Ligand-Substitution Processes in Tetranuclear Carbonyl Clusters. 5. A Kinetic and Infrared Investigation of ^{13}CO Incorporation into $Co_4(CO)_9(\mu\text{-}CO)_3$ and Its Monosubstituted Derivatives

Donald J. Darensbourg,* Bradley Scott Peterson, and Raymond E. Schmidt, Jr.

Department of Chemistry, Tulane University, New Orleans, Louisiana 70118

Received July 22, 1981

A kinetic investigation of carbon monoxide exchange processes in the parent tetranuclear cobalt carbonyl cluster, $Co_4(CO)_{12}$, and its monosubstituted analogues $Co_4(CO)_{11}L$ (where L = phosphorus donor ligand) is reported. The $Co_4(CO)_{11}L$ derivatives were concluded to be isostructural on the basis of ν(CO) infrared and ^{13}C NMR spectroscopy aided by X-ray structural analysis of a representative species. The carbonyl-exchange reactions were monitored by infrared spectroscopy in the ν(CO) bridging region employing ^{13}C-labeled carbon monoxide, which has allowed as well for a detailed vibrational analysis of the ν(CO) stretching vibrations for the bridging carbonyl ligands. The activation parameters for CO dissociation in $Co_4(CO)_{12}$ and $Co_4(CO)_{11}P(OEt)_3$ were determined to be $\Delta H^* = 24.9 \pm 1.9$ and 27.5 ± 3.3 kcal/mol, and $\Delta S^* = 2.9 \pm 5.9$ and 11.0 ± 10.2 eu, respectively. Although there was no significant effect on the rate parameters for dissociative CO substitution in the tetranuclear cluster upon replacement of CO by a ligand of comparable spatial requirements (e.g., $P(OMe)_3$ or $P(OEt)_3$), dissociative CO loss was enhanced when the cluster substrate contained sterically more demanding ligands. A summary of comparative kinetic results in the stepwise phosphine or phosphite substitutional processes in $Co_4(CO)_{12}$ and $Ir_4(CO)_{12}$ species is included.

Introduction

Dissociation of a neutral ligand from low-valent metal centers, thus providing a vacancy in the coordination sphere of the metal, pervades the mechanistic literature as a principal occurrence prior to substrate binding in catalytic processes involving transition-metal complexes.[1] Kinetic investigations of representative metal complexes furnish vital information pertinent to an understanding of the influences of the various steric and electronic factors which govern ligand-substitution processes. To date much is known concerning these substitution processes in low-valent mononuclear metal carbonyl derivatives, including the reactivity of and ligand mobility in the unsaturated intermediates afforded en route to product formation.[2]

On the other hand our knowledge of the similar intricacies pertaining to ligand-substitution processes in metal clusters, the homogeneous role models for metal surfaces in both chemisorption and catalytic processes,[3-5] is just beginning to emerge. Indeed it would be fair to characterize detailed kinetic investigation in metal-cluster chemistry as a rather untested area of chemical research. These comments are not intended to detract from the many fine contributions which are presently in the chemical literature,[6-10] but their purpose is to emphasize the importance of continuing vigorous efforts in these directions.

Our attentions have been centered on displacement reactions involving dissociative loss of carbon monoxide and phosphorus donor ligands in tetranuclear metal carbonyl cluster derivatives of the group 8 metals, Co, Rh, and Ir.[7-10] Special emphasis has been placed on discernment of steric effects attributable to prior substitution by phosphorus donor ligands on subsequent ligand-substitution processes. Herein we report the kinetic and activation parameters for ^{13}CO exchange reactions with the parent dodecacarbonyl, $Co_4(CO)_9(\mu\text{-}CO)_3$ (eq 1).[8] These observations are employed

$$Co_4(CO)_{12} + n^{13}CO \rightleftharpoons Co_4(CO)_{12-n}(^{13}CO)_n + n^{12}CO \quad (1)$$

as a basis for comparison with analogous data in monosubstituted derivatives, $Co_4(CO)_8(\mu\text{-}CO)_3L$, where L is a phosphine or phosphite ligand of varying steric and electronic character (eq 2). This methodology (i.e., measurement of ^{13}CO exchange rates) minimizes the incoming ligand's associative term which often prevails in the rate expression for ligand-substitution processes where L is the entering ligand.[6a,d,g] Hence, more accurate evaluation of the dissociative CO rate parameters is achievable.

$$Co_4(CO)_{11}L + n^{13}CO \rightleftharpoons Co_4(CO)_{11-n}(^{13}CO)_nL + n^{12}CO \quad (2)$$

(1) Henrici-Olivé, G.; Olivé, S. "Coordination and Catalysis"; Verlag Chemie: New York, 1977.

(2) A short listing of some of the published work in this area includes the following: (a) Angelici, R. J. *Organomet. Chem. Rev.* **1968**, *3*, 173. (b) Werner, H. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 930. (c) Brown, D. A. *Inorg. Chim. Acta Rev.* **1967**, *1*, 35. (d) Hyde, C. L.; Darensbourg, D. J. *Inorg. Chem.* **1973**, *12*, 1286. (e) Dobson, G. R. *Acc. Chem. Res.* **1976**, *9*, 300. (f) Lichtenberger, D. L.; Brown, T. L. *J. Am. Chem. Soc.* **1978**, *100*, 366, and other members of this series of papers. (g) Kelly, J. M.; Hermann, H.; Koerner, von Gustorf, E. *J. Chem. Soc., Chem. Commun.* **1973**, 105. (h) Darensbourg, D. J.; Graves, A. H. *Inorg. Chem.* **1979**, *18*, 1257. (i) Dobson, G. R. *Inorg. Chem.* **1980**, *19*, 1413.

