J. Am. Chem. Soc. 1982, 104, 2113-2116

Labilization of CO Dissociation from Metal Clusters: An Investigation of the Substitution Reactions of Monosubstituted Derivatives of Tetrairidium, $Ir_4(CO)_{11}L$ (L = PBu_3, PPh_3, $AsPh_3$, and $P(OPh)_3$)

David C. Sonnenberger and Jim D. Atwood*

Contribution from the Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214. *Received August 31, 1981*

Abstract: The reactions of $Ir_4(CO)_{11}L$ with additional ligand have been investigated for L = PPh_3, PBu_3, $AsPh_3$, and $P(OPh)_3$. Good first-order kinetics are seen for each complex, except when PBu_3 is the entering ligand. The PBu_3 reactions apparently proceed by ligand attack. Activation parameters are evaluated for each reaction. The predominant reaction mode is CO dissociation. Examination of the rates of CO dissociation from the series of compounds $Ir_4(CO)_{11}L$ (L = CO, PBu_3, PPh_3, $P(OPh)_3$, and $AsPh_3$) shows a remarkable labilization in the order CO < $P(OPh)_3$ < $AsPh_3$ < PPh_3 < PBu_3. These ligands span two orders of magnitude in the CO dissociation rate. It is suggested that this labilization of dissociation by the ligand L occurs at the substituted metal with bridging carbonyls transferring the coordinative unsaturation to a different iridium. This kinetic labilization probably arises from a transition-state stabilization.

The effect of the ligand environment around a metal on reactivity at that metal has been an important area of inorganic and organometallic chemistry.[1] There are several examples where subtle ligand changes dramatically affect the reactivity of metal complexes. In transition-metal carbonyl complexes, which have been often studied, the presence of ligands such as CH_3, H, and NO has an important effect on the mechanism of reaction.[2-5] Other ligands may not affect the mechanism but may have large effects on the rate of reaction.[6-11] The rates of CO dissociation from a number of octahedral metal carbonyls were explained in terms of cis labilization, a labilization toward dissociation of the CO cis to a ligand.[8] The cis labilization order CO < $P(OPh)_3$ < PPh_3 < I^- < Br^- < Cl^- was ascribed to a stabilization of the square-pyramidal transition state by the labilizing ligand. The effect of the trans ligand on dissociations from chromium complexes, $Cr(CO)_4LL'$, has also been investigated.[10,11] There was a very significant relationship between the π bonding of the trans ligand and the rate of ligand dissociation. In examining *cis*-$Mo(CO)_4LL'$ complexes, Darensbourg noted that steric interactions were of primary importance in determining rates of dissociation.[12]

Complexes with more than one metal center could show the same effects as mononuclear species but have the additional feature of ligands at one metal center affecting the rate of reaction at another metal center. The dimers, $Mn_2(CO)_9L$, illustrate the type of effects which can be operative.[13]

$$Mn_2(CO)_9L + L \rightarrow Mn_2(CO)_8L_2 + CO$$

The second ligand substitutes on the Mn which was not previously substituted. The relative rates for substitution on $Mn_2(CO)_9L$[13] for L = PPh_3, PBu_3, $P(OPh)_3$, and CO are 44, 12, 1.5, and 1, respectively. This order and magnitude were very similar to that observed for cis labilization in mononuclear complexes, and it was suggested that labilization for dissociation of the cis carbonyls at the substituted metal, transfer of the unsaturated center by a bridging CO, and substitution at the previously unsubstituted manganese occur.[8] Transfer of unsaturation from one metal center to another has been implicated in substitution reactions of $MnRe(CO)_{10}$.[14]

Table I. Relative Rates of CO Dissociation from Transition-Metal Carbonyl Clusters[24]

n	$Ru_3(CO)_{12-n}$-$(PPh_3)_n$	$Co_4(CO)_{12-n}$-$(P(OMe)_3)_n$	$Ir_4(CO)_{12-n}$-$(PPh_3)_n$
0	1	1	1
1	55	0.9	220
2	40	1.3	3500

