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Kinetic Studies of Ligand Substitution for Carbon Monoxide on Dodecacarbonyltetrairidium, $Ir_4(CO)_{12}$

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The kinetics of ligand substitution for CO on $Ir_4(CO)_{12}$ have been investigated for the ligands $P(C_4H_9)_3$, $P(C_6H_5)_3$, $P(OC_6H_5)_3$, and $As(C_6H_5)_3$ between 30 and 125 °C. The rates show a dependence on the nature and concentration of the entering ligand with the rate law rate = $(k_1 + k_2[L])[Ir_4(CO)_{12}]$. For reasonably nucleophilic ligands [$P(C_4H_9)_3$, $P(OC_6H_5)_3$, and $P(C_6H_5)_3$] the second-order term contributes more than 95% of the total rate. The k_2 term involves nucleophilic attack at an iridium center, and the k_1 term involves CO dissociation. The product of the substitution reaction depends on the ligand and on the reaction conditions. Many of the possible intermediates are identified by infrared spectroscopy. The mechanism of ligand substitution is discussed.

Studies of transition-metal clusters have proliferated in recent years. Initial work, dealing with preparation of clusters and structural determinations, was reviewed comprehensively in 1972.[1] Aspects of the chemistry of metal carbonyl clusters[2,3] and the relationship between metal clusters and metal surfaces have been reviewed more recently.[4-6] Especially intriguing have been recent studies of the reactions of unsaturated metal clusters with unsaturated hydrocarbons[7-10] and the use of transition-metal clusters as homogeneous catalysts.[11-13]

Despite the increasing number of studies of metal clusters there have been very few kinetic or mechanistic studies on transition-metal cluster complexes. Important questions about the mechanisms such as whether the cluster fragments during reactions can be answered with careful kinetic studies.[14] The most thoroughly studied cluster is $Ru_3(CO)_{12}$ (see eq 1).[15,17-21]

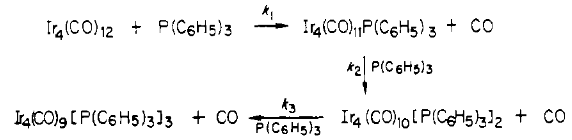
$$Ru_3(CO)_{12} + 3L \rightarrow Ru_3(CO)_9L_3 + 3CO \qquad (1)$$

Candlin and Shortland studied CO substitution by $P(C_6H_5)_3$, $P(C_6H_5)_2(C_2H_5)$, $P(C_6H_5)(C_2H_5)_2$, $P(C_4H_9)_3$, and $P(OC_6H_5)_3$.[15] These reactions were reported to give only the trissubstituted complex with no evidence of the mono- or bissubstituted species.[15] The rate law observed was of the form

$$\text{rate} = (k_1 + k_2\,[L])[Ru_3(CO)_{12}] \qquad (2)$$

very similar to that observed for mononuclear species such as $Mo(CO)_6$.[15,16] Significantly, $Ru(CO)_4P(C_6H_5)_3$ did not yield $Ru_3(CO)_9[P(C_6H_5)_3]_3$ under conditions where CO was known to dissociate from $Ru(CO)_4P(C_6H_5)_3$.[15] They suggested CO dissociation from the intact triruthenium complex as the mechanism for reaction.[15] Subsequent work has confirmed these observations and shown that during reaction with $P(C_6H_5)_3$ the dissociation of CO is accelerated from $Ru_3(CO)_{11}P(C_6H_5)_3$ and $Ru_3(CO)_{10}[P(C_6H_5)_3]_2$ with respect to $Ru_3(CO)_{12}$.[17-21]

Scheme I



Reaction of the iron and osmium analogues with phosphines have also been reported.[22,23] For the osmium complex $Os_3(CO)_{12}$, both the mono- and bissubstituted species were seen as intermediates, suggesting that the presence of $P(C_6H_5)_3$ coordinated to an osmium center had little effect on the CO dissociation rate.[22] Reactions of $Fe_3(CO)_{12}$ with nucleophiles led to mononuclear products [$Fe(CO)_4L$ and $Fe(CO)_3L_2$] with the fragmentation increasing with the nucleophilicity of the entering ligand.[23] Fox, Gladfelter, and Geoffroy have recently reported kinetics studies on tetranuclear mixed-metal clusters of iron, osmium, and ruthenium.[24]

