of these with the butadiene moiety probably dominates in the transition state. Approach of the $Cr(CO)_3$ group toward the butadiene moiety is rather *less* hindered on the exo side than on the endo side—the dihedral angle between the butadiene plane and the cyclic double bond C(17)–C(18) (plane Ene 2) is only 87.5°, while the dihedral angle made with the coordinated semicyclic olefin is 116.3° (as seen by an approaching $Cr(CO)_3$ group, see also Figure 3 and Table VIII). In addition, at distances where the Cr–butadiene interaction is weak, interaction with the terminal methylene carbon atom is possible. Thus, for certain directions of approach, the methylene semicyclic double bond could serve to guide the approaching $Cr(CO)_3$ group toward the butadiene component, thereby further enhancing exo approach.

Comparison with Other $M(CO)_3$(triene) Species. Among structurally characterized complexes containing the $Cr(CO)_3$ or $Mo(CO)_3$ moiety, it is only rarely that two carbonyl lgands approach trans geometry and then only as a result of coordination of the central atom to a phosphine ligand and a diolefin.[16,18] In other cases,[3–15,17,19–24] particularly among the more precisely determined structures, deviations of the C_{CO}–Cr–C_{CO} bond angles from 90° are small. It should be noted that these angles generally average to a value less than 90°, presumably from the steric demands of the olefinic or other ligands. Thus, the C(1)–Cr–C(2) angle, which we have observed, is one of the largest found, while the average angle of 87.8° is entirely normal. While some apparently significantly short Cr–C_{CO} bonds are known, these are invariably in structures of low precision; for example, a Cr–C_{CO} bond of 1.72 (2) Å is associated with a C–O separation of 1.27 (2) Å.[23] Among the conjugated triene complexes the values observed here for the Cr–C_{CO} bonds are entirely comparable.

The Cr—$C_{C=C}$ bonds lie comfortably within the range which has been observed for triene and diene complexes, although it is only in the curious homoaromatic systems[11–13] that bonds longer than the 2.386 (3) Å for the Cr—C(16) bond determined here have been found.

As noted earlier, butadiene–olefin and triolefin complexes are exceedingly scarce and only the $Mo(CO)_3$(5,6-dimethylenebicyclo[2.2.1]hept-2-ene) complex is available for comparison. Here there is an angle of ~60° between the olefin plane and the butadiene plane.

Concluding Remarks. Studies on appropriately substituted derivatives of I with extension to molybdenum and tungsten tricarbonyl complexes are planned, in order to probe further the binding properties of this ligand and equally important the coordinating properties of the $M(CO)_3$ species.

Acknowledgment. We gratefully acknowledge Professor H. R. Oswald and the Swiss National Science Foundation for the use of X-ray diffraction facilities and for financial support.

Registry No. $Cr(CO)_3(CH_3CN)_3$, 16800-46-7; $Cr(CO)_3(C_{10}H_{10})$, 70585-10-3.

Supplementary Material Available: A table of thermal parameters (Table III) and a listing of structure amplitudes (Table IV) (9 pages). Ordering information is given on any current masthead page.

Labilization of CO Dissociation from Metal Clusters. 2. An Investigation of Substitution Reactions of Bissubstituted Derivatives of Tetrairidium Dodecacarbonyl, $Ir_4(CO)_{10}L_2$ (L = PPh_3, $P(OPh)_3$, PBu_3, and $AsPh_3$)

David C. Sonnenberger and Jim D. Atwood*

Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214

Received December 3, 1981

The reactions of $Ir_4(CO)_{10}L_2$ with an additional ligand have been studied for L = PPh_3, $P(OPh)_3$, $AsPh_3$, and PBu_3. Good pseudo-first-order kinetics were observed for each cluster, and the activation parameters were evaluated for each reaction. The primary reaction pathway involves CO dissociation from the cluster in the rate-determining step. Examination of the rates of CO loss from the series of complexes $Ir_4(CO)_{10}L_2$, L = PPh_3, $P(OPh)_3$, $AsPh_3$, PBu_3, and CO, reveals a dramatic labilization in the order CO < $P(OPh)_3$ < PBu_3 < PPh_3 ≤ $AsPh_3$. These ligands span 3 orders of magnitude in the CO dissociation rate. It is proposed that CO dissociation occurs at a substituted metal center with bridging carbonyls transferring the coordinative unsaturation to a second unsubstituted center. The kinetic labilization by the presence of the substituent ligand L arises from a stabilization of the transition state.