Table II. Infrared Spectra of Monosubstituted Derivatives of $Ir_4(CO)_{12}$

compound	IR, cm^{-1}
$Ir_4(CO)_{11}PPh_3$	2086 (m), 2068 (w), 2053 (vs), 2032 (m), 2021 (s), 2013 (m), 1997 (vw), 1850 (m), 1825 (m)
$Ir_4(CO)_{11}P(OPh)_3$	2095 (m), 2068 (sh), 2057 (vs), 2040 (s), 2017 (m), 1870 (m), 1830 (m, br)
$Ir_4(CO)_{11}AsPh_3$	2089 (m), 2056 (vs), 2030 (m), 2020 (s), 1842 (m), 1820 (m)
$Ir_4(CO)_{11}PBu_3$	2085 (m), 2067 (w), 2052 (vs), 2030 (w), 2020 (s), 2011 (s), 1883 (w), 1850 (m), 1823 (m)

The presence of ligands on metal clusters has also shown an ability to accelerate CO dissociation as shown in Table I, although insufficient ligand variation has been reported to establish a pattern.[15-19] To further expand our understanding of the role of ligand environment on rates of metal cluster reactions, we have investigated further ligand substitution on the clusters, $Ir_4(CO)_{11}L$ (L = PPh_3, $P(OPh)_3$, PBu_3, $AsPh_3$).[20]

$$Ir_4(CO)_{11}L + L' \rightarrow \text{further substituted products}$$

---

(1) See, for example: Basolo, F.; Pearson, R., "Mechanisms of Inorganic Reactions"; Wiley: New York, 1967.

(2) Cawse, J. W.; Fiato, R. A.; Pruett, R. L. *J. Organomet. Chem.* **1979**, *172*, 405.

(3) Byers, B. H.; Brown, T. L. *J. Am. Chem. Soc.* **1977**, *99*, 2527.

(4) Thorsteinson, E. M.; Basolo, F. *J. Am. Chem. Soc.* **1966**, *88*, 3929.

(5) Wawersik, H.; Basolo, F. *J. Am. Chem. Soc.* **1967**, *89*, 4626.

(6) Atwood, J. D.; Brown, T. L. *J. Am. Chem. Soc.* **1975**, *97*, 3380.

(7) Atwood, J. D.; Brown, T. L. *J. Am. Chem. Soc.* **1976**, *98*, 3155.

(8) Atwood, J. D.; Brown T. L. *J. Am. Chem. Soc.* **1976**, *98*, 3160.

(9) Lichtenberger, D. L.; Brown. T. L. *J. Am. Chem. Soc.* **1978**, *100*, 366.

(10) Wovkulich, M. J.; Atwood, J. D. *J. Organomet. Chem.* **1980**, *184*, 77.

(11) Wovkulich, M. J.; Feinberg, S. J.: Atwood, J. D. *Inorg. Chem.* **1980**, *19*, 2608.

(12) Darensbourg, D. J.; Graves, A. H. *Inorg. Chem.* **1979**, *18*, 1257.

(13) Wawersik, H.; Basolo, F. *Inorg. Chim. Acta* **1969**, *3*, 113.

(14) Sonnenberger, D.; Atwood, J. D. *J. Am. Chem. Soc.* **1980**, *102*, 3484.

(15) Malik, S. K.; Poë, A. *Inorg. Chem.* **1978**, *17*, 1484.

(16) Darensbourg, D. J.; Incorvia, M. J. *J. Organomet. Chem.* **1979**, *171*, 89.

(17) Darensbourg, D. J.; Incorvia, M. J. *Inorg. Chem.* **1980**, *19*, 2585.

(18) Darensbourg, D. J.; Incorvia, M. J. *Inorg. Chem.* **1981**, *20*, 1911.

(19) Karel, K. J.; Norton, J. R. *J. Am. Chem.* **1974**, *96*, 6812.

(20) Stuntz, G. F.; Shapley, J. R. *Inorg. Chem.* **1976**, *15*, 1994.

0002-7863/82/1504-2113$01.25/0

Table III. Conditions for the Reaction of L′ with $Ir_4(CO)_{11}L$

compound	entering ligand	temp range, °C	IR absorption,[a] cm^{-1}
$Ir_4(CO)_{11}PPh_3$	PPh_3	80–90	2086
	$P(OPh)_3$	80–90	2086
	PBu_3	21	2036
$Ir_4(CO)_{11}P(OPh)_3$	$P(OPh)_3$	90–100	2096
	PPh_3	90–100	2096
$Ir_4(CO)_{11}AsPh_3$[b]	$AsPh_3$	80–90	2090
$Ir_4(CO)_{11}PBu_3$	PPh_3	75–90	2085

[a] The band reported was used to obtain the quantitative data. [b] Studied in decane and chlorobenzene.

