantly, it is recognized that electronic factors are influential to varying extents in these processes. However, this electronic effect may be akin to cis labilization in mononuclear metal complexes (a transition-state phenomenon),[36] as suggested by Sonnenberger and Atwood,[2] and would thus require loss of a ligand (CO) from a prior phosphine-substituted metal center. Hence, the rate-determining step (rds) in this latter mechanism (the skeletal sequence shown in reaction 7) does not necessitate the presence of more than one metal center or, in other words, does not define cooperativity, i.e., metal atoms working together for a common purpose (ligand dissociation). On the other hand, steric acceleration arguments only require the ligand which is dissociated to be close proximity to the metal center which has been previously substituted.[37] Thus this steric mode of inducing ligand dissociation may better fit the definition for cooperativity by virtue of the cluster's framework dictating spatial confrontations between ligands.



(7)

Acknowledgment. The financial support of the National Science Foundation through Grant CHE 80-09233 is greatly appreciated.

Registry No. $Ir_4(CO)_9(PMe_3)_3$, 81616-62-8; $Ir_4(CO)_9(PPh_3)_3$, 19631-23-3; $Ir_4(CO)_9(P\text{-}i\text{-}Pr_3)_3$, 40919-64-0; $Ir_4(CO)_9(PEt_3)_3$, 28829-02-9; $Ir_4(CO)_9(P\text{-}n\text{-}Bu_3)_3$, 40919-66-2; $Ir_4(CO)_8(PMe_3)_4$, 78715-94-3; $Ir_4(CO)_8(PEt_3)_4$, 28829-04-1; $Ir_4(CO)_8(P\text{-}n\text{-}Bu_3)_4$, 28829-05-2; $Ir_4(CO)_8(P(POMe)_3)_4$, 81616-63-9; $Ir_4(CO)_8(P(OPh)_3)_4$, 81616-64-0; $Ir_4(CO)_8(PPh_2Me)_4$, 52390-85-9; $Ir_4(CO)_{12}$, 18827-81-1.

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[35] Attempts at providing information in this regard are planned employing metal clusters containing mixed phosphine ligands.

[36] Lichtenberger, D. L.; Brown, T. L. *J. Am. Chem. Soc.* **1978**, *100*, 366 and other contributions to this series.

[37] The origin of the steric accelerations may be a ground-state property (e.g., as seen in the $Ir_4(CO)_8(PR_3)_4$ species), but it is often a transition-state property where the relief of interligand steric repulsions upon ligand dissociation allows the remaining metal–ligand bonds to attain values closer to their electronic equilibrium positions.

Peptide Formation in the Presence of a Metal Ion Protecting Group. 4. Synthesis of Penta- and Hexapeptide Sequences with the Pentaamminecobalt(III) Complex

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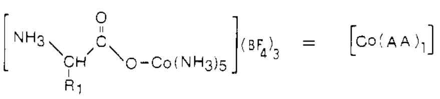
Abstract: Kinetically inert metal ion protecting groups provide radically different approaches to the protection of the terminals and side chains of amino acids and peptides. Pentaamminecobalt(III) is a useful C-terminal protecting group for sequential peptide synthesis. This is demonstrated by the synthesis of a number of amino acid complexes of the type



$$\left[NH_3CH(R_1)C(=O)O{-}Co(NH_3)_5\right](BF_4)_3 = [Co(AA)_1]$$

where R = hydrophilic, hydrophobic, aliphatic, and aromatic amino acid side chains. The reaction of these complexes with Boc-amino acid active esters or Boc symmetric anhydrides results in the formation of $[Co(AA)_1(AA)_2Boc]$. The Boc group is removed with 95% trifluoroacetic acid to form $[Co(AA)_1(AA)_2]$, which is further used for sequential peptide synthesis. Alternatively, the $[(NH_3)_5Co^{III}–]$ group is selectively removed by rapid reduction with $NaBH_4$ or NaHS to form the N-protected peptide fragment, $[(AA)_1(AA)_2Boc]$, under extremely mild conditions. Tests for racemization of the amino acid directly bound to cobalt showed no detectable loss of chirality of $[(AA)_1]$. The detailed synthesis, monitoring, purification, and analysis of cobalt pentaammine derivatives of Leu-enkephalin (TyrGlyGlyPheLeu), Met-enkephalin (TyrGlyGlyPheMet), and the hexapeptide sequence HisGlyHisGlyHisGly are described and so is a general procedure for peptide synthesis with the cobalt(III) protecting group. The individual fragments of these peptide sequences are characterized by HPLC. The attractive features of the $[(NH_3)_5Co^{III}–]$ protecting group include its color, tripositive charge, ease of introduction, and removal. Such properties are invaluable in the purification of synthetic peptides.

During the development of synthetic peptide chemistry, many references were made to the potential use of metal ions in the protection and activation of amino acid derivatives.[1-4] One of the early uses of metal ion chelates in peptide synthetic chemistry

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