Introduction

In an earlier paper dealing with the substitution processes of $Ir_4(CO)_{11}L$, we reported a significant enhancement in the rate of CO dissociation from the monosubstituted clusters, as compared to the parent cluster, $Ir_4(CO)_{12}$.[1] The degree of acceleration in the rate of CO loss varied with the nature of the substituent ligand

$$CO < P(OPh)_3 < AsPh_3 < PPh_3 < PBu_3 \tag{1}$$

This labilization of CO loss was ascribed to a stabilization of the resulting transition state by the presence of the substituent ligand. This phenomenon is not unique to the tetrairidium carbonyl clusters; CO dissociation was 55 times more rapid from $Ru_3(CO)_{11}PPh_3$ than from $Ru_3(CO)_{12}$.[2]

---

(1) Sonnenberger, D. C.; Atwood, J. D. *J. Am. Chem. Soc.*, in press.

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

0276-7333/82/2301-0694$01.25/0

Table I. Infrared Spectra of the $Ir_4(CO)_{10}L_2$ Clusters[a]

compd	ν(CO), cm^{-1}
$Ir_4(CO)_{10}(PPh_3)_2$	2068 (m), 2041 (s), 2000 (s, br), 1820 (w), 1790 (m, br)
$Ir_4(CO)_{10}(P(OPh)_3)_2$	2072 (m), 2050 (s), 2021 (s), 1835 (m), 1820 (m)
$Ir_4(CO)_{10}(AsPh_3)_2$	2068 (s), 2041 (s), 2006 (s, br), 1825 (m), 1787 (w)
$Ir_4(CO)_{10}(PBu_3)_2$	2059 (m), 2032 (s), 1995 (s, br), 1825 (m), 1787 (m)

[a] In dichloromethane.

The ability of a unique ligand to affect the reactivity at a metal center has been well documented in organometallic chemistry. The presence of such ligands as Cp, Me, and NO in a transition-metal carbonyl complex has been found to alter the mechanism of reaction on the complex.[4-6] Other ligands, although not affecting the reaction mechanism, have been observed to alter the energetics.[7-16] The rates of CO dissociation from a number of six-coordinate metal carbonyls was explained in terms of cis labilization, a labilization toward dissociation of the CO cis to the unique ligand.[12] The cis labilization order

$$CO < P(OPh)_3 < PPh_3 < I^- < Br^- < Cl^- \qquad (2)$$

was ascribed to a stabilization of the resulting square-pyramidal transition state by the labilizing ligand.

The presence of a second noncarbonyl ligand in an octahedral metal carbonyl complex leads to a further acceleration of CO toward dissociation, though usually the magnitude of the labilization is less than when the ligand is the only labilizing ligand. Thus the presence of PPh_3 in $Mn(CO)_4PPh_3Br$ accelerates CO dissociation by a factor of 10 over the rate seen in $Mn(CO)_5Br$[11] while the presence of PPh_3 in $Cr(CO)_5PPh_3$ accelerates the rate of CO dissociation by a factor of 100 over the rate observed from $Cr(CO)_6$.[12]

The presence of a second unique ligand on a transition-metal carbonyl cluster has been observed to affect the energetics of the CO dissociation process from that cluster.[2,17,18] In these studies, however, there was no variation in the nature of the substituent ligand, so that, as a result, there exists insufficient data to understand the reactivity. To increase our understanding of the effects of the ligand environment on the reactivity at the metal centers of transition-metal clusters, we have followed the further substitution on the bissubstituted tetrairidium clusters, $Ir_4(CO)_{10}L_2$ (L = PPh_3, $P(OPh)_3$, $AsPh_3$, and PBu_3). A previous study of $Ir_4(CO)_{10}(PPh_3)_2$ has indicated a substantial acceleration of CO dissociation.[17]

Table II. Rate Constants for the Reaction of $Ir_4(CO)_{10}(PPh_3)_2$ with PPh_3[a]

temp, °C	10^2[L], M	$10^5 k_{obsd}$, s^{-1}
64	1.5	33.5 ± 0.3
	0.76	33.3 ± 0.5
59	0.76	16.7 ± 0.2
49	0.76	3.90 ± 0.16

[a] 95% confidence limits.

Experimental Section

Preparations. Iridium trichloride dihydrate (Matthey Bishop Co.), lithium chloride (Fisher Reagent Grade), trimethylamine *N*-oxide (Aldrich Chemical Co.), triphenylarsine (Aldrich Chemical Co.), and triphenyl phosphite (Aldrich Chemical Co.), and triphenylphosphine (Aldrich Chemical Co.) were used as received; tri-*n*-butylphosphine 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.

