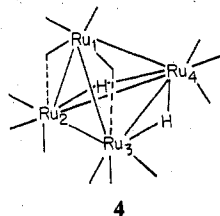the other hand, Os certainly possesses a greater amount of electron density than does Ru, and this could be the important factor in determining the activation energies.

An interesting comparison can be made to the homonuclear cluster $H_2Ru_4(CO)_{13}$, **4**, which is isostructural with the mix-


4

ed-metal clusters reported herein.[16] The exchange processes which this cluster undergoes have been found by Milone and co-workers[17] to be quite similar to those of the mixed-metal analogues. However, bridge-terminal interchange localized on Ru_1 is not the lowest temperature process in $H_2Ru_4(CO)_{13}$, but instead the cyclic exchange of CO's around the Ru_1–Ru_2–Ru_3 face occurs rapidly even at -72 °C. It was proposed that the lower activation barrier observed for $H_2Ru_4(CO)_{13}$ compared to $H_2FeRu_3(CO)_{13}$ results from the increased stability of bridging carbonyls bound to first-row metals.[17] This proposal is further supported here. In Scheme IV the intermediates **2** and **3** have one of the bridging carbonyls bridging either a Ru–Ru, a Ru–Os, or an Os–Os bond. The least favorable case would involve migration of the CO's around the Fe–Os_1–Os_2 face of the C_s isomer of $H_2FeRuOs_2(CO)_{13}$. Accordingly, we find this to have the highest activation barrier observed for the cyclic process in any of the clusters. The energy difference between the tautomers **1–3** in Scheme IV is least in the case where all the metals are Ru and is greatest when one metal is Fe and the other two are Os.

Intrametallic Rearrangement. The last exchange process in $H_2FeRu_3(CO)_{13}$ and the last two processes in $H_2FeRuOs_2$-$(CO)_{13}$ and $H_2FeRu_2Os(CO)_{13}$ involve reorganization of the metal framework. The actual magnitude of the shifts within the framework is relatively small, yet it still significantly contributes to the final averaging process. The metal framework of $H_2FeRu_3(CO)_{13}$ is shown below
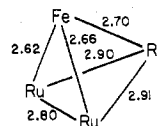
with the average metal–metal bond distances derived from the reported crystal structure.[13] These values indicate that the greatest change that would occur in any one bond length during the rearrangement is 0.11 Å. We tend to view the reorganization process as more of a breathing motion of the metal framework, but one which has coupled to it motions of the carbonyl and hydride ligands.

It appears that intrametallic rearrangement processes are not at all uncommon, as noted by Band and Muetterties[1] in a recent review, but they are still poorly understood. In our case we would particularly like to understand how the various motions contribute to the overall rearrangement process. For example, what percentage of the 15.6-kcal/mol activation barrier for isomerization of $H_2FeRuOs_2(CO)_{13}$ is due to reorganization of the metal framework and what percentage is due to hydrogen migration? We expect that such matters will be the subject of future publications from this and other research groups.

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Ligand Substitution Processes in Tetranuclear Metal Carbonyl Clusters. 2. $Co_4(CO)_9(\mu\text{-}CO)_3$ Derivatives

DONALD J. DARENSBOURG* and MICHAEL J. INCORVIA

Kinetic and mechanistic studies of carbon monoxide substitution processes in the tetranuclear metal clusters Co_4-$(CO)_{12-n}[P(OCH_3)_3]_n$ ($n = 0, 1, 2$) are reported. Entering ligands employed in these investigations were trimethyl phosphite, triphenylphosphine, or ^{13}CO. The CO substitutional rates in $Co_4(CO)_{12}$ with $P(OCH_3)_3$ or $P(C_6H_5)_3$ were too rapid to be studied by conventional techniques and were unaffected by the addition of the radical scavenger 2,6-di-*tert*-butylphenol; nevertheless, the rate of ^{13}CO incorporation into $Co_4(CO)_{12}$ occurs at only a moderate velocity. The exchange reaction between ^{13}C-labeled carbon monoxide and $Co_4(CO)_{12}$ has allowed for a detailed analysis of the $\nu(CO)$ stretching vibrations for the bridging carbonyl ligands. Although the rate of reaction of $Co_4(CO)_{11}[P(OCH_3)_3]$ with $P(OCH_3)_3$ to afford $Co_4(CO)_{10}[P(OCH_3)_3]_2$ has been shown to be strongly dependent on the concentration of trimethyl phosphite, the comparable rate for formation of the mixed-ligand complex $Co_4(CO)_{10}[P(OCH_3)_3][P(C_6H_5)_3]$ from $Co_4(CO)_{11}[P(OCH_3)_3]$ and triphenylphosphine follows a first-order dissociative path. Rate constants and activation parameters for dissociative CO loss in $Co_4(CO)_{12-n}[P(OCH_3)_3]_n$ ($n = 0, 1, 2$) were found not to be significantly dependent upon the value of n.