Darensbourg and Incorvia have investigated the reactions of $P(OCH_3)_3$ substituted derivatives of $Co_4(CO)_{12}$.[25,26] Reaction of the monosubstituted complex $Co_4(CO)_{11}P(OCH_3)_3$ with $P(OCH_3)_3$ proceeded by a second-order reaction, while reaction of the bis complex $Co_4(CO)_{10}(P(OCH_3)_3)_2$ with $P(OCH_3)_3$ to give $Co_4(CO)_9[P(OCH_3)_3]_3$ was first order in $Co_4(CO)_{10}[P(OCH_3)_3]_2$ and independent of $P(OCH_3)_3$.[25,26] A very interesting feature of metal cluster reactivity was noted by Karel and Norton in substitution of $Ir_4(CO)_{12}$ with $P(C_6H_5)_3$[27] (Scheme I). The rate constant for the first reaction, k_1, was an associative rate constant, while k_2 and k_3 were dissociative rate constants. The relative rates were $k_3 = 30k_2 = 920k_1$.[27] These results are indicative of a cooperative effect, $P(C_6H_5)_3$ on one metal having a large effect on the rate of reaction at a different metal center.

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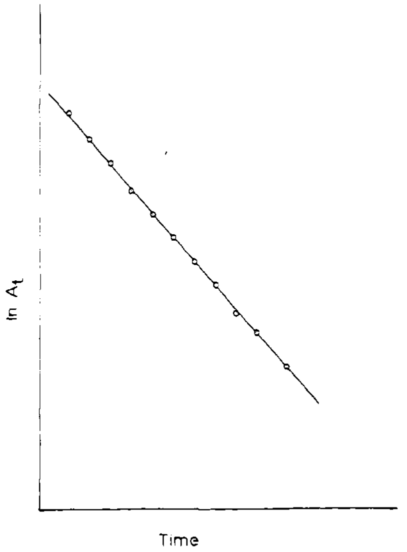

Figure 1. Plot of ln A_t vs. time from reaction of $Ir_4(CO)_{12}$ with $As(C_6H_5)_3$ at 119 °C in chlorobenzene.

Because of the potential which transition-metal clusters have shown as catalysts and the scarcity of kinetic data, we have begun a program of kinetic studies of metal clusters. We have elected to investigate CO substitution reactions on $Ir_4(CO)_{12}$ with several different ligands: $P(C_4H_9)_3$, $P(C_6H_5)_3$, $P(OC_6H_5)_3$, and $As(C_6H_5)_3$ (see eq 3). The results of this investigation are reported herein.

$$Ir_4(CO)_{12} + nL \rightarrow Ir_4(CO)_{12-n}L_n + nCO \qquad (3)$$

Experimental Section

Tetrairidium dodecacarbonyl (Strem Chemical Co.) and triphenylphosphine (Aldrich Chemical Co.) were used as received. Triphenyl phosphite and tri-*n*-butylphosphine were purified by vacuum distillation over sodium and stored under argon.[28] Triphenylarsine was recrystallized from dry ethanol and stored under argon. Chlorobenzene, used as the primary solvent for kinetic studies, was dried with calcium hydride and stored under vacuum over molecular sieves. Decane, used as the solvent in the identification reactions, was purified by mixing with sulfuric acid, washing with water, passing down an alumina column, and storing over sodium. Tetrahydrofuran, used as a solvent in the tri-*n*-butylphosphine reactions, was dried over sodium and stored under argon. Methylene chloride, also used as a solvent in the tri-*n*-butylphosphine reactions, was dried over calcium hydride.

The reactions were accomplished under an argon atmosphere in foil-wrapped vessels in darkened hoods and followed by IR, with use of a Beckman IR 4240 spectrophotometer and matched 1.0-mm NaCl cells. All reactions were performed under pseudo-first-order conditions, with a ligand excess of greater than 30 times that of the $Ir_4(CO)_{12}$. A Haake FS constant-temperature circulator was used to maintain the reactions at the desired temperature, to within ±0.1 °C.