$Ir_4(CO)_{10}(PPh_3)_2$ and $Ir_4(CO)_{10}(P(OPh)_3)_2$ were prepared as previously described,[19] with isolated yields of 27% and 25%, respectively. The infrared spectra (reported in Table I) are in agreement with the literature values.

$Ir_4(CO)_{10}(AsPh_3)_2$ was prepared by a method similar to the triphenylphosphine analogue. Purification was accomplished by preparative-scale TLC (cyclohexane–dichloromethane, 7:1) of the reaction mixture. Recrystallization, using a 4:1 hexane–THF mixture, gave orange crystals, in an isolated yield of 21%. The infrared spectrum is listed in Table I.

$Ir_4(CO)_{10}(PBu_3)_2$ was also prepared by a procedure similar to the triphenylphosphine derivative. Purification was achieved by preparative-scale TLC (cyclohexane). Recrystallization from a 10:1 hexane–THF mixture gave dark yellow crystals in a 25% isolated yield. The infrared spectrum (Table I) is in agreement with previous assignment.[20]

Kinetic Studies. Triphenylphosphine (Aldrich Chemical Co.) was used as received. Triphenyl phosphite, tri-*n*-butylphosphine, and decane were purified as previously described.[21] Chlorobenzene was dried by refluxing over calcium hydride, vacuum distilled, and stored under vacuum over molecular sieves. Triphenylarsine was recrystallized from dry ethanol.

The reactions were accomplished in foil-wrapped vessels in darkened hoods and followed by IR, using a Beckman 4240 infrared spectrophotometer and matched 1.0-mm NaCl cells, for a minimum of 3 half-lives. All reactions were performed under pseudo-first-order conditions, with a ligand concentration greater than 20 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. All reactions were performed in chlorobenzene under an argon atmosphere.

$Ir_4(CO)_{10}(PPh_3)_2$. The reaction of $Ir_4(CO)_{10}(PPh_3)_2$ with PPh_3 in chlorobenzene was investigated at temperatures between 49 and 64 °C. The kinetics were followed by monitoring the decrease in absorbance at 2069 cm^{-1} due to $Ir_4(CO)_{10}(PPh_3)_2$.

$Ir_4(CO)_{10}(P(OPh)_3)_2$. The reactions of $Ir_4(CO)_{10}(P(OPh)_3)_2$ with PPh_3, PBu_3, and $P(OPh)_3$ in chlorobenzene were studied at temperatures between 89 and 99 °C. The substitution kinetics were followed by monitoring the decrease in absorbance at 2072 cm^{-1}, due to $Ir_4(CO)_{10}(P(OPh)_3)_2$.

$Ir_4(CO)_{10}(AsPh_3)_2$. The reactions of $Ir_4(CO)_{10}(AsPh_3)_2$ with $AsPh_3$ and PPh_3 in chlorobenzene were investigated at temperatures between 49 and 69 °C. The kinetics of the reaction with PPh_3 were followed by monitoring the decrease in absorbance at 2066 cm^{-1}, due to $Ir_4(CO)_{10}(AsPh_3)_2$. No kinetic data could be

---

[3] See, for example: Basolo, F.; Pearson, R. "Mechanisms of Inorganic Reactions"; Wiley: New York, 1967.

[4] Mawby, R. J.; Basolo, F.; Pearson, R. G. *J. Am. Chem. Soc.* **1964**, *86*, 3994.

[5] Schuster-Woldan, H. G.; Basolo, F. *J. Am. Chem. Soc.* **1966**, *88*, 1657.

[6] Thorsteinson, E. M.; Basolo, F. *J. Am. Chem. Soc.* **1966**, *88*, 3929.

[7] Angelici, R. J.; Basolo, F. *Inorg. Chem.* **1963**, *2*, 728.

[8] Zingales, F.; Sartorelli, V.; Trovati, A. *Inorg. Chem.* **1967**, *6*, 1246.

[9] Wawersik, H.; Basolo, F. *Inorg. Chim. Acta* **1969**, *3*, 113.

[10] Atwood, J. D.; Brown, T. L. *J. Am. Chem. Soc.* **1975**, *97*, 3380.

[11] Atwood, J. D.; Brown, T. L. *J. Am. Chem. Soc.* **1976**, *98*, 3155.

[12] Atwood, J. D.; Brown, T. L. *J. Am. Chem. Soc.* **1976**, *98*, 3160.

[13] Lichtenberger, D. L.; Brown, T. L. *J. Am. Chem. Soc.* **1978**, *100*, 366.