Introduction

Muetterties has articulated the presumption that transition-metal clusters may serve as simple homogeneous models of metal surfaces in both chemisorption and catalytic processes.[1–3] Indeed, several recent reports have appeared of

homogeneous catalysis employing metal clusters as catalysts for such important processes as the water-gas shift reaction,[4–6]

(1) Muetterties, E. L. *Bull. Soc. Chim. Belg.* **1975**, *84*, 959.
(2) Muetterties, E. L. *Bull. Soc. Chim. Belg.* **1976**, *85*, 451.

methanation,[7] Fischer–Tropsch synthesis of aliphatic hydrocarbons,[8] hydrogenation,[9] and the production of ethylene glycol from synthesis gas.[10] One of the special features of metal clusters that is not present in mononuclear metal species is the possibility of cooperation between metal centers. It is thus hoped that this electronic interaction will be transmitted from neighboring metal atoms to the active catalytic center in the cluster. Some support for this cooperativity has been gleaned from Karel and Norton's study of the stepwise phosphine substitution of $Ir_4(CO)_{12}$ to eventually afford the $Ir_4(CO)_9$-$[P(C_6H_5)_3]_3$ derivative.[11] These researchers found that the progressive substitution in $Ir_4(CO)_{12}$ by triphenylphosphine was accelerated greatly by prior incorporation of PPh_3 into the cluster despite the fact that the substitution (as viewed from the end product) was occurring at different iridium atoms. Nevertheless, Chini and Heaton have pointed out from less direct observations, based on synthetic reactions of $Co_4(CO)_{12}$ and $Rh_4(CO)_{12}$ with phosphines and phosphites to afford the substituted derivatives that the kinetic conclusions noted in CO substitutional processes of $Ir_4(CO)_{12}$ are not easily generalized.[12]

In order to obtain direct kinetic evidence on the CO substitutional process in the $Co_4(CO)_{12}$ and $Rh_4(CO)_{12}$ derivatives, we have begun investigations of ligand substitution reactions in these members of the homologous group 8 series and wish to summarize our results for the cobalt species in this report.[13]

Experimental Section

$Co_4(CO)_{12}$ and $P(OCH_3)_3$ were obtained from Strem Chemicals, Inc. $Co_4(CO)_{12}$ was used without further purification. $P(OCH_3)_3$ was doubly distilled from sodium metal under nitrogen immediately prior to use. $P(C_6H_5)_3$ was recrystallized from hot methanol. Hexane and heptane were distilled from $CaSO_4$ under a nitrogen atmosphere. Carbon monoxide (93.3 atom % ^{13}CO) was obtained from Prochem, B.O.C. Ltd., London. $Co_4(CO)_{11}[P(OCH_3)_3]$ and $Co_4(CO)_{10}[P(O-CH_3)_3]_2$ were prepared as previously described[13] by a modification of the procedures reported by Labroue and Poilblanc.[14] All manipulations were carried out in an inert-atmosphere box (under argon) or in Schlenkware under a nitrogen atmosphere.

$Co_4(CO)_{11}[P(C_6H_5)_3]$. A hexane solution of $Co_4(CO)_{12}$ (0.52 g or 0.91 mmol in 75 mL of hexane) and $P(C_6H_5)_3$ (0.24 g or 0.91 mmol) was stirred at room temperature for 2 h, followed by solvent removal under vacuum. The resulting residue was taken up in a minimum quantity of hexane and chromatographed on a silica gel column eluting first with hexane to remove any unreacted $Co_4(CO)_{12}$. The desired product,[15] $Co_4(CO)_{11}[P(C_6H_5)_3]$, was then eluted with a 20% (v/v) toluene/hexane mixture and isolated upon solvent evaporation.

$Co_4(CO)_{10}[P(OCH_3)_3][P(C_6H_5)_3]$. The mixed-ligand cluster $Co_4(CO)_{10}[P(OCH_3)_3][P(C_6H_5)_3]$ was obtained by the reaction of $Co_4(CO)_{11}[P(OCH_3)_3]$ with a 5 molar excess of $P(C_6H_5)_3$ in a hexane solution. The reaction was monitored by infrared spectroscopy until