(3) Muetterties, E. L. *Bull. Soc. Chim. Belg.* **1975**, *84*, 959.

(4) Muetterties, E. L. *Bull. Soc. Chim. Belg.* **1976**, *85*, 451.

(5) Muetterties, E. L. *Science (Washington, D.C.)* **1977**, *196*, 839.

(6) Some of the published reports dealing with this subject from other laboratories include the following: (a) Karel, K. J.; Norton, J. R. *J. Am. Chem. Soc.* **1974**, *96*, 6812. (b) Malik, S. K.; Poë, A. *Inorg. Chem.* **1978**, *17*, 1484. (c) Bor, G.; Dietler, U. K.; Pino, P.; Poë, A. *J. Organomet. Chem.* **1978**, *154*, 301. (d) Sonnenberger, D.; Atwood, J. D. *Inorg. Chem.* **1981**, *20*, 3243. (e) Candlin, J. P.; Shortland, A. C. *J. Organomet. Chem.* **1969**, *16*, 289. (f) Malik, S. K.; Poë, A. *Inorg. Chem.* **1979**, *18*, 1241. (g) Stuntz, G. F.; Shapley, J. R. *J. Organomet. Chem.* **1981**, *213*, 389.

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

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

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

(10) Darensbourg, D. J.; Baldwin-Zuschke, B. J. *Inorg. Chem.*, in press.

0276-7333/82/2301-0306$01.25/0 © 1982 American Chemical Society

Experimental Section

$Co_4(CO)_{12}$ and all phosphorus donor ligands were obtained from Strem Chemicals, Inc., and were used without further purification. Hexane and heptane were distilled over sodium under a nitrogen atmosphere. Carbon monoxide (93.3 atom % ^{13}CO) was obtained from Prochem, B.O.C. Ltd., London.

Preparation of $Co_4(CO)_{11}L$ Compounds. The monosubstituted cobalt cluster carbonyls $Co_4(CO)_{11}L$ (L = $(MeO)_3P$, $(EtO)_3P$, $(o\text{-}CH_3C_6H_4O)_3P$, PEt_3, and $AsPh_3$) were all prepared in a completely analogous manner.[11] Reactions were carried out with Schlenkware under an inert atmosphere.

An equimolar mixture (2 mmol) of $Co_4(CO)_{12}$ and ligand was stirred at ambient temperature in 75 mL of hexane for 4–5 h, at which point the solution was reduced to approximately 3–4 mL. The sample was then chromatographed by using flash chromatography to remove any unreacted $Co_4(CO)_{12}$ utilizing nitrogen pressure.[12] This procedure drastically reduces the amount of time the sample spends on the column, as the entire separation could be accomplished in approximately 10 min. The column (40 cm × 20 mm) was packed with silica gel (60–200 mesh) by using a hexane slurry. Eluting the sample with hexane removed the unreacted $Co_4(CO)_{12}$, and the desired product was obtained by eluting with a 20% (v/v) toluene–hexane solvent mixture.

Preparation of ^{13}CO-Enriched $Co_4(CO)_{11}L$ Compounds. Samples of $Co_4(CO)_{11-n}(^{13}CO)_nL$ for ^{13}C NMR investigations were synthesized and purified as described above from enriched $Co_4(CO)_{12}$ (prepared from $Co_4(CO)_{12}$ under an atmosphere of ^{13}CO at 40 °C for 24 h). Alternatively, ^{13}CO incorporation was achieved by direct CO exchange with $Co_4(CO)_{11}L$ at 40 °C for ~1 day, followed by purification by column chromatography. This latter procedure is not applicable for the ^{13}CO enrichment of $Co_4(CO)_{11}L$ derivatives where L is a labile ligand (e.g., L = PPh_3 or $AsPh_3$).

Kinetic Measurements of ^{13}CO-Exchange Reactions. A 100-ml Schlenk flask, containing the preweighed sample, was fitted with a rubber septum secured by copper wire and was evacuated under vacuum. The flask was then equilibrated in a constant-temperature bath, and an atmosphere (760 torr) of ^{13}CO (93.3 atom % ^{13}C) was introduced into it. Heptane (15 mL, distilled over sodium) was then syringed into the flask. The reaction flask was agitated to effect sample dissolution (~15 s), and the timer was started immediately thereafter. Samples (~0.7 mL) were withdrawn at noted time intervals with a hypodermic syringe for infrared analysis.

Infrared Measurements and Vibrational Analysis. The infrared spectra were recorded in 1.0-mm matched NaCl sealed cells on a Perkin-Elmer 283B spectrophotometer equipped with an Infrared Data Station. Spectra recorded for the ^{13}CO-exchange reactions were the average of four (added repetitively) scanned spectra employing the PECDS software package provided by Perkin-Elmer. The spectra were calibrated against a water-vapor spectrum below 2000 cm^{-1} and against a CO spectrum above 2000 cm^{-1}.