The reactions of $Ir_4(CO)_{12}$ with $P(C_6H_5)_3$, $P(OC_6H_5)_3$, and $As(C_6H_5)_3$ were studied at temperatures between 80 and 125 °C. In these reactions, the kinetics were followed by monitoring the decrease in absorbance at 2068 cm^{-1}, due to $Ir_4(CO)_{12}$, for a minimum of 3 half-lives. In the $P(OC_6H_5)_3$ studies, a Du Pont 310 curve resolver was employed to separate the absorbances due to $Ir_4(CO)_{12}$ and the reaction products in this region. A plot of ln A_t vs. time yielded the pseudo-first-order rate constants, k_{obsd}, quoted herein. The reaction of $Ir_4(CO)_{12}$ with $P(C_4H_9)_3$ proceeded at a conveniently measurable rate ($t_{1/2}$ > 10 min) at temperatures less than 50 °C. At these temperatures, however, $Ir_4(CO)_{12}$ is only very slightly soluble. As a result of this limited solubility of $Ir_4(CO)_{12}$ and the facile nature of its reaction with $P(C_4H_9)_3$, only an average lower limit on the relative rate of reaction was obtained. Plots of k_{obsd} vs. ligand concentration yielded the rate constants k_1 and k_2. From an Arrhenius plot using k_{obsd}, the activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, were obtained.

Table I. Rate Constants for Reaction of $Ir_4(CO)_{12}$ with L[a]

ligand	temp, °C	10^2[L], M	$10^5 k_{obsd}$, s^{-1}
$P(C_6H_5)_3$	109	7.6	45.2 ± 0.7
		3.8	25.3 ± 0.9
		1.9	15.0 ± 0.2
		0.96	10.0 ± 0.3
	99	7.6	20.1 ± 0.6
	89	7.6	9.05 ± 0.25
$As(C_6H_5)_3$	124	7.6	44.3 ± 0.2
	119	7.6	26.1 ± 0.5
	109	7.6	8.49 ± 0.16
		6.7	8.24 ± 0.03
		5.7	7.97 ± 0.06
$P(OC_6H_5)_3$	109	1.9	30.0 ± 1.0
		1.3	22.4 ± 0.5
		0.95	18.0 ± 1.6
	99	7.6	56.3 ± 0.6
	89	7.6	27.1 ± 1.5
	79	7.6	13.8 ± 0.2

[a] Error limits are quoted at 95% confidence interval.

Table II. Activation Parameters[a] for $Ir_4(CO)_{12}$ + L

ligand	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
$P(C_6H_5)_3$	22.0 ± 0.1	−16.6 ± 0.3
$P(OC_6H_5)_3$	17.6 ± 1.4	−26.7 ± 3.8
$As(C_6H_5)_3$	32.1 ± 0.7	6.4 ± 1.8

[a] Error limits are quoted as 95% confidence interval.

Table III. Relative Rates of Reaction of Metal Carbonyls with L

compd	$P(C_4H_9)_3$	$P(OC_6H_5)_3$	$P(C_6H_5)_3$	$As(C_6H_5)_3$
$Ir_4(CO)_{12}$	~120[a]	2.8	1	0.19
$Co(CO)_3NO$[b]	90	0.03	1	0.002
$Mn(CO)_4NO$[c]	40	0.09	1	0.01
$Co_2(CO)_8$[d]	40		1	0.01

[a] Lower limit for rate of reaction with $P(C_4H_9)_3$. [b] Reference 32. [c] Reference 33. [d] Reference 34.

Table IV. Ligand-Independent and -Dependent Rate Constants[a] for $Ir_4(CO)_{12}$ + L at 109 °C

ligand	$10^5 k_1$, s^{-1}	$10^5 k_2$, M^{-1} s^{-1}
$P(C_6H_5)_3$	5.0 ± 0.3	530 ± 10
$As(C_6H_5)_3$	6.4 ± 0.1	27 ± 1
$P(OC_6H_5)_3$	5.8 ± 0.1	1300 ± 100

[a] Error limits are quoted as 95% confidence interval.