Comparison of these data to the substitutions on $Ir_4(CO)_{12}$ allows an interpretation of transition-metal cluster substitution reactions in terms of cis labilization.[21]

Experimental Section

Preparations. Iridium trichloride dihydrate (Matthey Bishop Co.), lithium chloride (Fisher reagent grade), trimethylamine *N*-oxide dihydrate (Aldrich Chemical Co.), *p*-toluidine (Fisher reagent grade), and carbon monoxide (Linde CP Grade) were used as received. Triphenylphosphine (Aldrich Chemical Co.), triphenylarsine (Aldrich Chemical Co.), and triphenylphosphite (Aldrich Chemical Co.) were used as received; tri-n-butylphosphine (PBu_3) was vacuum distilled over sodium before use.

All preparative-scale thin-layer chromatography was accomplished by using 1.0-mm thick silica gel (VWR Scientific Co.) plates with calcium sulfate binder. All substituted tetrairidium clusters were stored in an inert atmosphere glovebox under argon, for they were found to be slightly air sensitive in the solid state.

(Triphenylphosphine)undecacarbonyltetrairidium, $Ir_4(CO)_{11}PPh_3$, was prepared as previously described.[20] The infrared spectrum, listed in Table II, is in agreement with previous assignment. Anal. Calcd for $Ir_4(CO)_{11}PPh_3$: Ir, 57.42; C, 26.01; P, 2.32; H, 1.13. Found: Ir, 57.65; C, 26.20; P, 2.17; H, 1.43.

(Triphenyl phosphite)undecacarbonyltetrairidium, $Ir_4(CO)_{11}P(OPh)_3$, was prepared as previously described.[20] The infrared spectrum, reported in Table II, is in agreement with previous assignment.

(Triphenylarsine)undecacarbonyltetrairidium, $Ir_4(CO)_{11}AsPh_3$, was prepared by methods similar to those for the triphenylphosphine analogue. Separation was accomplished via preparative-scale TLC (cyclohexane–methylene chloride, 7:1) of the reaction mixture. Recrystallization, using a 4:1 hexane–THF mixture, gave the yellow, monosubstituted derivative. The infrared spectrum, listed in Table II, is similar to closely related arsine-substituted clusters.[25] Anal. Calcd for $Ir_4(CO)_{11}AsPh_3$: Ir, 55.59; C, 25.18; H, 1.10. Found: Ir, 56.10; C, 27.36; H, 1.71.

(Tri-*n*-butylphosphine)undecacarbonyltetrairidium, $Ir_4(CO)_{11}PBu_3$, was prepared by methods similar to those for the triphenylphosphine analogue. Separation of the product mixture was achieved by preparative-scale TLC (cyclohexane). The infrared spectrum is reported in Table II. Anal. Calcd for $Ir_4(CO)_{11}PBu_3$: Ir, 60.10; C, 21.59; H, 2.13. Found: Ir, 60.87; C, 21.85; H, 2.30.

Kinetic Studies. Triphenylphosphine (Aldrich Chemical Co.) was used as received. Triphenyl phosphite, tri-*n*-butylphosphine, and decane were purified as described earlier.[14] Triphenylarsine was recrystallized from dry ethanol and stored under argon. Chlorobenzene was dried with calcium hydride and stored under vacuum over molecular sieves.

The reactions were accomplished under an argon atmosphere in foil-wrapped vessels in darkened hoods and followed by IR, using a Beckman 4240 IR spectrophotometer and matched 1.0-mm NaCl cells, for a minimum of three half-lives. All reactions were performed under pseudo-first-order conditions, with a ligand concentration of greater than 30 times that of the cluster. A Haake FS constant-temperature circulator was used to maintain the reactions at the desired temperature, to within ±0.1 °C.

In the reaction of $Ir_4(CO)_{11}PPh_3$ with PBu_3, a plot of $\ln [(A_t - A_\infty)/(A_0 - A_\infty)]$ vs. time was used to determine k_{obsd}. In all other reactions, a plot of $\ln A_t$ vs. time yielded the pseudo-first-order rate constants, k_{obsd}, quoted herein. Plots of k_{obsd} vs. ligand concentration afforded the rate constants k_1 and k_2. From an Arrhenius plot using k_{obsd}, the activation parameters ΔH^* and ΔS^* were obtained. The reaction conditions for $Ir_4(CO)_{11}L$ complexes are presented in Table III.