Initial CO stretching force constants for the bridging CO region in the $Co_4(CO)_{11}L$ derivatives were obtained by altering the parameters computed for the parent, $Co_4(CO)_{12}$, species.[8] That is, both F_{CO} values in $Co_4(CO)_{11}L$ were slightly lowered relative to that in $Co_4(CO)_{12}$, with the F_{CO} parameter corresponding to the two CO groups bridging the cobalt atom bearing the unique substituent being lowered to the greater extent. The trial force constants were refined by use of the ^{13}CO frequency data and an iterative computer program that adjusts a set of force constants common to a group of isotopically substituted molecules to give simultaneously a least-squares fit between the observed and calculated frequencies for all the molecules. The trial force constants were refined to reproduce the observed ^{12}CO and ^{13}CO vibrations to within an average of ≤0.8 cm^{-1}.

^{13}C NMR Measurements. The ^{13}C NMR spectra were recorded on a JEOL FX60 operated at 15.03 MHz with an internal deuterium lock. Samples were run in either $CDCl_3$ or CD_2Cl_2 solvents in 10-mm tubes. Spectra were determined by employing a sweep width of 4000 Hz (16K data block) with an acquisition time of 2 s, a pulse repetition rate of 5 s, and a flip angle of 30°.

(11) This is a modification of that previously reported: Cetini, G.; Gambino, O.; Rossetti, R.; Stanghellini, P. L. *Inorg. Chem.* **1968**, *7*, 609.
(12) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

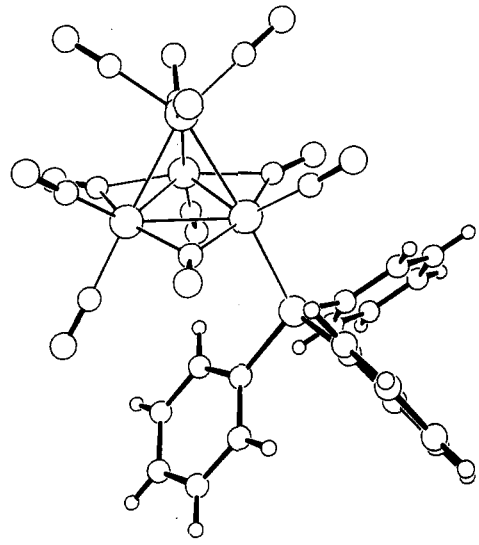

Figure 1. Perspective ORTEP drawing of the $Co_4(CO)_{11}[PPh_3]$ molecule (taken from ref 9).

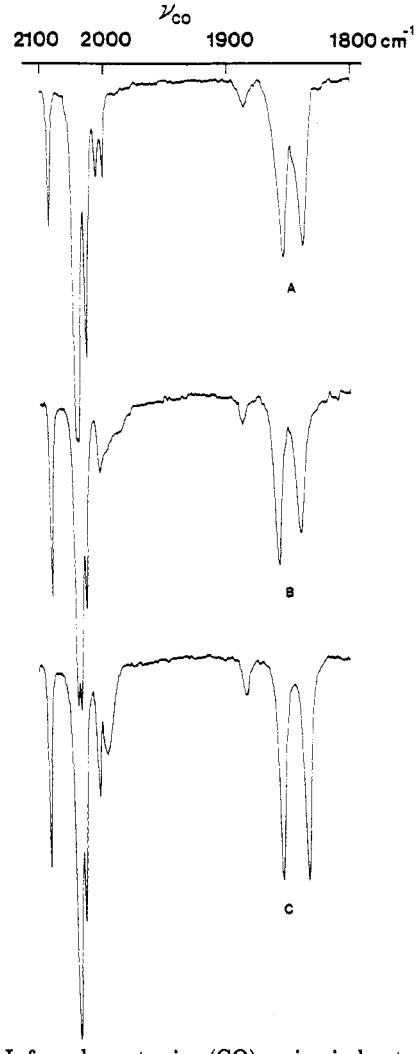

Figure 2. Infrared spectra in ν(CO) region in heptane solution. (A) $Co_4(CO)_{11}P(OEt)_3$; (B) $Co_4(CO)_{11}PPh_3$; (C) $Co_4(CO)_{11}PEt_3$.

Results and Discussion

The salient features of the solid-state structure of $Co_4(CO)_{11}PPh_3$ are reiterated in Figure 1, where the triphenylphosphine ligand is seen to occupy an axial coordination site in the tetranuclear cluster.[9] The solution