Table I. Calculated and Observed CO Stretching Frequencies in the Bridging Region of $Co_4(CO)_{12}$[a]

molecule	$\nu(CO)$, cm^{-1} obsd[b]	calcd[c]	symmetry	symmetry coordinate
all-^{12}CO	1899.7	1900.3	A_1	$(1/3^{1/2})(r_1 + r_2 + r_3)$
	1867.0	1866.0	E	$(1/6^{1/2})(2r_2 - r_1 - r_3)$
		1866.0		$(1/2^{1/2})(r_3 - r_1)$
mono-^{13}CO	1891.5	1893.3	A'	$(1/2^{1/2})(r_2 + r_3)$
	1831.2	1831.2	A'	r_1
	1867.0	1866.0	A''	$(1/2^{1/2})(r_3 - r_2)$
di-^{13}CO	1882.9	1884.3	A'	r_3
	1840.5	1840.0	A'	$(1/2^{1/2})(r_1 + r_2)$
	1825.0	1824.4	A''	$(1/2^{1/2})(r_2 - r_1)$
all-^{13}CO		1858.0	A_1	$(1/3^{1/2})(r_1 + r_2 + r_3)$
	1825.0	1824.4	E	$(1/6^{1/2})(2r_2 - r_1 - r_3)$
		1824.4		$(1/2^{1/2})(r_3 - r_1)$

[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 was $F_{CO} = 14.23_2$ and $F_{CO,CO} = 0.17_4$ mdyn/Å. A similar value for F_{CO} (14.23 mdyn/Å) has been reported in ref 16.

all the $Co_4(CO)_{11}[P(OCH_3)_3]$ had reacted. The volume of the solution was reduced and then chromatographed on silica gel. The column was first eluted with a 5–10% hexane/toluene (v/v) mixture to remove any traces of unreacted $Co_4(CO)_{11}[P(OCH_3)_3]$. The product, Co_4-$(CO)_{10}[P(OCH_3)_3][P(C_6H_5)_3]$, was then eluted with toluene. Crystals were obtained by removing the toluene solvent under vacuum. Anal. Calcd for $C_{31}H_{24}O_{13}Co_4P_2$: C, 41.26; H, 2.66. Found: C, 41.15; H, 2.53.

^{13}CO Exchange Reaction with $Co_4(CO)_{12}$. These reactions were carried out in Schlenk storage tubes (25-mL capacity) under an atmosphere of carbon monoxide in heptane solvent. The tubes were fitted with septum caps secured by copper wire. The heptane solutions of $Co_4(CO)_{12}$ were degassed several times to remove traces of oxygen prior to the introduction of an atmosphere of ^{13}CO (93.3 atom % ^{13}C). The reaction flasks were covered with aluminum foil to exclude light and then placed in a constant-temperature bath. Samples were withdrawn at regular time intervals with a hypodermic syringe for infrared analysis. During the course of the exchange reaction the flask was evacuated under vacuum and refilled with 93.3% ^{13}C carbon monoxide. After $Co_4(CO)_{12}$ had reached maximum ^{13}CO enrichment, the reaction solution was degassed and an atmosphere of ^{12}CO was admitted to the flask with the reverse exchange process being observed in a similar manner.

Kinetic Measurements. All thermal substitution reactions with phosphorus-donor ligands were carried out in oxygen-free hexane solutions (in the dark) by using the techniques previously reported.[13]

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 reaction with $Co_4(CO)_{12}$ 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 were calculated by use of the ^{12}CO vibrational data. 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}.

Results and Discussion

The rates of the ligand substitution reactions of $Co_4(CO)_{12}$ by L (L = $P(OCH_3)_3$ or $P(C_6H_5)_3$) to form $Co_4(CO)_{11}L$ in dried oxygen-free hexane solution were too fast to monitor by conventional techniques. Addition of the radical scavenger 2,6-di-*tert*-butylphenol had no effect on the reaction rate. Even under the conditions of 1 mol of $P(C_6H_5)_3$/mol of $Co_4(CO)_{12}$ and a 20-fold excess of the radical scavenger, the formation

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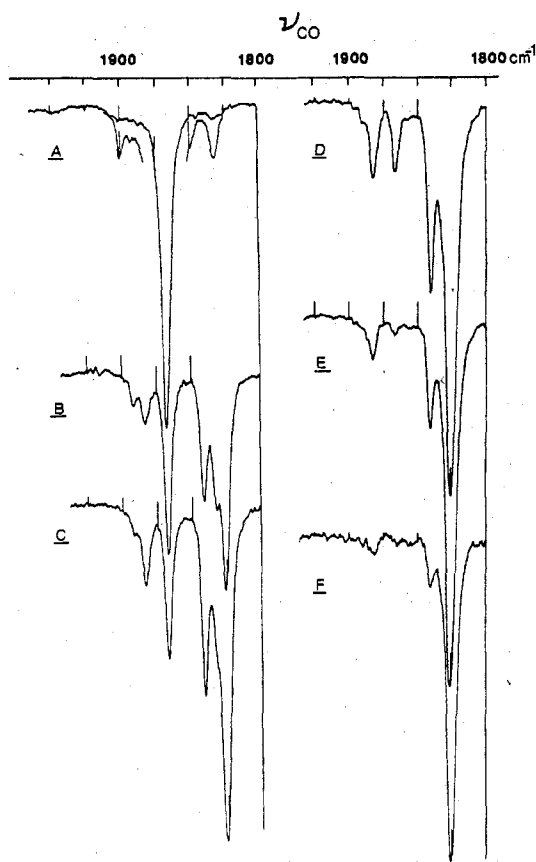
Figure 1. Time-dependent infrared spectra in the ν(CO) bridging region for the exchange reaction between $Co_4(CO)_9(\mu\text{-}CO)_3$ and ^{13}CO: A, initial spectrum (overlay at very high concentration); B, spectrum after 42 h; C, spectrum after 62 h; D, spectrum after 90 h; E, spectrum after 120 h; F, spectrum after 132 h.