For the purpose of identifying the reaction products, decane was used as the solvent. All other conditions were identical with those employed in the kinetics experiments. The assignment of reaction products was based on a comparison of IR product spectra obtained in this study with the spectra of substituted $Ir_4(CO)_{12}$ derivatives reported in the literature (see Table V).

Results

In the reactions of $Ir_4(CO)_{12}$ with $P(C_6H_5)_3$, $P(OC_6H_5)_3$, and $As(C_6H_5)_3$, under pseudo-first-order conditions, plots of ln A_t vs. time were linear for a minimum of 3 half-lives, as demonstrated in Figure 1. The pseudo-first-order rate constants, k_{obsd}, obtained from such plots at the various temperatures and ligand concentrations investigated are given in Table I. The activation parameters for the reactions with these ligands are listed in Table II. Due to the low solubility of $Ir_4(CO)_{12}$ and the facile nature of its reaction with $P(C_4H_9)_3$, only an average lower limit on the relative rate of reaction could be determined.

The rate of reaction was dependent upon both the nature and concentration of the incoming ligand. As shown in Table III, the reaction rate varies greatly with the nucleophiles studied. Also, the rate depended linearly on the ligand con-

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(28) If the ligands were not freshly distilled, significant deviations from linearity were observed in the plots of ln A vs. time.

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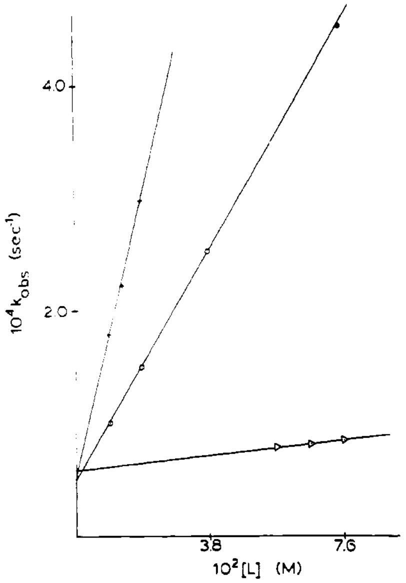

Figure 2. Plot of k_{obsd} vs. [L] for a series of reactions with $Ir_4(CO)_{12}$ at 109 °C in chlorobenzene: ○, $P(C_6H_5)_3$; △, $As(C_6H_5)_3$; +, $P(OC_6H_5)_3$.

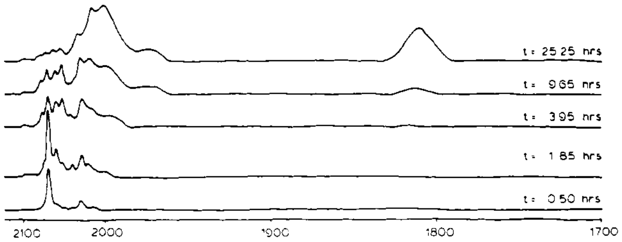

Figure 3. Infrared spectra during the reaction of $Ir_4(CO)_{12}$ with $P(OC_6H_5)_3$ at 79 °C in decane.

centration, as demonstrated in Figure 2. For the ligands, $P(OC_6H_5)_3$, $P(C_6H_5)_3$, and $As(C_6H_5)_3$, the dependence on the concentration of ligand is quite different as shown by the different slopes (k_2). However, the intercepts are virtually identical, indicating the constancy of k_1. The ligand-independent and -dependent rate constants, k_1 and k_2, respectively, obtained from this plot are listed in Table IV.

Reaction of $Ir_4(CO)_{12}$ with $P(C_6H_5)_3$. As the reaction proceeded, a number of IR absorbances grew in. First to appear are bands corresponding to $Ir_4(CO)_{11}[P(C_6H_5)_3]$, as assigned in Table V. Later, absorbances assigned to $Ir_4(CO)_9[P(C_6H_5)_3]_3$ appeared. The trissubstituted cluster was the primary reaction product under all conditions studied. At no time was any $Ir_4(CO)_{10}[P(C_6H_5)_3]_2$ detected.