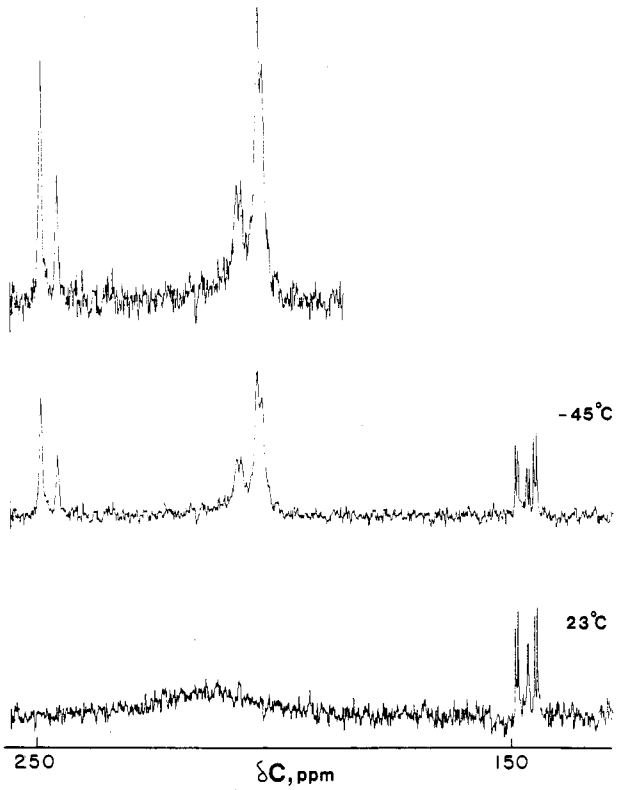

Figure 3. ^{13}C FT NMR spectrum of $Co_4(CO)_{11}PPh_3$ in $CDCl_3$ at −45 °C and ambient temperature.

Table I. ^{13}C Chemical Shifts (Ppm) in $CO_4(CO)_{11}L$

	L			
	PPh_3 [a]	PEt_3 [b]	$P(OMe)_3$ [c]	CO [d]
bridging	249.8	249.2	248.2	
	245.8	245.7	245.6	243.1
equatorial	202.1	201.3	198.0	
	201.0	199.7	197.2	
axial	197.1	196.7	196.1	195.9
apical	195.9		193.7	191.9

[a] Spectrum determined in $CDCl_3$ at −45 °C (see Figure 3 3). [b] Spectrum determined in CD_2Cl_2 at −69 °C. [c] Taken from ref 13. [d] Taken from: Evans, J.; Johnson, B. F. G.; Lewis, J.; Matheson, T. W. *J. Am. Chem. Soc.* 1975, *97*, 1245.

structure of this derivative, as evinced by ν(CO) infrared and ^{13}C NMR spectroscopy, is consistent with this formulation (see Figure 2B and 3). Brown and co-workers[13] have reported the low-temperature ^{13}C NMR spectrum for $Co_4(CO)_{11}P(OMe)_3$ which displays a very close resemblance to that noted here for the PPh_3 analogue (Table I). The most distinguishing feature in both these spectra lies in the bridging CO region (most downfield peaks) where two carbon resonances in relative intensity ratio 1:2 are observed, with the two bridging CO groups bonded to the basal cobalt atom bearing the phosphorus ligand being more downfield as anticipated.[14] Assignment of the terminal carbon resonances are on a more tenuous basis. Quadrupole broadening by the ^{59}Co nucleus prohibits the observation of ^{13}C–P coupling in the ^{13}C NMR spectra of these derivatives. If we assume the generally observed trend of an upfield shift of carbonyl carbon peaks with decreasing metal–carbon interaction, as revealed by the M–C bond distances, the peak assignments are as listed in Table I. This designation is congruous with that made by Stuntz and Shapley[15] for $Ir_4(CO)_{11}PPh_2Me$.

Table II. Infrared Spectra in the ν(CO) Region of $Co_4(CO)_{11}L$ Derivatives[a]

L	ν(CO), cm^{-1}
PEt_3	2086, 2040, 2030, 2006, 1996, 1885, 1856, 1836
PPh_3	2084, 2044, 2039, 2029, 2006, 1993, 1881, 1854, 1835
$AsPh_3$	2085, 2046, 2041, 2031, 2007, 1995, 1881, 1853, 1834
$P(OMe)_3$	2091, 2051, 2046, 2032, 2017, 2003, 1889, 1858, 1843
$P(OEt)_3$	2089, 2048, 2044, 2030, 2013, 2001, 1887, 1857, 1841
$P(Otolyl)_3$	2090, 2049, 2042, 2033 2011, 2002, 1885, 1856, 1844

[a] Measured in heptane solution, accurate to ±2 cm^{-1}.

Table III. Rate Data for CO-Exchange Processes in $Co_4(CO)_{11}L$ Species[a]

L	temp, °C	$k \times 10^4$, s^{-1} [b]
CO	40.0	3.27 ± 0.20
	43.0	5.10 ± 0.26
	45.0	6.10 ± 0.15
	45.0	5.53 ± 0.08
	52.0	14.5 ± 0.35
	56.0	24.5 ± 3.8
	56.0	23.5 ± 3.0
$P(OEt)_3$	35.0	1.50 ± 0.14
	37.5	2.05 ± 0.14
	40.0	3.37 ± 0.13
	45.0	6.79 ± 0.41
	50.0	12.1 ± 1.6
PEt_3	35.0	8.87 ± 0.61
	40.0	15.6 ± 0.62

[a] Determined in heptane solution under an atmosphere of ^{13}CO. [b] Error limits for rate constants represent 95% confidence limits.