Table IV. Rate Constants[a] for the Reaction of $Ir_4(CO)_{11}PPh_3$ with L

ligand	temp, °C	$10^3[L]$, M	$10^5 k_{obsd}$, s^{-1}
PPh_3	89.5	7.7	50.5 ± 0.7
		5.5	49.6 ± 0.2
		3.7	48.7 ± 0.2
	89	7.6	49.1 ± 1.4
	84	7.6	25.1 ± 1.3
	79	7.6	13.2 ± 0.3
$P(OPh)_3$	89.5	7.6	57.0 ± 0.5
		3.8	54.2 ± 1.5
PBu_3	22	7.6	35.1 ± 4.2

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

Table V. Ligand Independent and Dependent Rate Constants[a] for $Ir_4(CO)_{11}L + L'$

substituent ligand	entering ligand	temp, °C	$10^5 k_1$, s^{-1}	$10^5 k_2$, M^{-1} s^{-1}
PPh_3	PPh_3	89.5	47 ± 1	460 ± 70
$P(OPh)_3$	$P(OPh)_3$	89	5.1 ± 0.6	630 ± 30
	PPh_3	89	5.7 ± 0.1	56 ± 6
$AsPh_3$	$AsPh_3$	89	34 ± 1	170 ± 10
PBu_3	PPh_3	89	93 ± 1	270 ± 30

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

Table VI. Activation Parameters[a] for $Ir_4(CO)_{11}L + L'$

substituent ligand	entering ligand	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
PPh_3	PPh_3	32.0 ± 1.0	14.3 ± 2.7
$P(OPh)_3$	$P(OPh)_3$	30.6 ± 0.8	7.0 ± 2.3
$AsPh_3$	$AsPh_3$	30.6 ± 1.3	9.7 ± 3.5
PBu_3	PPh_3	33.0 ± 0.4	18.4 ± 1.1

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

Results

Reaction of $Ir_4(CO)_{11}PPh_3$ with PPh_3, $P(OPh)_3$, and PBu_3. The reaction with PPh_3 followed pseudo-first-order kinetics for a minimum of three half-lives. The pseudo-first-order rate constants, k_{obsd}, at the various temperatures and ligand concentrations investigated are listed in Table IV. The ligand-independent and -dependent rate constants, k_1 and k_2, respectively, are given in Table V. The activation parameters are reported in Table VI.

During the reaction, IR absorbances appeared at 2065 (w), 2042 (m), 2012 (w), 1994 (sh), 1981 (s), 1962 (m), 1790 (sh), and 1780 (m) cm^{-1}. The bands at 2065, 2012, and 1790 cm^{-1} were assigned to $Ir_4(CO)_{10}(PPh_3)_2$, whereas those at 2042, 1994, 1981, 1962, and 1780 cm^{-1} were assigned to $Ir_4(CO)_9(PPh_3)_3$. Under all conditions studied, the trisubstituted cluster was the primary reaction product.[21]

The reaction of $Ir_4(CO)_{11}PPh_3$ with $P(OPh)_3$ obeyed pseudo-first-order kinetics for at least three half-lives. The pseudo-first-order rate constants, k_{obsd}, at the ligand concentrations studied are reported in Table IV. As the reaction proceeded, IR bands appeared at 2030 (m), 2000 (vs, br), and 1805 (s) cm^{-1}. These bands have been tentatively assigned to $Ir_4(CO)_9[P(OPh)_3]_2(PPh_3)$,[22] by comparison to complexes substituted by only one ligand.

Due to the limited solubility of $Ir_4(CO)_{11}PPh_3$ at room temperature and the facile nature of its reaction with PBu_3, only an approximate pseudo-first-order rate constant, k_{obsd}, listed in Table IV, could be determined.

---

[21] Sonnenberger, D.; Atwood, J. D. *Inorg. Chem.* **1981**, *20*, 3243.