[14] Darensbourg, D. J.; Graves, A. H. *Inorg. Chem.* **1979**, *18*, 1257.

[15] Wovkulich, M. J.; Atwood, J. D. *J. Organomet. Chem.* **1980**, *184*, 77.

[16] Wovkulich, M. J.; Feinberg, S. J.; Atwood, J. D. *Inorg. Chem.* **1980**, *19*, 2608.

[17] Karel, K. J.; Norton, J. R. *J. Am. Chem. Soc.* **1974**, *96*, 6812.

[18] Darensbourg, D. J.; Incorvia, M. J. *Inorg. Chem.* **1980**, *19*, 2585.

[19] Stuntz, G. F.; Shapley, J. R. *Inorg. Chem.* **1976**, *15*, 1994.

[20] Drakesmith, A. J.; Whyman, R.; *J. Chem. Soc., Dalton Trans.* **1973**, 362.

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

Table III. Rate Constants for the Reaction of $Ir_4(CO)_{10}(P(OPh)_3)_2$ with L[a]

ligand	temp, °C	10^2[L], M	10^5k_{obsd}, s^{-1}
$P(OPh)_3$	99	0.76	45.5 ± 0.6
	94	0.76	25.2 ± 2.7
	89	3.1	15.5 ± 0.4
		1.5	14.8 ± 0.9
		0.76	14.2 ± 0.7
PPh_3	89	0.76	13.2 ± 0.5
PBu_3	89	0.80	41.5 ± 1.7

[a] 95% confidence limits.

Table IV. Rate Constants for the Reaction of $Ir_4(CO)_{10}(AsPh_3)_2$ with PPh_3[a]

temp, °C	10^2[L], M	10^5k_{obsd}, s^{-1}
69	0.76	88.6 ± 1.0
59	1.5	27.3 ± 0.7
	1.2	26.4 ± 0.9
	0.76	25.0 ± 0.6
54	0.76	11.8 ± 0.3

[a] 95% confidence limits.

Table V. Rate Constants for the Reaction of $Ir_4(CO)_{10}(PBu_3)_2$ with PBu_3[a]

temp, °C	10^2[L], M	10^5k_{obsd}, s^{-1}
74	0.80	63.5 ± 2.7
69	0.80	34.8 ± 0.4
68.5	1.6	33.7 ± 1.6
	1.2	33.4 ± 1.0
	0.80	33.0 ± 0.5
59	0.80	8.93 ± 0.09

[a] 95% confidence limits.

obtained in the reaction with $AsPh_3$ due to an overlap of IR absorbances in this spectral region.

$Ir_4(CO)_{10}(PBu_3)_2$. The reaction of $Ir_4(CO)_{10}(PBu_3)_2$ with PBu_3 in chlorobenzene was studied at temperatures between 59 and 74 °C. The kinetics were followed by monitoring the decrease in absorbance at 2068 cm^{-1} ($Ir_4(CO)_{10}(PBu_3)_2$).

For the purpose of product identification, decane was used as the reaction solvent. All other reaction conditions were identical with those employed in the kinetic experiments.

Results

The reactions of $Ir_4(CO)_{10}L_2$ (L = PPh_3, $P(OPh)_3$, $AsPh_3$, and PBu_3) with PPh_3, $P(OPh)_3$, or PBu_3 followed pseudo-first-order kinetics for at least 2 half-lives, after which overlap of product absorbances interferred with the kinetic measurements. The pseudo-first-order rate constants, k_{obsd} are given in Tables II (L = PPh_3), III (L = $P(OPh)_3$), IV (L = $AsPh_3$), and V (L = PBu_3). The ligand independent and dependent rate constants, k_1 and k_2, respectively, obtained from plots of k_{obsd} vs. [L′], as shown in Figure 1 (L = $P(OPh)_3$), and eq 3, are listed in Table VI, while the activation parameters are reported in Table VII.

During the substitution on $Ir_4(CO)_{10}(PPh_3)_2$ by PPh_3, IR bands appeared at 2040 (m), 1980 (s, br), 1960 (sh), and 1780 (m, br) cm^{-1}, all of which can be assigned to $Ir_4(CO)_9(PPh_3)_3$. In the reaction of $Ir_4(CO)_{10}(PBu_3)_2$ with PBu_3, IR absorbances grew in at 1990 (sh), 1980 (m), 1950 (s), 1942 (sh), 1780 (sh), and 1767 (s) cm^{-1}. These bands can be assigned to $Ir_4(CO)_9(PBu_3)_3$ and $Ir_4(CO)_8(PBu_3)_4$, with the latter being the predominant product under all conditions studied.