Table II contains the ν(CO) spectra for a series of $Co_4(CO)_{11}L$ derivatives where L is varied over a wide range of donor/acceptor ratios,[16] and Figure 2 further illustrates the great deal of conformity evident in these spectra. Hence, the spectral data strongly suggest that all the $Co_4(CO)_{11}L$ species are isostructural, with the lowest energy isomer being that in which the unique ligand (L) resides at an axial location. Therefore, variations in the reactivity of these $Co_4(CO)_{11}L$ 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.

We have previously reported a rough estimate for the rate of CO dissociation in the parent $Co_4(CO)_{12}$ species as determined by ^{13}CO incorporation at ambient temperature.[8] It is of utmost importance to more accurately quantify the rate parameters associated with dissociative CO loss in the dodecacarbonyl derivative in order to make meaningful comparisons with the corresponding values obtained as a function of substitution with electron-donor ligands at the metal centers. Table III lists the rate constants for ^{13}CO exchange with the substrate $Co_4(CO)_{12}$ as a function of temperature. These rate constants were measured by employing the ν(CO) vibrational modes in the bridging CO region as described in our previous publication[8] and were calculated by assuming three dissociative CO ligands in $Co_4(CO)_{12}$.[17] This procedure is based on

(13) Cohen, M. A.; Kidd, D. R.; Brown, T. L. *J. Am. Chem. Soc.* 1975, *97*, 4408.
(14) Todd, L. J.; Wilkinson, J. R. *J. Organomet. Chem.* 1974, *77*, 1.
(15) Stuntz, G. F.; Shapley, J. R. *J. Am. Chem. Soc.* 1977, *99*, 607.
(16) Bodner, G. M.; May, M. P.; McKinney, L. E. *Inorg. Chem.* 1980, *19*, 1951.

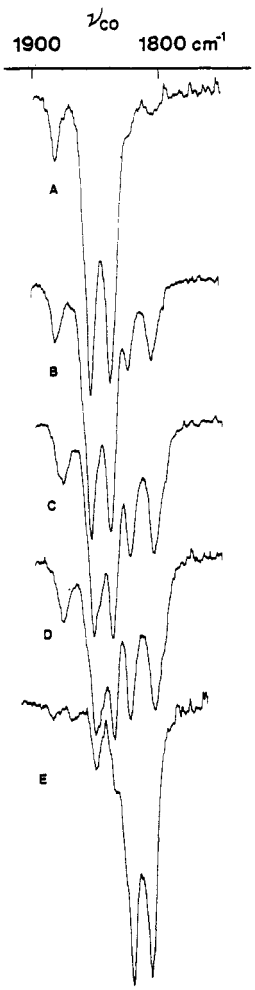

Figure 4. Time-dependent infrared spectra in the ν(CO) bridging region for the exchange reaction between $Co_4(CO)_{11}P(OEt)_3$ and ^{13}CO at 40 °C. (A) Spectrum after 5 min; (B) Spectrum after 52 min; (C) Spectrum after 119 min; (D) Spectrum after 185 min; (E) Spectrum at "infinity" reading.

the fact that intramolecular CO rearrangement is fast relative to the CO dissociation process. No observable variations in the rate of ^{13}C incorporation were noted for CO pressures ranging from 380 to 1140 torr.

Reaction 3 has been demonstrated to be strongly dependent on the nature of the incoming ligand (L), with measurable rates by conventional techniques being possible only when L is isotopically labeled carbon monoxide.[8]

$$Co_4(CO)_{12} + L \rightarrow Co_4(CO)_{11}L + CO \qquad (3)$$

Similar ^{13}CO exchange rate data were determined in the monosubstituted $Co_4(CO)_{11}L$ species. This procedure of obtaining rate data for CO dissociation eliminates the incoming ligand's associative term which is often dominant in the rate expression for ligand-substitution processes.

The infrared traces in the ν(CO) bridging region observed during the incorporation of ^{13}CO into $Co_4(CO)_{11}P(OEt)_3$ are depicted in Figure 4. For the $Co_4(CO)_{12}$ complex it has previously been demonstrated that the interaction force constants between terminal and bridging CO groups may be considered as being zero.[9,18] By using this assumption in the $Co_4(CO)_{11}L$ derivatives, it should be possible to analyze their spectra in the ν(CO) bridging region (Figure 4) in terms of progressive formation of *only* five ^{13}CO-substituted cluster fragments in addition to the starting all-^{12}CO species (see Figure 5). This is indeed found to be the case, for the spectral band assignments compiled in Tables IV and V were computed by employing a restricted CO force field involving only the bridging CO ligands. Table VI lists comparative CO stretching force constants for the bridging CO groups in $Co_4(CO)_{11}L$ species where L varies in donor/acceptor ratio from that of PEt_3

(17) Because of the accuracy with which these parameters are measured, no correction for the fact that 93.3 atom % ^{13}C-labeled carbon monoxide was employed in these investigations.

(18) Bor, G.; Sbrignadello, G.; Noack, K. *Helv. Chim. Acta* **1975**, *58*, 815.

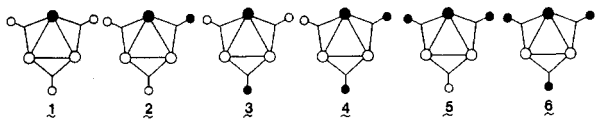

Figure 5. Possible isotopic species involving the bridging CO ligands in $Co_4(CO)_{11}L$.