[22] Assignment of the mixed ligand products was based on comparison to the homoligated analogues. The assigned products and infrared spectra (cm^{-1}) are as follows: $Ir_4(CO)_9PBu_3(PPh_3)_2$ 2038 (m), 1992 (sh), 1985 (s), 1960 (m), 1782 (m); $Ir_4(CO)_{10}PPh_3(PBu_3)$ 2065 (s), 2038 (s), 2012 (sh), 2000 (s, br), 1828 (m), 1790 (m); $Ir_4(CO)_9P(OPh)_3(PPh_3)_2$ 2045 (m), 2020 (sh), 1990 (s, br), 1785 (s, br); $Ir_4(CO)_{10}(P(OPh)_3)PBu_3$ 2072 (m), 2048 (s), 2022 (sh), 2015 (s), 1995 (sh), 1965 (sh), 1832 (m), 1805 (m); $Ir_4(CO)_9PPh_3(P(OPh)_3)_2$ 2030 (m, sh), 2000 (s, br), 1802 (s, br).

Table VII. Rate Constants[a] for the Reaction of $Ir_4(CO)_{11}P(OPh)_3$ with L

ligand	temp, °C	$10^2[L]$, M	10^5k_{obsd}, s^{-1}
$P(OPh)_3$	89	0.76	9.67 ± 0.12
		1.5	14.8 ± 0.3
		3.1	24.1 ± 0.7
	94	0.76	17.0 ± 0.2
	99	0.76	30.1 ± 0.6
PPh_3	89	0.39	5.96 ± 0.18
		0.75	6.14 ± 0.09
		1.2	6.41 ± 0.32

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

Table VIII. Rate Constants[a] for Reaction of $Ir_4(CO)_{11}AsPh_3$ with $AsPh_3$ and $Ir_4(CO)_{11}PBu_3$ with PPh_3

complex	temp, °C	$10^2[L]$, M	10^5k_{obsd}, s^{-1}
$Ir_4(CO)_{11}AsPh_3$	89	0.37	34.4 ± 0.9
		0.56	34.7 ± 0.2
		0.76	35.1 ± 0.7
			32.3 ± 0.6[b]
		1.2	35.8 ± 0.1
		1.5	32.2 ± 0.4[b]
	84	0.76	18.3 ± 0.6
	79	0.76	9.95 ± 0.13
$Ir_4(CO)_{11}PBu_3$	89	0.38	93.6 ± 3.7
		0.78	94.1 ± 0.5
		1.1	94.6 ± 0.8
	79	0.76	25.1 ± 0.6
	74	0.76	12.4 ± 0.5

[a] Error limits are quoted as 95% confidence intervals. [b] In chlorobenzene.

As the reaction occurred, IR absorbances at 2064 (s), 2037 (s), 2005 (sh), 1995 (s), 1982 (sh), 1825 (m), and 1790 (m) cm^{-1} grew in. These absorbances have been tentatively assigned to $Ir_4(CO)_{10}(PPh_3)(PBu_3)$.[22]

Reaction of $Ir_4(CO)_{11}P(OPh)_3$ with $P(OPh)_3$ and PPh_3. The reaction with $P(OPh)_3$ followed pseudo-first-order kinetics for a minimum of three half-lives. The pseudo-first-order rate constants, k_{obsd}, at the different temperatures and ligand concentrations investigated are listed in Table VII. The ligand-independent and -dependent rate constants, k_1 and k_2, respectively, are given in Table V. The activation parameters are reported in Table VI.

During the reaction, a series of IR absorbances grew (2075 (w), 2032 (m), 2025 (w), 2000 (s), 1807 (m, br) cm^{-1}). These bands have been assigned to $Ir_4(CO)_{10}[P(OPh)_3]_2$ and $Ir_4(CO)_8[P(OPh)_3]_4$. Under all conditions studied, the tetrasubstituted cluster is the primary reaction product.[21]

The reaction of $Ir_4(CO)_{11}P(OPh)_3$ with PPh_3 obeyed pseudo-first-order kinetics for at least three half-lives. The pseudo-first-order rate constants, k_{obsd}, at the various ligand concentrations studied are reported in Table VII. The ligand-independent and -dependent rate constants, k_1 and k_2, respectively, are listed in Table V. As the reaction proceeded, IR bands appeared at 2045 (m), 1995 (s, br), and 1785 (m, br) cm^{-1}, which were tentatively assigned to $Ir_4(CO)_9(PPh_3)_2P(OPh)_3$.[22]

Reaction of $Ir_4(CO)_{11}AsPh_3$ with $AsPh_3$. These reactions followed pseudo-first-order kinetics for a minimum of two half-lives, after which the reactions slowed somewhat, apparently by reaction of CO with the intermediate ($Ir_4(CO)_{10}AsPh_3$). The pseudo-first-order rate constants, k_{obsd}, at the various temperatures and ligand concentrations investigated are given in Table VIII. The ligand-independent and -dependent rate constants, k_1 and k_2, respectively, are reported in Table V. The activation parameters are listed in Table VI.