Figure 2. Possible isotopic species involving the bridging CO ligands in $Co_4(CO)_{12}$.

of $Co_4(CO)_{11}[P(C_6H_5)_3]$ took place in less than 1 min (minimum time from mixing to completion of IR scan). However, ^{13}CO incorporation into $Co_4(CO)_{12}$ was found to occur at only a moderate velocity.

The infrared spectra in the ν(CO) bridging region for the carbon monoxide exchange reaction of $Co_4(CO)_9(\mu\text{-}CO)_3$ with ^{13}CO (eq 1) in hydrocarbon solution at 24.6 °C are illustrated

$$Co_4(^{12}CO)_{12} + {}^{13}CO \rightarrow Co_4(^{12}CO)_{12-n}(^{13}CO)_n \quad (1)$$
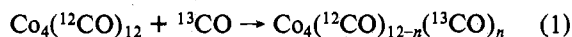
in Figure 1 at various stages during the ligand substitution process. Since it has been demonstrated previously (on the basis of partial ^{13}CO substitution in $Co_4(CO)_{12}$) that the interaction constants between terminal and bridging CO groups in the cobalt dodecacarbonyl species may be considered as being zero, the bridging CO region will be indicative of progressive formation of three ^{13}CO-substituted cluster fragments in addition to the starting all-^{12}CO species (see Figure 2).[16] Spectral band assignments for the various species are provided in Table I and Figure 3, where a restricted CO force field involving only the bridging CO ligands was employed in the computation of ν(CO) positions.
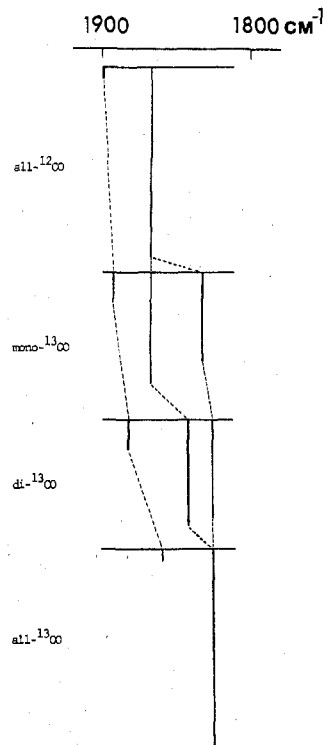

Figure 3. Line drawings of the ν(CO) bridging region for the various ^{13}CO-substituted $Co_4(CO)_{12}$ species. The relative intensities are only approximate.

On the other hand, examination of the ν(CO) spectral changes in the terminal CO stretching region for the $Co_4(CO)_9$ molecular fragment accompanying progressive ^{13}CO incorporation presents a much more complicated situation. That is, 80 *different isotopic molecules* are to be expected for the $Co_4(^{12}CO)_{9-n}(^{13}CO)_n$ (n = 0–9) fragments. Using the terminal CO stretching force field reported by Bor et al.,[16] it is possible to generate the positions of all the anticipated terminal ν(CO) vibrational modes afforded by systematic ^{12}CO replacement by ^{13}CO in a completely fluxional metal-cluster species.[17-19] This has been done, and as expected many of the vibrations in the isotopically related molecules are degenerate or are very close in energy to one another. Figure 4 shows the terminal ν(CO) vibrational changes which occur as the ligand substitution process depicted in eq 1 proceeds to completion.

For further verification that *all* the ν(CO) vibrational changes which were noted for $Co_4(CO)_{12}$ in the presence of ^{13}CO were due to isotopic substitution into the $Co_4(CO)_{12}$ cluster, the once formed highly ^{13}CO-enriched $Co_4(CO)_{12}$ sample was subjected to the reverse reaction with ^{12}CO. As illustrated in Figure 5, the ν(CO) bands reverted back to those assigned to the $Co_4(^{12}CO)_{12}$ species. Thus the exchange reaction carried out in the absence of oxygen and light appears to be quite clean, with no side reactions occurring.