Table IV. Calculated and Observed CO Stretching Frequencies in the Bridging Region of $Co_4(CO)_{11}P(OEt)_3$ [a]

molecule	ν(CO), cm^{-1} obsd [b]	calcd [c]	symmetry
all-^{12}CO, 1	1879.4	1879.3	A′
	1849.7	1849.0	A′
	1834.3	1835.0	A″
mono-^{13}CO, 2		1878.8	A
	1843.0	1843.3	A
	1801.3	1800.2	A
mono-^{13}CO, 3		1853.1	A′
	1833.4	1833.4	A′
		1835.0	A″
di-^{13}CO, 4		1846.9	A
	1833.4	1833.6	A
		1800.0	A
di-^{13}CO, 5		1878.3	A′
	1808.2	1808.8	A′
	1798.8	1794.1	A″
all-^{13}CO, 6	1838.3	1837.4	A′
	1807.4	1807.9	A′
	1794.6	1794.1	A″

[a] Spectra were recorded in heptane solution. [b] The observed frequencies are accurate to ±1.0 cm^{-1}. [c] The CO stretching force field arrived at in this computation is summarized in Table VI. Average error in calculated frequencies = 0.5 cm^{-1} or 0.029%.

Table V. Calculated and Observed CO Stretching Frequencies in the Bridging Region of $Co_4(CO)_{11}PEt_3$ [a]

molecule	ν(CO), cm^{-1} obsd [b]	calcd [c]	symmetry
all-^{12}CO, 1	1876.6	1872.8	A′
	1848.4	1848.6	A′
	1827.2	1827.6	A″
mono-^{13}CO, 2		1868.8	A
	1841.8	1842.7	A
	1796.2	1796.5	A
mono-^{13}CO, 3	1862.8	1861.8	A′
	1819.6	1818.1	A′
		1827.6	A″
di-^{13}CO, 4		1851.7	A
	1819.6	1819.0	A
	1796.2	1795.8	A
di-^{13}CO, 5		1865.8	A′
	1814.1	1814.2	A′
	1787.4	1786.9	A″
all-^{13}CO, 6		1831.1	A′
	1806.9	1807.4	A′
	1787.4	1786.9	A″

[a] Spectra were recorded in heptane solution. [b] The observed frequencies are accurate to ±1.0 cm^{-1}. [c] The CO stretching force field arrived at in this computation is summarized in Table VI. Average error in calculated frequencies = 0.8 cm^{-1} or 0.044%.

Table VI. Comparative Bridging CO Stretching Force Constants in $Co_4(CO)_{11}L$ Derivatives

L	force constant, mdyn/Å[a] F_{CO} (1)	F_{CO} (2)	$F_{CO,CO}$ (1)	$F_{CO,CO}$ (2)
CO	14.23_2		0.17_4	
$P(OEt)_3$	13.71_1	14.23_6	0.07_1	0.11_6
PEt_3	13.71_5	14.01_4	0.12_6	0.22_9

[a] F_{CO} (1) (bridging to Co atom bearing L) and $F_{CO,CO}$ (1) (both interacting CO groups bound to Co atom bearing L).

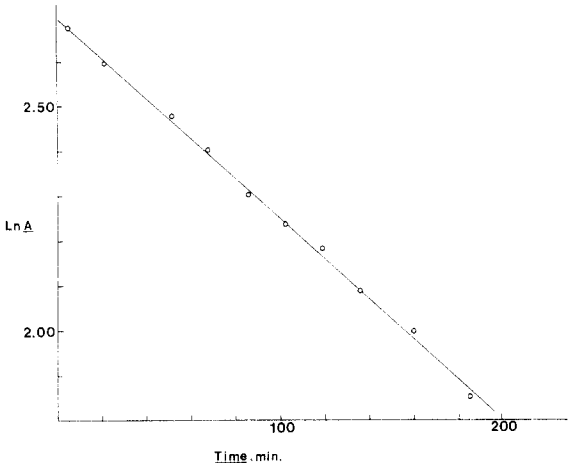

Figure 6. First-order rate plot for the disappearance of substrate for the reaction of $Co_4(CO)_{11}P(OEt)_3$ with ^{13}CO in heptane at 40 °C. $k_{obsd} = 7.49 \times 10^{-5}\ s^{-1}$, which when multiplied by 9 and divided by 2 affords $k = 3.37 \times 10^{-4}\ s^{-1}$. Because reactions were monitored in the ν(CO) bridging region, and hence incorporation of ^{13}CO at the eight terminal CO positions goes unnoticed, the k_{obsd} must be multiplied by the factor 9, i.e., there are nine positions which among the single incoming ^{13}CO ligand may distribute itself. Division of k_{obsd} by the factor 2 arises from the assumption that there is selective dissociation of one of the two axial CO groups.

to CO. As is apparent in Table VI these vibrational parameters indicate some increase in electron density, which is passed on to the CO groups, at the metal atom bearing the phosphine substituent. On the other hand, the carbonyl ligand bridging unsubstituted cobalt atoms appears to be unaffected. A similar conclusion can be reached from ^{13}C NMR data, where the CO group bridging unsubstituted cobalt atoms has a carbon resonance resembling that of the bridging CO groups in $Co_4(CO)_{12}$.[13]