As the reaction occurred, IR absorbances appeared at 2065 (w), 2040 (w), 1990 (w, br), and 1780 (w) cm^{-1}. These bands can be assigned to $Ir_4(CO)_{10}(AsPh_3)_2$ and $Ir_4(CO)_9(AsPh_3)_3$.[21]

Reaction of $Ir_4(CO)_{11}PBu_3$ with PPh_3. These reactions obeyed pseudo-first-order kinetics for at least three half-lives. The pseudo-first-order rate constants, k_{obsd}, at the various temperatures and ligand concentrations investigated are given in Table VIII. The ligand-independent and -dependent rate constants, k_1 and k_2, respectively, are reported in Table V. The activation parameters are listed in Table VI. During the reaction, IR bands appeared at 2038 (m), 1992 (sh), 1985 (s), 1960 (m), and 1782 (m) cm^{-1}. These absorbances have been assigned to $Ir_4(CO)_9(PPh_3)_2PBu_3$.[22]

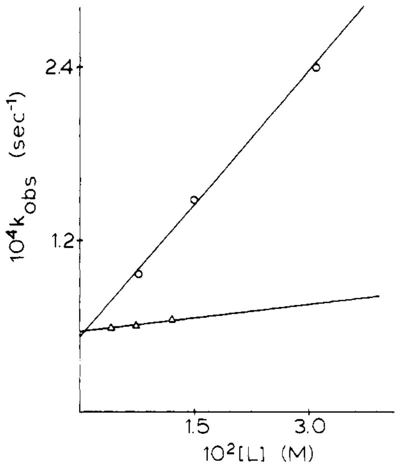

Figure 1. Plot of k_{obsd} vs. [L] for $Ir_4(CO)_{11}P(OPh)_3$ at 89 °C for L = $P(OPh)_3$ (○), PPh_3 (△).

Table IX. Rate Constants for CO Dissociation Adjusted to 109 °C[24]

complex	$k_1 \times 10^5$, s^{-1}
$Ir_4(CO)_{12}$	6.0
$Ir_4(CO)_{11}P(OPh)_3$	50
$Ir_4(CO)_{11}AsPh_3$	320
$Ir_4(CO)_{11}PPh_3$	520
$Ir_4(CO)_{11}PBu_3$	1100

Discussion

The reaction under consideration is the further substitution of a ligand for CO on $Ir_4(CO)_{11}L$, L = PBu_3, PPh_3, $P(OPh)_3$, and $AsPh_3$.

$$Ir_4(CO)_{11}L + xL' \rightarrow Ir_4(CO)_{11-x}LL'_x + xCO$$

These reactions were studied between 20 and 100 °C in decane and in chlorobenzene. The specific product depended on the ligand and the reaction temperature. For further substitution by the same ligand the products were the same as those observed previously.[14] For reaction of L' with $Ir_4(CO)_{11}L$, the products were assigned by comparison of infrared spectra with the homoligated products.[22]

Good pseudo-first-order kinetic plots were obtained for each of the ligands by following the decrease in the infrared absorbance of $Ir_4(CO)_{11}L$, and the rate constants, k_{obsd}, were obtained from the slope. Plots of k_{obsd} vs. [L'] were linear with nonzero intercepts. A sample plot is shown in Figure 1. This kinetic behavior is consistent with a two-term rate law.

$$\text{rate} = k_{obsd}[Ir_4(CO)_{11}L] = (k_1 + k_2[L'])[Ir_4(CO)_{11}L]$$

The values of k_1 and k_2 for the different complexes are shown in Table V. The relative contributions of k_1 and k_2 are dramatically reversed for $Ir_4(CO)_{11}L$ in comparison to $Ir_4(CO)_{12}$.[21] The ligand-dependent term dominated for $Ir_4(CO)_{12}$ but is minor for $Ir_4(CO)_{11}L$. This reduction of importance of the ligand-dependent term is primarily the result of the enhanced rate for the ligand-independent term. The values of k_2 for $Ir_4(CO)_{11}L$ in Table V are larger than those observed for $Ir_4(CO)_{12}$.[21] However, the solvent difference (decane for $Ir_4(CO)_{11}L$ and chlorobenzene for $Ir_4(CO)_{12}$) would easily account for the increase.[23] Since the total