A noteworthy qualitative observation derived from an examination of the bridging ν(CO) region of the $Co_4(CO)_9(\mu\text{-}CO)_3$ species is the very weak intensity of the totally symmetric vibration involving all three bridging CO groups. That is, the intensity of the A_1 mode (1899.7 cm^{-1}) in the all-^{12}CO derivative is less than 50% as great as the ^{13}C satellite of the E mode of this species (hence about 0.7% the intensity of the E mode).[20,21] This in turn requires the three bridging CO

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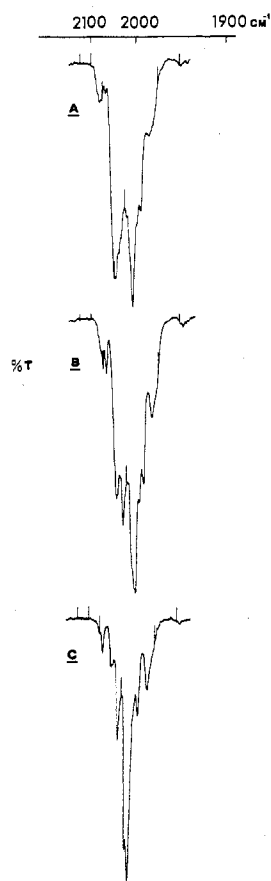(19) Aime, S.; Milone, L.; Osella, D.; Poli, A. *Inorg. Chim. Acta* **1978**, *30*, 45.

Figure 4. Time-dependent infrared spectra in the terminal $\nu(CO)$ region for the exchange reaction between $Co_4(CO)_9(\mu\text{-}CO)_3$ and ^{13}CO: A, after 62 h; B, after 90 h; C, after 132 h.

Figure 5. Infrared spectra in the $\nu(CO)$ region during the exchange reaction of $Co_4(CO)_{12}$ and carbon monoxide: A, initial spectrum; B, spectrum after 168 h of reaction with ^{13}CO at 24.6 °C; C, spectrum after ^{13}CO atmosphere in part B was removed and replaced by ^{12}CO for an additional 288 h at 24.6 °C.

groups to be coplanar to within 4–5°, which further corroborates a consistency of solid-state and solution structures for the $Co_4(CO)_{12}$ species.[22,23]

These studies have provided also for a semiquantitative value for the rate for CO dissociation in the $Co_4(CO)_{12}$ species in hydrocarbon solvent at 24.6 °C. A rate constant value of $(1.5 \pm 0.4) \times 10^{-5}$ s^{-1} at 24.6 °C for CO dissociation in $Co_4(CO)_{12}$ was determined.

The substitution reactions of $Co_4(CO)_{11}[P(OCH_3)_3]$ with either $P(OCH_3)_3$ or $P(C_6H_5)_3$ were studied in hexane solution. Although the reaction of $Co_4(CO)_{11}[P(OCH_3)_3]$ with P(OC-H$_3$)$_3$ proceeds almost completely by a second-order pathway, carbon monoxide was observed to inhibit the rate of this reaction; for example, for obtainment of linear kinetic plots, the reaction mixture was swept constantly with an argon stream to remove the carbon monoxide generated during the course of the reaction. Currently, we have no explanation for this rather unanticipated observation.[24] The second-order rate
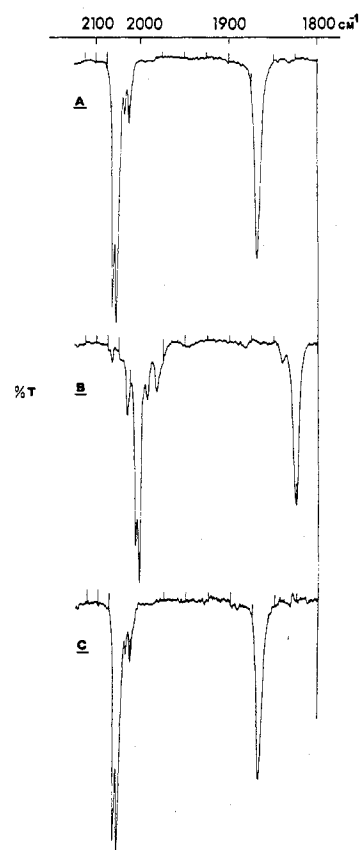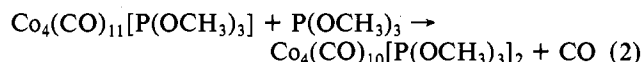
constant (k_2) at 20.6 °C for the thermal substitution process of $Co_4(CO)_{11}[P(OCH_3)_3]$ to afford $Co_4(CO)_{10}[P(OCH_3)_3]_2$ (eq 2) was determined to be 0.197 ± 0.10 M^{-1} s^{-1}; due to the