Table III presents the kinetic parameters for CO-exchange processes in the monosubstituted $Co_4(CO)_{11}L$ derivatives, where L = $P(OEt)_3$ and PEt_3. The rate constants were calculated by assuming two dissociative CO ligands in $Co_4(CO)_{11}L$. Figures 6 and 7 contain representative plots of the data employed in computing rate constants and activation parameters for dissociative CO loss in these cobalt cluster species. Comparative rate constants and activation parameters for the system investigated herein, as well as those previously reported,[7,8] are collected in Table VII. Attempts at measuring the rate of ^{13}CO incorporation into the PPh_3 and $AsPh_3$ analogues were hampered by the more facile reaction involving donor-ligand replacement (eq 4), where the $AsPh_3$ ligand was observed to dissociate more rapidly than PPh_3.

$$Co_4(CO)_{11}L + {}^{13}CO \rightarrow Co_4(CO)_{11}(^{13}CO) + L \quad (4)$$

At high pressures of carbon monoxide, declusterification of $Co_4(CO)_{12}$ to afford $Co_2(CO)_8$ is proposed to proceed via a mechanism involving $Co_4(CO)_{13}$, which is formed by the breaking of one Co–Co bond with concomitant formation

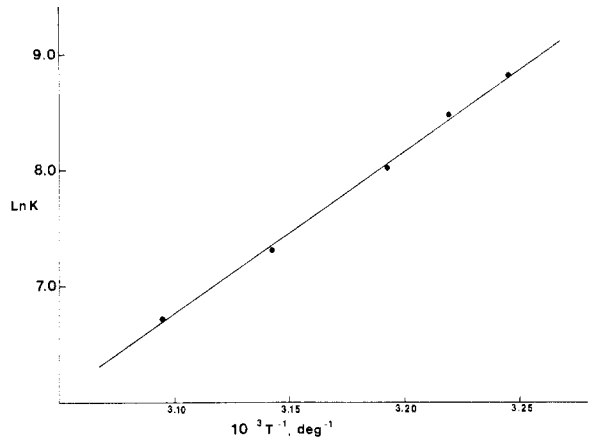

Figure 7. Arrhenius plot of $-\ln k$ vs. $1/T$ for the CO exchange reaction of $Co_4(CO)_{11}P(OEt)_3$ with ^{13}CO in heptane.

Table VII. Comparative Rate and Activation Parameters for Carbon Monoxide Displacement in $Co_4(CO)_{11}L$

L	cone angle,[a] deg	10^4k, s^{-1} [b]	ΔH^* [c]	ΔS^* [c]
$P(OMe)_3$ [d]	107	2.03 (1.00)	26.8 ± 1.0	8.2 ± 3.5
CO	~95	3.27 (1.61)	24.9 ± 1.9	2.9 ± 5.9
$P(OEt)_3$	109	3.37 (1.66)	27.5 ± 3.3	11.0 ± 10.2
PEt_3	132	15.6 (7.68)	e	e
$P(OMe)_3$ [f]	107	4.77 (2.35)	27.1 ± 1.1	10.7 ± 3.7

[a] Taken from: Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313. [b] Relative rate data are listed in parentheses. Reactions were carried out at 40.0 °C. [c] Error limits for activation parameters represent 95% confidence limits. [d] Taken from ref 8 where the incoming ligand employed was PPh_3. [e] These parameters were not measured in this instance. [f] Taken from ref 8 for CO displacement in $Co_4(CO)_{10}[P(OMe)_3]_2$ where $P(OMe)_3$ was the incoming ligand employed.

of a Co–CO bond and a repositioning of one bridging CO ligand.[6c] In this connection it is noteworthy that the kinetic parameters, coupled with the absence of dimer production under the mild temperature and CO pressure of this study, strongly argue against the formation of an intermediate or transition state of this type for these CO-exchange reactions. That is, CO exchange is a lower energy process than declusterification (as shown, e.g., in eq 5 where $rate_1 > rate_2$).

$$Co_4(CO)_{12} + n^{13}CO \underset{}{\overset{rate_1}{\rightleftharpoons}} Co_4(CO)_{12-n}(^{13}CO)_n + n^{12}CO \xrightarrow{rate_2} Co_2(CO)_8 \quad (5)$$

A slightly revised relative order of reactivity for dissociative CO substitutional processes in $Co_4(CO)_{12}$ with progressive substitution of $P(OMe)_3$ is provided in Table VII and eq 6. These data dramatically illustrate the

$$Co_4(CO)_{12} \xrightarrow{1.00} Co_4(CO)_{11}P(OMe)_3 \xrightarrow{0.62} Co_4(CO)_{10}[P(OMe)_3]_2 \xrightarrow{1.46} Co_4(CO)_9[P(OMe)_3]_3 \quad (6)$$

absence of an 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. However, there is a small, yet significant, increase in the rate of dissociative CO loss as L is altered in the $Co_4(CO)_{11}L$ derivatives, increasing in the order $P(OMe)_3 < P(OEt)_3 < PEt_3$. Unfortunately, our efforts to extend these investigations to sterically more demanding ligands, e.g., PPh_3, was prohibited by the ready loss of the ligand L. More extensive

studies of the rate of dissociative CO loss in Ir_4 cluster species as a function of the phosphorus donor ligand indicate the spatial requirements of these ligands to be a major consideration in determining these rates.[10,19] Similar, more pronounced, arguments should apply in the Co_4 systems reported upon herein and are indeed consistent with the rate constant vs. cone-angle data summarized in Table VII.[20]