In the reaction of $Ir_4(CO)_{10}(P(OPh)_3)_2$ with $P(OPh)_3$, IR absorbances at 2050 (vw), 2030 (w), 2015 (sh), 1995 (s, br), and 1805 (m, br) cm^{-1} grew in. These bands can be assigned to $Ir_4(CO)_9(P(OPh)_3)_3$ and $Ir_4(CO)_8(P(OPh)_3)_4$,[22] with the latter the major substitution product. During the reaction with PPh_3, IR bands appeared at 2040 (m), 2015 (sh), 1987 (s, br), and 1790 (m, br) cm^{-1}, which have been assigned to $Ir_4(CO)_8(P(OPh)_3)_2(PPh_3)_2$. In the reaction with PBu_3, IR absorbances grew in at 2062 (sh), 1980 (m), 1950 (s), 1942 (sh), and 1767 (s) cm^{-1}. The band at 2062 cm^{-1} appeared early in the reaction but disappeared by the end, when the absorbance at 2050 cm^{-1} ($Ir_4(CO)_{10}(P(OPh)_3)_2$) was minimal. The last four IR product bands, identical with those observed in the reaction of $Ir_4(CO)_{10}(PBu_3)_2$ with PBu_3, can be assigned to $Ir_4(CO)_8(PBu_3)_4$.

During the reaction of $Ir_4(CO)_{10}(AsPh_3)_2$ with PPh_3, IR bands grew in at 2043 (m), 1982 (s, br), and 1780 (m) cm^{-1}, all assigned to $Ir_4(CO)_9(AsPh_3)_2PPh_3$. In the substitution by $AsPh_3$, the observed product was $Ir_4(CO)_9(AsPh_3)_3$ (2042 (m), 1985 (s, br), and 1780 (m) cm^{-1}).

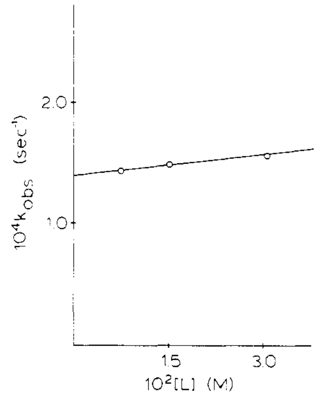

Figure 1. Plot of k_{obsd} vs. [L′] for the reaction of $Ir_4(CO)_{10}(P(OPh)_3)_2$ with $P(OPh)_3$ at 89 °C in chlorobenzene.

Table VI. Ligand Independent and Dependent Rate Constants for $Ir_4(CO)_{10}L_2$ + L′[a]

substituent ligand	entering ligand	temp, °C	10^5k_1, s^{-1}	10^5k_2, M^{-1} s^{-1}
PPh_3	PPh_3	64	33 ± 1	
$P(OPh)_3$	$P(OPh)_3$	89	14 ± 1	52 ± 13
$AsPh_3$	PPh_3	59	23 ± 1	310 ± 30
PBu_3	PBu_3	68.5	32 ± 1	88 ± 14

[a] 95% confidence limits.

Table VII. Activation Parameters for $Ir_4(CO)_{10}L_2$ + L′[a]

substituent ligand	entering ligand	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
PPh_3	PPh_3	32.0 ± 0.9	20.2 ± 2.8
$P(OPh)_3$	$P(OPh)_3$	30.5 ± 1.0	7.6 ± 2.7
$AsPh_3$	PPh_3	27.9 ± 0.9	8.6 ± 2.7
PBu_3	PBu_3	29.4 ± 1.1	11.3 ± 3.3
PPh_3[b]	PPh_3	31.0	17

[a] 95% confidence limits. [b] Reference 17.

Discussion

The reaction (eq 3) under consideration is the further substitution on $Ir_4(CO)_{10}L_2$ by L′ (L, L′ = PPh_3, $P(OPh)_3$, $AsPh_3$, and PBu_3). The reactions were studied at temperatures between 49 and 99 °C in chlorobenzene. The specific substitution product varied with the entering ligand, the substituent ligand, and the reaction tempera-

$$Ir_4(CO)_{10}L_2 + nL' \xrightarrow{\text{argon}} Ir_4(CO)_{10-n}L_2L'_n + nCO \qquad (3)$$

---

[22] Cattermole, P. E.; Orrell, K. G.; Osborne, A. G. *J. Chem. Soc., Dalton Trans.* **1974**, 328.