$$Co_4(CO)_{11}[P(OCH_3)_3] + P(OCH_3)_3 \rightarrow$$
$$Co_4(CO)_{10}[P(OCH_3)_3]_2 + CO \quad (2)$$

large magnitude of k_2 it was rather difficult to obtain an accurate value of k_1, the dissociative rate constant.[13] Nevertheless, it was possible to establish an upper limit for k_1 of 8.5×10^{-5} s^{-1} at 20.6 °C. This is to be compared with the k_1 value of 2.8×10^{-5} s^{-1} at 20.6 °C observed for reaction 3.

$$Co_4(CO)_{10}[P(OCH_3)_3]_2 + P(OCH_3)_3 \rightarrow$$
$$Co_4(CO)_9[P(OCH_3)_3]_3 + CO \quad (3)$$
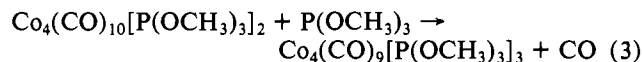
We have therefore undertaken an investigation of the substitution reaction of $Co_4(CO)_{11}[P(OCH_3)_3]$ with the less nucleophilic and sterically more demanding triphenylphosphine ligand in order to accurately ascertain the kinetic and activation parameters for dissociative CO displacement in Co_4-$(CO)_{11}[P(OCH_3)_3]$. Triphenylphosphine was found to react with $Co_4(CO)_{11}[P(OCH_3)_3]$ to form $Co_4(CO)_{10}[P(OC-H_3)_3][P(C_6H_5)_3]$ species in a well-behaved manner with a decrease in absorbance of the infrared bands assignable to $Co_4(CO)_{11}[P(OCH_3)_3]$ coupled with increasing absorbance for bands assignable to the mixed-ligand cluster $Co_4(CO)_{10}$-$[P(OCH_3)_3][P(C_6H_5)_3]$ (eq 4). Infrared spectral data ob-

$$Co_4(CO)_{11}[P(OCH_3)_3] + P(C_6H_5)_3 \rightarrow$$
$$Co_4(CO)_{11}[P(OCH_3)_3][P(C_6H_5)_3] + CO \quad (4)$$

served in the $\nu(CO)$ region for the two derivatives, $Co_4(C-O)_{10}[P(OCH_3)_3]_2$ and $Co_4(CO)_{10}[P(OCH_3)_3][P(C_6H_5)_3]$, are extremely similar in both band positions and relative inten-

(20) Since 3% of the $Co_4(CO)_{12}$ molecules have one bridging ^{13}CO and two ^{12}CO ligands, which give rise to two vibrational modes at 1867.0 and 1831.2 cm^{-1} (see Table I) derived from the E mode at 1867.0 cm^{-1} of the all-^{12}CO species, the intensity of the 1831.2-cm^{-1} ^{13}CO satellite is expected to be ~0.5 of 3% or 1.5% as great as the E mode of the all-^{12}CO species. The ratio of intensities of the A_1:E modes in the all-^{12}CO species is equal to the $\tan^2 \theta$, where θ represents the degree of nonplanarity of the three bridging CO groups, on the assumption of equivalent dipole moment derivatives for the two different symmetry modes.[21]
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(24) A tentative suggestion is that the $P(OCH_3)_3$ ligand assists in the dissociative loss of CO without concerted cobalt–phosphorus bond formation; i.e., this assistance (the associative term in the rate law) leads to a coordinatively unsaturated species.

Table II. Comparative Rate Constants and Activation Parameters for Dissociation of Carbon Monoxide in $Co_4(CO)_{12-n}[P(OCH_3)_3]_n$ ($n = 1, 2$) Derivatives[a]

| temp, °C | $10^4 k_{obsd}$, s^{-1} | |
	$Co_4(CO)_{11}$- $[P(OMe)_3]$[b]	$Co_4(CO)_{10}$- $[P(OMe)_3]_2$[c]
25.6	0.505 (0.253)	0.589
35.0	2.15 (1.08)	2.39
39.4	3.83 (1.92)	4.48
46.6	10.6 (5.30)	11.7
$\Delta H^{*,d}$ kcal·mol^{-1}	26.8 ± 1.0 (112.2)	27.1 ± 1.1 (113.4)
$\Delta S^{*,d}$ cal·mol^{-1}·deg^{-1}	8.2 ± 3.5 (40.2)	10.7 ± 3.7 (44.8)