If steric acceleration is a governing factor in the enhancement of the rate of CO loss as the size of the phosphorus donor ligand increases in these $Co_4(CO)_{11}L$ derivatives, then the coordination site of the CO group which is dissociated must be in rather close proximity to the phosphorus ligand. Crystallographically defined models reveal this to be either the equatorial CO group on the phosphorus-bearing cobalt atom or one of the two axial CO groups.[21] X-ray structural results show these latter CO groups to be slightly more weakly bound than the equatorial CO ligand of the Co–P moiety,[9] hence making them more likely candidates for dissociation. Nevertheless, CO loss at the metal center which bears the phosphorus donor ligand with a concomitant facile CO migration leading to unsaturation at an adjacent metal site cannot be ruled out.[22-24] Unfortunately, because of intramolecular ligand rearrangements in the substrate molecule, which occur on a time scale faster than dissociative ligand loss, definitive answers to questions of this type will go unresolved.

In light of the prominence of steric effects in substitutional processes in metal carbonyl clusters, a consideration of importance in any general discussion of progressive rate enhancement for dissociative CO loss with ligand substitution must take account of structural differences. For example, in the cobalt complex containing the small trimethyl phosphite ligands, $Co_4(CO)_{10}[P(OMe)_3]_2$, the two phosphite ligands occupy axial sites[9] whereas in $Ir_4(CO)_{10}[PPh_3]_2$ and $Rh_4(CO)_{10}[PPh_3]_2$ the phosphine ligands are found in both axial and equatorial positions,[25,26] apparently as a result of spatial requirements.

The enormous rate acceleration for CO dissociation observed during the stepwise phosphine substitution of $Ir_4(CO)_{12}$ to give $Ir_4(CO)_9[PPh_3]_3$ is often regarded as being supportive evidence that electronic interactions can be transmitted from neighboring metal atoms to the active catalytic center in a cluster. Such a conclusion is arrived at by neglecting steric factors. Indeed, our work,[19,27] as well as that of others,[28] demonstrates that this observation is not a general one for a wide range of phosphorus donor ligands. It is our contention that a sizable contribution to the rate acceleration for stepwise substitution in the Ir_4 system arises from sterically induced dissociation.

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

Registry No. $Co_4(CO)_{12}$, 17786-31-1; $Co_4(CO)_{11}(PEt_3)$, 79664-00-9; $Co_4(CO)_{11}(PPh_3)$, 12336-57-1; $Co_4(CO)_{11}(AsPh_3)$, 12336-56-0; $Co_4(CO)_{11}(P(OMe)3)$, 56277-17-9; $Co_4(CO)_{11}(P(OEt)_3)$, 79664-01-0; $Co_4(CO)_{11}(P(o\text{-tolyl})_3)$, 79664-02-1.

(19) Darensbourg D. J.; Baldwin-Zusche, B. J. "Abstracts of Papers", 181st National Meeting of the American Chemical Society, Atlanta, GA, March 1981; American Chemical Society: Washington, D.C., 1981; INOR 190.

(20) As evident in Table VII the rates of CO dissociation in the closely related $Co_4(CO)_{11}L$ derivatives, where L = $P(OMe)_3$ and $P(OEt)_3$, are quite similar. An important difference, however, is that the incoming ligand was PPh_3 for the $Co_4(CO)_{11}P(OMe)_3$ rate study and ^{13}CO for the corresponding $Co_4(CO)_{11}P(OEt)_3$ investigation. These observations would support the conclusion that the measured rate constants are dissociative in character. It also argues strongly against a mechanism involving phosphorus ligand dissociation (eq 4) followed by rapid intramolecular rearrangement of the incorporated ^{13}CO and replacement of CO by the phosphorus ligand via the reverse of eq 4.

(21) This is the assumption employed in the derivation of the specific rate constants as computed from k_{obsd} (see Table III).

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

(23) Darensbourg, M. Y.; Atwood, J. L.; Burch, R. R., Jr.; Hunter, W. E.; Walker, N. *J. Am. Chem. Soc.* **1979**, *101*, 2631.

(24) Darensbourg, D. J.; Burch, R. R., Jr.; Darensbourg, M. Y. *Inorg. Chem.* **1978**, *17*, 2677.

(25) Albano, V.; Bellon, P.; Scatturin, V. *Chem. Commun.* **1967**, 730.

(26) Heaton, B. T.; Longhetti, L.; Mingos, D. M. P.; Briant, C. E.; Minshall, P. C.; Theobald, B. R. C.; Garlaschelli, L.; Sartorelli, U. *J. Organomet. Chem.* **1981**, *213*, 333.

(27) Darensbourg, D. J.; Baldwin-Zuschke, B. J., Tenth International Conference on Organometallic Chemistry, Toronto, Canada, August 1981, p 25.

(28) Sonnenberger, D. C.; Atwood, J. D., Tenth International Conference on Organometallic Chemistry, Toronto, Canada, August 1981, p 24.