Reaction of $Ir_4(CO)_{12}$ with $P(OC_6H_5)_3$. As this reaction proceeded, a number of IR bands grew in, as shown in Figure 3. On the basis of the assignments of these absorbances as listed in Table V, the reaction products observed were $Ir_4(CO)_{12-x}[P(OC_6H_5)_3]_x$, where $x = 1$–4. At the end of the reaction, when the absorbance at 2068 cm^{-1}, due to $Ir_4(CO)_{12}$, was minimal, $Ir_4(CO)_9[P(OC_6H_5)_3]_3$ and $Ir_4(CO)_8[P(OC_6H_5)_3]_4$ were the major products, with the latter being predominant at higher reaction temperatures (>80 °C).

Reaction of $Ir_4(CO)_{12}$ with $P(C_4H_9)_3$. As this reaction occurred, a series of IR absorbances appeared. These bands were assigned to $Ir_4(CO)_{12-x}[P(C_4H_9)_3]_x$, with $x = 2$–4, from Table V. At no time during the reaction was any $Ir_4(CO)_{11}[P(C_4H_9)_3]$ observed. At low reaction temperatures (<60 °C), the trissubstituted species was the major reaction product, whereas at higher temperatures the tetrakissubstituted cluster dominated. At these high reaction temperatures, all IR bands could not be assigned.

Table V. Assignment (cm^{-1}) of Absorbances in Infrared Product Spectra[a]

	ligand			
compd	$P(C_6H_5)_3$	$P(OC_6H_5)_3$	$P(C_4H_9)_3$	$As(C_6H_5)_3$
$Ir_4(CO)_{11}L$	2087 (w)	2096 (w)		
	2054 (m)	2060 (m)		2062 (w)
	2036 (w)	2040 (w)		2012 (w)
	2012 (w)	2017 (w)		
	1850 (w)			
$Ir_4(CO)_{10}L_2$		2077 (m)	2060 (m)	2052 (sh)
		2052 (m)	2032 (m)	2044 (s)
		2028 (m)	2000 (m)	2012 (m)
			1825 (w)	
			1780 (w)	
$Ir_4(CO)_9L_3$	2042 (m)			2035 (w)
	1985 (s)	2018 (s)	1980 (s)	2008 (w)
	1960 (sh)	1975 (w)	1960 (m)	1992 (s)
	1780 (m)		1780 (m, br)	1960 (s)
$Ir_4(CO)_8L_4$		2000 (s)	1980 (s)	
		1810 (s, br)	1950 (vs)	
			1917 (m)	
			1768 (vs)	

[a] Assignments of the distinct absorptions for $P(C_6H_5)_3$, $P(OC_6H_5)_3$, and $P(C_4H_9)_3$ are based on literature values as follows: $P(C_6H_5)_3$, ref 26 and 27; $P(OC_6H_5)_3$, ref 26 and 28; $P(C_4H_9)_3$, ref 27. The $As(C_6H_5)_3$ assignments are based on analogy to $P(C_6H_5)_3$ systems[31] and by independent preparations of the products.[39]

Reaction of $Ir_4(CO)_{12}$ with $As(C_6H_5)_3$. As the reaction proceeded, a number of IR bands grew in. From Table V, these absorbances were assigned to $Ir_4(CO)_{12-x}[As(C_6H_5)_3]_x$, where $x = 1$–3. The bis- and trissubstituted clusters were the major reaction products under the conditions investigated.

Discussion

The reaction under consideration is the substitution of a ligand for CO on $Ir_4(CO)_{12}$ (eq 4). The ligands used were

$$Ir_4(CO)_{12} + nL \rightarrow Ir_4(CO)_{12-n}L_n + nCO \qquad (4)$$

$P(C_6H_5)_3$, $P(OC_6H_5)_3$, $P(C_4H_9)_3$, and $As(C_6H_5)_3$. These reactions were studied between 30 and 125 °C. The low solubility of $Ir_4(CO)_{12}$ presented some problems, especially at low temperatures. The reaction led to different products depending on the temperature and the ligand employed.