ture.[23] For the reaction of a ligand L′ with $Ir_4(CO)_{10}L_2$ ($L \neq L'$), the products were assigned by comparison of their infrared spectra with those of the homoligated analogues.[24]

By following the decrease in concentration of the initial cluster, $Ir_4(CO)_{10}L_2$, good pseudo-first-order rate constants, k_{obsd}, were obtained, with a rate law

$$\text{rate} = (k_1 + k_2[L'])[Ir_4(CO)_{10}L_2] \qquad (4)$$

where the $k_2[L']$ term is minor in comparison to k_1. This type of expression has been ascribed to both dissociative interchange[25] and competing associative and dissociative paths.[26] It has been postulated that the substitution processes on $Ir_4(CO)_{12}$,[21] $Ir_4(CO)_{11}L$,[1] and $Ru_3(CO)_{12}$[27] occur via competing ligand attack and CO dissociative paths. In the $Ir_4(CO)_{10}L_2$ system, we propose that the ligand independent k_1 term arises from a CO dissociative rate-determining step. All evidence is consistent with a CO dissociative pathway for the first-order term.[28] The relatively minor k_2 term is more difficult to assign. For the complexes $Ir_4(CO)_{10}(PPh_3)_2$, $Ir_4(CO)_{10}(PBu_3)_2$, and $Ir_4(CO)_{10}(P(OPh)_3)_2$, the k_2 term probably arises from a dissociative interchange mechanism, although we cannot completely rule out an associative step. The small dependence on the nature of the incoming ligand would be more consistent with an I_d mechanism. Reactions of $Ir_4(CO)_{10}(AsPh_3)_2$ show a more marked dependence on the nature of the incoming ligand and probably proceed by nucleophilic attack on the cluster. The reason for this change is unclear although $AsPh_3$ complexes have been previously observed to have different behavior.[29]

The k_1 term is dominant in all of the reactions of $Ir_4(CO)_{10}L_2$ which we have investigated, usually accounting for greater than 90% of the total reaction rate. Nucleophilic attack by the entering ligand on the cluster is of less importance in the $Ir_4(CO)_{10}L_2$ clusters than on the $Ir_4(CO)_{12}$ and $Ir_4(CO)_{11}L$ systems. This is evident when one examines the results of the reactions where PBu_3 is the incoming ligand. We have observed that both $Ir_4(CO)_{12}$ and the $Ir_4(CO)_{11}L$ clusters react with PBu_3 at room temperature, presumably by nucleophilic attack.[1,21] The observations that the product of the room-temperature reactions of $Ir_4(CO)_{11}L$ with PBu_3 was exclusively the bis-substituted cluster[1] and that the reaction of $Ir_4(CO)_{10}L_2$ with PBu_3 only occurred at elevated temperatures imply that the addition of a second substituent ligand to the Ir_4 framework makes the cluster less reactive toward PBu_3, i.e., renders the associative mode of substitution a considerably less favorable reaction pathway. A possible cause for this effect may be that the addition of a second noncarbonyl ligand increases the electron density on the Ir_4 framework by an amount significant enough so that nucleophilic attack would not be as favorable. An alternate explanation is that the presence of two ligands renders the cluster less susceptible to ligand attack for steric reasons.

Table VIII. Relative Rates of CO Dissociation from the Tetrairidium Carbonyl Clusters

cluster	relative rate[a]
$Ir_4(CO)_{12}$[b]	1
$Ir_4(CO)_{11}P(OPh)_3$[c]	8
$Ir_4(CO)_{10}(P(OPh)_3)_2$	21
$Ir_4(CO)_{11}AsPh_3$[c]	54
$Ir_4(CO)_{11}PPh_3$[c]	82
$Ir_4(CO)_{11}PBu_3$[c]	170
$Ir_4(CO)_{10}(PBu_3)_2$	540
$Ir_4(CO)_{10}(PPh_3)_2$	1200
$Ir_4(CO)_{10}(AsPh_3)_2$	1200

[a] Rate from $Ir_4(CO)_{12}$ was defined as unity. [b] Reference 21. [c] Reference 7.

We have ascribed the ligand independent term to rate-determining CO dissociation from the clusters followed by rapid reaction with the incoming ligand L′. The effect of the substituent ligand L in $Ir_4(CO)_{10}L_2$ on the rate of CO loss is quite dramatic as shown in Table VIII. The order of enhancement in the rate of CO dissociation from these clusters

$$CO < P(OPh)_3 < PBu_3 < PPh_3 \leq AsPh_3 \qquad (5)$$

is similar to that observed for cis labilization on mononuclear complexes,[10-13] to that seen for the dimers $Mn_2(CO)_9L$,[9] and to the monosubstituted species $Ir_4(CO)_{11}L$. This similarity strongly suggests that similar factors are responsible for the labilization of CO dissociation in mononuclear, dinuclear, and polynuclear systems.