---

(23) We measured the solvent dependence for the reaction of $Ir_4(CO)_{11}AsPh_3$ with $AsPh_3$ at 89 °C. In decane the value of k_1 was 3.4×10^{-4} s^{-1}, while in chlorobenzene the value of k_1 was 3.2×10^{-4} s^{-1}. The value of k_2 was 1.7×10^{-3} s^{-1} M^{-1} in decane and was too small to be evaluated in chlorobenzene.

Table X. Relative Labilization of CO Dissociation in Different Complexes[24]

L	$Cr(CO)_5L$	$Mn_2(CO)_9L$	$Ir_4(CO)_{11}L$
CO	1	1	1
$P(OPh)_3$		1.5	10
$AsPh_3$	100^a		34
PBu_3		12	93
PPh_3	300	44	50

[a] The comparison is for $W(CO)_6$ and $W(CO)_5SbPh_3$.

contribution to the rate by the ligand-dependent term is very small, the most that can be said is that the rate of ligand attack is about the same for $Ir_4(CO)_{11}L$ and $Ir_4(CO)_{12}$.

The ligand-independent (first-order) term predominates in further substitutions on $Ir_4(CO)_{11}L$. We ascribe this first-order term to rate-determining CO dissociation from the cluster followed by rapid reactions with L. The activation parameters, $\Delta H^{\ddagger}$ of ~ 31 kcal/mol and positive $\Delta S^{\ddagger}$, and the very small dependence of k_1 on the solvent are consistent with CO dissociation. The effect of the ligand L in $Ir_4(CO)_{11}L$ on the rate of CO dissociation is quite remarkable, as shown in Table IX.[24] The ligands show a relatively large labilization of CO toward dissociation with the order and amount shown: L = CO < $P(OPh)_3$ < $AsPh_3$ < PPh_3 < PBu_3; relative rates = 1, 8, 50, 90, and 180, respectively. The relative ordering and quantitative labilization are very similar to those observed for cis labilization on mononuclear complexes and to those seen for the dimers, $Mn_2(CO)_9L$.[6-9,13,25] The comparison is shown in Table X. The similarity strongly suggests that the same factors are responsible for the labilization of CO dissociation in mononuclear, dinuclear, and polynuclear complexes.[6-9,13,15-19] For $Mn_2(CO)_9L$, intermediates with bridging CO's similar to those suggested for substitutions on $MnRe(CO)_{10}$ could allow the unsaturation at the substituted manganese to be transferred to the unsubstituted manganese.[14] Thus the PPh_3 could labilize one of the four cis CO's, a bridging CO would transfer the unsaturation to the other manganese center, and the phosphine would add to the previously unsubstituted manganese center. Similar considerations of $Ir_4(CO)_{11}L$ are complicated by the structural change from no bridging CO's to bridging CO's.[26,27] In addition these molecules are fluxional, undergoing three distinct averaging processes at low temperature.[28] Thus it is impossible to suggest the detailed geometry of the complex $Ir_4(CO)_{11}L$ just prior to CO dissociation. The facility of CO exchange would certainly make transfer of the unsaturation from the substituted iridium to an unsubstituted iridium likely, if the ligand labilized CO dissociation from the substituted iridium center as we suggest.