By following the decrease in the absorbance of $Ir_4(CO)_{12}$ at 2068 cm^{-1}, good pseudo-first-order kinetic plots were obtained for each of the ligands and the rate constants, k_{obsd}, were obtained from the slope. A plot of k_{obsd} vs. [L] was linear with a nonzero intercept. These plots are shown in Figure 2. The plots for the different ligands have the same intercept. This kinetic behavior is consistent with the rate law

$$\text{rate} = k_{obsd}[Ir_4(CO)_{12}] = (k_1 + k_2\,[L])[Ir_4(CO)_{12}] \qquad (5)$$

The value of k_1 (at 109 °C) as determined from the intercept of the plots is $(6.0 \pm 0.5) \times 10^{-5}$ s^{-1}. This type of rate law has been commonly observed in metal carbonyl kinetics.[14] However very significant differences in the relative values of k_1 and k_2 exist for $Ir_4(CO)_{12}$. In other systems the second-order term is quite small, contributing less than 5% to the total rate. In substitutions on $Ir_4(CO)_{12}$ by the ligands $P(C_4H_9)_3$, $P(C_6H_5)_3$, and $P(OC_6H_5)_3$, the second-order term (k_2) contributes 95% of the total rate.

The dependence on the nature of the ligand is quite dramatic as shown by the relative rates given in Table III: $P(C_4H_9)_3 >> P(OC_6H_5)_3 > P(C_6H_5)_3 > As(C_6H_5)_3$. This dependence is very similar to that observed in the reactions of $Co(CO)_3NO$ and $Mn(CO)_4NO$.[31,32] These complexes react purely by a

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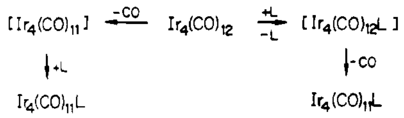
Scheme II



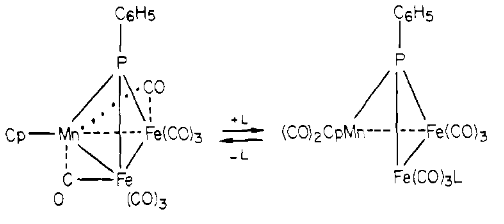
ligand-dependent rate expression involving nucleophilic attack on the metal carbonyl complex. Thus nucleophilic attack on $Ir_4(CO)_{12}$ is strongly implicated in the mechanism. The dependence is not just nucleophilic however, or reaction of $P(C_6H_5)_3$ would occur more rapidly than reaction of $P(OC_6H_5)_3$. We believe that the slowness of $P(C_6H_5)_3$ relative to $P(OC_6H_5)_3$ is the result of steric interactions.

The mechanisms which have typically been suggested for metal–metal bonded species, CO dissociation and homolytic fission of a metal–metal bond, are clearly inconsistent with the marked dependence on the nature and concentration of the incoming ligand. The first step must be nucleophilic attack on an iridium center. This type of attack has not often been observed in metal carbonyl kinetics. The best examples are seen in the nitrosyl complexes $Co(CO)_3NO$ and $Mn(CO)_4NO$[33,34] although $Co_2(CO)_8$ may provide a more pertinent example.[35] Table III shows the variation in rate with ligand for each of these complexes. We believe that $Ir_4(CO)_{12}$ is more susceptible to nucleophilic attack than most metal carbonyl complexes because of the more accessible metal center. Iridium, as a third-row metal, is, large and the metal–metal bonds are constrained to 60° angles so that the OC–Ir–CO angles are widened to 100°.[36] Thus, the iridium center is not as sterically constrained as most metal carbonyl complexes. Steric size of the entering ligand should be important, and our data show small steric effects.

The first step of the reaction with nucleophilic reagents is formation of the adduct (as a transition state or intermediate), $Ir_4(CO)_{12}L$ by nucleophilic attack on an iridium center (eq 6). A possible model for the adduct has been reported in the

$$Ir_4(CO)_{12} + L \rightarrow Ir_4(CO)_{12}L \tag{6}$$

chemistry of $Cp(CO)_2MnP(C_6H_5)Fe_2(CO)_8$.[37] Reaction with nucleophiles led to an adduct without one Mn–Fe bond (eq 7).