[a] Rate data were determined in hexane solution. [b] Values in parentheses represent k_{obsd} divided by 2. Incoming ligand employed was $P(C_6H_5)_3$. The concentration of the substrate, $Co_4(CO)_{11}P(OCH_3)_3$, was 1.91×10^{-3} M; $[PPh_3] = (1.07–5.16) \times 10^{-2}$ M. [c] Data taken from ref 13 corrected for temperature differences from Arrhenius plot. Incoming ligand employed was $P(OCH_3)_3$. [d] Values in parentheses are given in SI units.

sities,[25] thus strongly suggesting that the two species are isostructural. The reaction of $Co_4(CO)_{11}[P(OCH_3)_3]$ with P-$(C_6H_5)_3$ was shown to be first order in substrate and to be independent of the concentration of $P(C_6H_5)_3$ over the concentration range investigated (Table II). No trimethyl phosphite displacement was noted (see elemental analysis in Experimental Section), and in addition, the rate of CO substitution was retarded in the presence of carbon monoxide.

In order to compare rate data for displacement of carbon monoxide in $Co_4(CO)_{11}[P(OCH_3)_3]$ and $Co_4(CO)_{10}[P(OCH_3)_3]_2$, it is necessary to take into account the difference in the number of dissociable CO groups in the two species. Since the solution structures of products derived from phosphine and phosphite substitution in these and related cluster species exhibit substitution in the terminal basal positions,[18,19,26] it would not be unreasonable to assume that there are three dissociable CO ligands in $Co_4(CO)_{12}$, two in $Co_4(CO)_{11}[P-(OCH_3)_3]$, and only one in $Co_4(CO)_{10}[P(OCH_3)_3]_2$.[27] Certainly this analysis of the rate data would provide for the greatest correction to be applied to the substitutional rate constants, for all other assumptions would lead to smaller ratio of dissociable CO ligands in the three species. (See Note Added in Proof.)

A comparison of the dissociative rate constant data and activation parameters for reactions 3 and 4, these latter values being presumably the same as the analogous parameters expected for reaction 2,[28] may be found in Table II. From Table II, it is readily seen that the maximum difference in the dissociative rate constants for progressive CO displacement in $Co_4(CO)_{11}[P(OCH_3)_3]$ and $Co_4(CO)_{10}[P(OCH_3)_3]_2$ is a factor of 2.3 at all temperatures studies. Although the CO stretching frequencies of the ground-state species do not support any weakening of the average Co–C bond in going from $Co_4(C-O)_{11}[P(OCH_3)_3]$ to $Co_4(CO)_{10}[P(OCH_3)_3]_2$, there may be some small site preference of the added $P(OCH_3)_3$ ligand in the transition state leading to a stabilizing effect with increased $P(OCH_3)_3$ substitution.[29,30] Unfortunately, we have not been able to obtain quantitative rate data for dissociative CO dis-
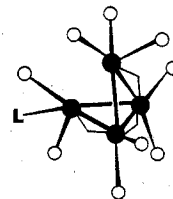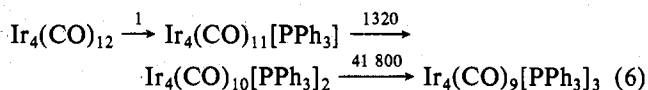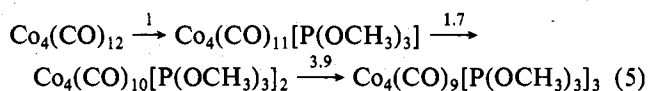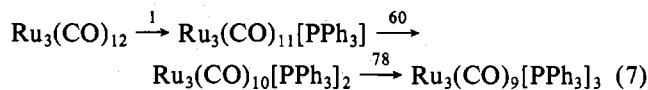

Figure 6. $Co_4(CO)_{12}L$ intermediate.

placement in the parent dodecacarbonyl species $Co_4(CO)_{12}$ in the presence of phosphine or phosphite ligands. However, semiquantitative rate data for ^{13}CO incorporation into Co_4-$(CO)_{12}$ indicate that this process occurs with a rate constant which is quite similar to that observed for CO dissociation in $Co_4(CO)_{11}[P(OCH_3)_3]$.