The presence of the second labilizing ligand on tetrairidium causes a further labilization, very similar to mononuclear complexes.[11,12] The second ligand does not labilize CO dissociation as much as the first ligand substituted on the cluster, and neither is the labilization additive. This similarity to mononuclear complexes suggests the *metal cluster complex* can be compared to mononuclear complexes, but that considering each metal center on a cluster to be a mononuclear complex is an oversimplification. The changes in infrared spectra upon substitution of a labilizing ligand for CO further show that the metal cluster functions as a unit. All infrared frequencies decrease (~30 cm^{-1}) upon substitution of one PBu_3 for CO.[30] If the metal centers acted as discreet units, one would anticipate that a few frequencies would be reduced but that the others would be relatively unaffected. Substitution on one metal by a labilizing ligand also affects the Co–CO bond length at the other Co atoms in the plane in $Co_4(CO)_{11}PPh_3$,[31] where the apical Co–CO distance is 0.04 Å longer than the average Co–CO distance for the unsubstituted cobalt atoms in the plane.

In CO dissociative processes from $Ir_4(CO)_{11}L$, we suggested that the CO dissociated from the substituted iridium center.[1] With loss from the substituted center, the incoming ligand would not fill the empty coordination site due to steric crowding. Similar to the $MnRe(CO)_{10}$ system,[32] the unsaturation could be transferred by a bridging (semibridging) carbonyl to a second, unsubstituted iridium center, which could then undergo substitution. The acceleration in the rate of CO dissociation from the clusters upon substitution of a ligand for a CO was proposed to result from a stabilization of the transition state, formed

---

(23) Only in the reaction of $Ir_4(CO)_{10}(P(OPh)_3)_2$ with PBu_3 was the replacement of the substituent ligand observed.

(24) Assignment of the mixed ligand products was based on a comparison to the homoligated analogues. The assigned products and infrared spectra (ν(CO), in cm^{-1}) are as follows. $Ir_4(CO)_9(AsPh_3)_2PPh_3$: 2043 (m), 1982 (s, br), 1780 (m) cm^{-1}. $Ir_4(CO)_8(P(OPh)_3)_2(PPh_3)_2$: 2040 (m), 2015 (sh), 1987 (s, br), 1790 (m, br) cm^{-1}.

(25) Covey, W. D.; Brown, T. L. *Inorg. Chem.* **1973**, *12*, 2820.

(26) Rossetti, R.; Stanghellini, P. L. *J. Coord. Chem.* **1974**, *3*, 217.

(27) Poë, A.; Twigg, M. V. *J. Chem. Soc., Dalton Trans.* **1974**, 1860.

(28) Reaction of $Ir_4(CO)_{10}(PPh_3)_2$ with PPh_3 under an atmosphere of CO caused the rate to slow from $(3.35 \pm 0.03) \times 10^{-4}\ s^{-1}$ to $(1.59 \pm 0.09) \times 10^{-4}\ s^{-1}$, fully consistent with expectations for CO dissociation although not a definitive experiment.

(29) Absi-Halabi, M.; Atwood, J. D.; Forbus, N. P.; Brown, T. L. *J. Am. Chem. Soc.* **1980**, *102*, 6248.

(30) This lowering in infrared stretching frequencies of the carbon monoxide ligands occurs for $Ir_4(CO)_{11}PBu_3$ going to $Ir_4(CO)_{10}(PBu_3)_2$ where no gross structural changes occur.

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

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

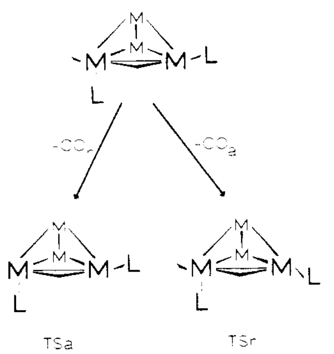

Figure 2. Possible transition states resulting from CO dissociation on $Ir_4(CO)_{10}L_2$. Carbonyl ligands on the unsubstituted iridium centers are omitted for clarity.