(7)

$L = CO, P(C_6H_5)_3$

This reaction was reversible; L dissociation led to formation of the Mn–Fe bond. For the iridium complex $Ir_4(CO)_{12}L$ either CO could dissociate leading to the substituted product or L could dissociate to the starting complex. Earlier work has shown that dissociation rates for L from organometallic chromium centers changes as is shown[38] by $As(C_6H_5)_3 > P(C_6H_5)_3 > P(OC_6H_5)_3 >> P(C_4H_9)_3$. This is the inverse order to that observed in the disappearance of $Ir_4(CO)_{12}$ by the nucleophilic attack term (k_2), which indicates the rate of L dissociation back to $Ir_4(CO)_{12}$ may be important in determining the rate of disappearance of $Ir_4(CO)_{12}$. The fact the k_1 is independent of the nature of the entering ligand strongly suggests that the first-order step is CO dissociation from $Ir_4(CO)_{12}$. Thus we believe that the mechanism of the ligand substitution reaction for $Ir_4(CO)_{12}$ can be summarized by Scheme II. We cannot suggest whether the bracketed species are intermediates or transition states. The ligand attack term predominates for ligands that are reasonably nucleophilic; only for very weak nucleophiles $[As(C_6H_5)_3]$ does CO dissociation compete with ligand attack. Steric effects which were suggested to be very important in reactions of isocyanides with $Ir_4(CO)_{12}$ cannot account for the differences seen in rates of reactions with $P(C_4H_9)_3$, $P(C_6H_5)_3$, $P(OC_6H_5)_3$, and $As(C_6H_5)_3$, although steric effects may account for the differences between $Ir_4(CO)_{12}$ and the other metal carbonyl complexes shown in Table III.

The entropies of activation, as listed in Table II, are in agreement with this mechanism. For the reaction of $Ir_4(CO)_{12}$ with $P(C_6H_5)_3$ and with $P(OC_6H_5)_3$, $\Delta S^{\ddagger} < 0$, indicative of an associative rate-determining step. Conversely, $\Delta S^{\ddagger} > 0$ for the reaction of $Ir_4(CO)_{12}$ with $As(C_6H_5)_3$, implying a dissociative pathway.

The research described has shown that substitution reactions of $Ir_4(CO)_{12}$ occur primarily by nucleophilic attack for the ligands, $P(C_4H_9)_3$, $P(OC_6H_5)_3$, and $P(C_6H_5)_3$, and by CO dissociation for weak nucleophiles such as $As(C_6H_5)_3$. The research does not answer the important question about ligand cooperative effects although the observation of many of the intermediates suggests that the rates of substitution on $Ir_4(CO)_{11}L$ and $Ir_4(CO)_{10}L_2$ are not very different than substitution on $Ir_4(CO)_{12}$. Experiments are in progress to investigate substitution on the complexes, $Ir_4(CO)_{11}L$ and $Ir_4(CO)_{10}L_2$, directly.

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Registry No. $Ir_4(CO)_{12}$, 18827-81-1; $P(C_6H_5)_3$, 603-35-0; $As(C_6H_5)_3$, 603-32-7; $P(OC_6H_5)_3$, 101-02-0; $P(C_4H_9)_3$, 998-40-3; $Ir_4(CO)_{11}P(C_6H_5)_3$, 53565-22-3; $Ir_4(CO)_{11}P(OC_6H_5)_3$, 59532-82-0; $Ir_4(CO)_{11}As(C_6H_5)_3$, 78128-47-9; $Ir_4(CO)_{10}[P(OC_6H_5)_3]_2$, 59532-57-9; $Ir_4(CO)_{10}[P(C_4H_9)_3]_2$, 40919-70-8; $Ir_4(CO)_{10}[As(C_6H_5)_3]_2$, 78128-48-0; $Ir_4(CO)_9[P(C_6H_5)_3]_3$, 19631-23-3; $Ir_4(CO)_9[P(OC_6H_5)_3]_3$, 78128-49-1; $Ir_4(CO)_9[P(C_4H_9)_3]_3$, 40919-66-2; $Ir_4(CO)_9[As(C_6H_5)_3]_3$, 78128-50-4; $Ir_4(CO)_8[P(OC_6H_5)_3]_4$, 51900-03-9; $Ir_4(CO)_8[P(C_4H_9)_3]_4$, 37366-38-4.

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