The source of a kinetic acceleration in rate can arise either from a ground-state destabilization or from a transition-state stabilization. There is no evidence for a ground-state destabilization. Crystal structure determinations on substituted tetrairidium clusters show no lengthening of the Ir–C distances on the substituted or other iridium atoms (Ir–C_{av}: $Ir_4(CO)_{12}$, 1.87 Å; $Ir_4(CO)_{11}$(CN-*t*-Bu), 1.87 Å (not substituted Ir), 1.84 Å (substituted Ir); $Ir_4(CO)_{10}$ diars (diars = 1,2-bis(dimethylarsino)benzene), 1.88 Å).[26,29,30] Infrared spectra of the substituted derivatives, $Ir_4(CO)_{11}L$, are shifted to lower frequency, suggesting a strengthening of the M–C bonds, not a weakening, which would be expected if the labilization arose from ground-state effects. Thus we suggest that the labilization of CO dissociation observed in $Ir_4(CO)_{11}L$ results from a transition-state stabilization by the presence of the ligand. The stabilization could arise from steric or electronic factors, although steric factors should be minimal on these iridium centers which are large and have bond angles for the three groups of 100°.[26,29,30] The ordering could be consistent with decreasing π-bonding capability or increasing σ-bonding strength. It was suggested that decreasing π-bonding capability was most important in mononuclear complexes. For the ligands we investigated, stabilization of the unsaturated intermediate by σ-bonding would be equally probable. If CO dissociation occurs at the substituted iridium, then there is considerable precedence for transition-state stabilization by the presence of ligands that are weaker π-bonding ligands than CO.[6-9] The quantitative agreement between cis labilization order and the order of labilization we observe for $Ir_4(CO)_{11}L$ suggest that the CO does dissociate from the iridium which is already substituted. At this point too little data exist to determine how the presence of these ligands (PPh_3, PBu_3, $P(OPh)_3$, $AsPh_3$) stabilizes the transition state for dissociative loss of CO from $Ir_4(CO)_{11}L$.

The other transition-metal clusters that have been investigated can be interpreted also in terms of a labilization of CO at the same metal. The rate of CO dissociation from $Ru_3(CO)_{11}PPh_3$ is 55 times that from $Ru_3(CO)_{12}$, as shown in Table I.[15] This is quite comparable to the labilization of CO dissociation by PPh_3 in $Cr(CO)_5PPh_3$,[8] $Mn_2(CO)_9PPh_3$,[13] and $Ir_4(CO)_{11}PPh_3$. $P(OMe)_3$ provides very little labilization when substituted for CO in $Co_4(CO)_{12}$.[16-18] This would be consistent with the very small labilization observed for phosphites in $Mn(CO)_4(P(OPh)_3)Br$[7] and $Ir_4(CO)_{11}P(OPh)_3$.

We have shown that the rate of CO dissociation from $Ir_4(CO)_{11}L$ depends on the ligand L and have offered an explanation of the ligand effects in terms of a labilization of the CO's on the substituted iridium. We suggest that this labilization (very similar to cis labilization in mononuclear complexes) is also operative in reactions of metal carbonyl dimers and other clusters. Initial results on $Ir_4(CO)_{10}L_2$ indicate a continued labilization of CO toward dissociation as the extent of substitution increases.

Acknowledgment. We acknowledge the financial support of the National Science Foundation, Matthey Bishop, Inc., for a loan of $IrCl_3 \cdot H_2O$, and helpful discussions with Professors J. B. Keister and M. R. Churchill.

Registry No. $Ir_4(CO)_{11}PPh_3$, 53565-22-3; $Ir_4(CO)_{11}PBu_3$, 80865-04-9; $Ir_4(CO)_{11}AsPh_3$, 80865-03-8; $Ir_4(CO)_{11}P(OPh)_3$, 59532-82-0; $Ir_4(CO)_{12}$, 18827-81-1; $P(OPh)_3$, 101-02-0; $AsPh_3$, 603-37-7; PBu_3, 998-40-3; PPh_3, 603-35-0.

---

[24] The rates we quoted in the tables are observed rates of reaction without any attempt to correct these values for statistical factors. We believe that until the site of CO dissociation is established a statistical correction is meaningless.

[25] The relative position of PPh_3 and PBu_3 in the orders of labilization is variable. We believe this to be the result of a stabilization of the ground state and the transition state by PBu_3. The relative amount of ground-state and transition-state effects causes the variation in position for different complexes.

[26] Churchill, M. R.; Hutchinson, J. P. *Inorg. Chem.* **1978**, *17*, 3528.

[27] Albano, V.; Bellon, P. L.; Scatturin, V. *Chem. Commun.* **1967**, 730.

[28] Stuntz, G. F.; Shapley, J. R. *J. Am. Chem. Soc.* **1977**, *99*, 607.

[29] Churchill, M. R.; Hutchinson, J. P. *Inorg. Chem.* **1979**, *18*, 2451.

[30] Churchill, M. R.; Hutchinson, J. P. *Inorg. Chem.* **1980**, *19*, 2765.