by CO loss, by the presence of the substituent ligand, similar to the cis labilization effect in mononuclear carbonyl complexes.[1] We believe that the predominant effects operative in $Ir_4(CO)_{10}L_2$ are also transition-state stabilization by the presence of the ligands. The order observed, however, is slightly different than observed for $Ir_4(CO)_{11}L$. We believe that the electron-deficient transition state is stabilized by a ligand which can relieve the unsaturation and that the energy of the transition states generated by CO dissociation from $Ir_4(CO)_{10}L_2$ would be in the order L = $PBu_3 < PPh_3 < AsPh_3 < P(OPh)_3 <$ CO which is that expected from consideration of the σ-donor strength of the ligands. The order of observed kinetic labilities of CO requires consideration of the M–CO bond strength (ground-state properties). Substituting two weak π-accepting ligands for CO on $Ir_4(CO)_{12}$ increases the π backbonding onto the remaining CO's, thereby increasing the Ir–CO bond strength. The observed order of CO lability from $Ir_4(CO)_{10}L_2$ is a consequence of two competing features, the stabilization of the transition state by σ donors and an increase in the Ir–CO bond strength by weak π acceptors. The order observed parallels the steric size,[33] but we believe that steric interactions play a small role in the acceleration of CO dissociation from these clusters. Steric interactions would involve weakening of the Ir–CO bonds by the presence of these labilizing ligands. No evidence exists for this bond weakening in these complexes; indeed evidence points toward a strengthening of the Ir–CO bonds as substitution occurs.

The site of CO dissociation in these Ir_4 clusters is difficult to predict. If CO dissociation occurs at the substituted iridium centers, there would be two sites for CO loss in the bissubstituted cluster and only one in the monosubstituted species.[34] Statistically one would expect a doubling of the rate for the bissubstituted complexes in comparison to the monosubstituted species. The rate of CO dissociation from any particular $Ir_4(CO)_{10}L_2$ cluster, however, was greater than twice the rate of CO loss from the corresponding $Ir_4(CO)_{11}L$ complex (Table VIII). Since, in the bissubstituted clusters, the two substituent ligands are not in equivalent coordination sites, with one in the axial site on a basal iridium and the other on a second basal iridium in a radial state, the two sites for CO dissociation are not equivalent. Thus, one would not necessarily expect the rate of CO loss from the $Ir_4(CO)_{10}L_2$ clusters to be twice the rate from the monosubstituted complexes. In $Ir_4(CO)_{11}L$ the substituent ligand occupies an axial coordination site on a basal iridium. Upon going to $Ir_4(CO)_{10}L_2$, the additional unique ligand is coordinated to a second basal iridium in a radial site. It has been proposed that the lowest energy conformer for the C_{3v} M_4 cluster is with the substituent ligand in a basal axial coordination site,[35] but steric repulsions force the second ligand on $Ir_4(CO)_{10}L_2$ to be in a basal equatorial position. If CO dissociation occurs at the radially substituted iridium center, the CO loss from the axial position on that center could permit the substituent ligand to drop down from its equatorial position into a semiaxial coordination site in the transition state (TSr),[36] as shown in Figure 2. The dissociation of CO from the axially substituted iridium center would lead to a transition state (TSa) similar to that formed in the loss of CO from $Ir_4(CO)_{11}L$. If the loss of CO from the radially substituted iridium did permit the substituent ligand to migrate toward the more energetically favorable axial coordination site, one might expect the resulting transition state, TSr, to be lower in energy than the TSa transition state, which results from CO loss at the axially substituted center. As a result of this transition-state labilization, the rate of CO dissociation from the radially substituted iridium would be greater than the rate from the axially substituted center. Hence, one would expect the rate of CO loss from a bissubstituted cluster to be greater than twice the rate of CO loss from the corresponding monosubstituted complex.

We have shown that the rate of CO dissociation from $Ir_4(CO)_{10}L_2$ depends on the substituent ligand L and have offered an explanation of the ligand effects in terms of a labilization of the CO's on the substituted iridium centers. We suggest that this labilization (very similar to cis labilization in mononuclear complexes) is also operative in the reactions of dinuclear and other polynuclear metal carbonyl complexes.

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

Registry No. $Ir_4(CO)_{10}(PPh_3)_2$, 59532-83-1; $Ir_4(CO)_{10}(P(OPh)_3)_2$, 59532-57-9; $Ir_4(CO)_{10}(AsPh_3)_2$, 78128-48-0; $Ir_4(CO)_{10}(PBu_3)_2$, 40919-70-8.

---

(33) Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2956.

(34) Each substituted iridium center has one terminal carbonyl.

(35) Johnson, B. F. G.; Benfield, R. E. *J. Chem. Soc., Dalton Trans.* **1978**, 1554.

(36) TSr means the transition state resulting from CO loss at the radially substituted iridium center.