Steric effects are often responsible for ligand dissociation reactivities in mononuclear metal carbonyl phosphine and phosphite derivatives[31,32] and should be considered when substitutional processes in multinuclear metal species are viewed as well. In this regard it is indeed possible that in progressive CO-substitution reactions with phosphine or phosphite ligands in metal-cluster species CO loss is occurring at the metal center which bears the phosphorus-donor ligand with a concomitant facile CO migration leading to unsaturation at an adjacent metal site.[30,33,34]

In conclusion, the kinetic investigations made thus far on substitutional processes in the tetranuclear carbonyl clusters of cobalt involving the sterically compact trimethyl phosphite ligand indicate that *substantial* rate enhancement for CO dissociation is not evident with progressive phosphite substitution (eq 5).[35] In contrast to the $Ir_4(CO)_{12}$ system (eq 6),

$$Co_4(CO)_{12} \xrightarrow{1} Co_4(CO)_{11}[P(OCH_3)_3] \xrightarrow{1.7}$$
$$Co_4(CO)_{10}[P(OCH_3)_3]_2 \xrightarrow{3.9} Co_4(CO)_9[P(OCH_3)_3]_3 \quad (5)$$

$$Ir_4(CO)_{12} \xrightarrow{1} Ir_4(CO)_{11}[PPh_3] \xrightarrow{1320}$$
$$Ir_4(CO)_{10}[PPh_3]_2 \xrightarrow{41\,800} Ir_4(CO)_9[PPh_3]_3 \quad (6)$$

during successive CO substitution with trimethyl phosphite in the $Co_4(CO)_{12}$ species, no structural change occurs upon the introduction of the first substituent. Structural integrity is maintained also during the reaction of $Ru_3(CO)_{12}$ with PPh_3 (eq 7) where an initial rate increase was observed to be greatly

$$Ru_3(CO)_{12} \xrightarrow{1} Ru_3(CO)_{11}[PPh_3] \xrightarrow{60}$$
$$Ru_3(CO)_{10}[PPh_3]_2 \xrightarrow{78} Ru_3(CO)_9[PPh_3]_3 \quad (7)$$

attenuated upon further substituent addition.[36]

We would be remiss not to mention alternative intermediates in substitution processes of the $Co_4(CO)_{12}$ species, especially in view of the investigation of the reaction of $Co_4(CO)_{12}$ with CO to afford $Co_2(CO)_8$ at elevated pressures by Bor and co-workers.[37] These researchers propose an intermediate of

(25) Infrared spectra in the ν(CO) region in hexane solution were as follows. $Co_4(CO)_{10}[P(OCH_3)_3]_2$: 2071, 2038, 2016, 2005, 1987, 1830, 1816 cm^{-1}. $Co_4(CO)_{10}[P(OCH_3)_3][P(C_6H_5)_3]$: 2070, 2034, 2017, 2000, 1996, 1828, 1812 cm^{-1}.
(26) Huie, B. T.; Knobler, C. B.; Kaesz, H. D. *J. Chem. Soc., Chem. Commun.* **1975**, 684.
(27) A similar distinction was made for CO substitutional processes in the iridium-cluster species.[11]
(28) The k_{obsd} for dissociative CO loss in $Co_4(CO)_{11}[P(OCH_3)_3]$ in the presence of $P(C_6H_5)_3$ lies within the limit defined for k_{obsd} for the analogous process involving $P(OCH_3)_3$ as the incoming ligand.
(29) This is the basis of Brown's cis-labilization proposal.[30]
(30) Atwood, J. D.; Brown, T. L. *J. Am. Chem. Soc.* **1976**, *98*, 3160.

(31) Darensbourg, D. J.; Graves, A. H. *Inorg. Chem.* **1979**, *18*, 1257.
(32) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.
(33) Darensbourg, M. Y.; Atwood, J. L.; Burch, R. R., Jr.; Hunter, W. E.; Walker, N. *J. Am. Chem. Soc.* **1979**, *101*, 1979.
(34) Darensbourg, D. J.; Burch, R. R., Jr.; Darensbourg, M. Y. *Inorg. Chem.* **1978**, *17*, 2677.
(35) Although the rate of dissociative CO loss in the initial step in eq 5, i.e., $Co_4(CO)_{12}$ plus $P(OCH_3)_3$ going to $Co_4(CO)_{11}[P(OCH_3)_3]$, occurs too rapidly to be observable by conventional techniques, the rate of ^{13}CO incorporation (a dissociative process) has been qualitatively determined to be slightly slower (less than a factor of 2) than the rate of dissociative CO loss in the $Co_4(CO)_{11}[P(OCH_3)_3]$ species. Accurate rate measurements, including determination of activation parameters, for ^{13}CO substitution into $Co_4(CO)_{12}$, are currently in progress.
(36) Malik, S. K.; Poë, A. *Inorg. Chem.* **1978**, *17*, 1484.

the type described in Figure 6 (where L = CO) which conforms with the 18-electron rule and is derived from tetracobalt dodecacarbonyl by cleavage of one Co–Co bond with the concomitant formation of a Co–CO bond and a repositioning of one bridging carbon monoxide ligand. Indeed an intermediate of this configuration where L = $P(OCH_3)_3$ may well account for the interchange or associative term in these substitutional processes. The exchange reaction of $Co_4(CO)_{12}$ with the poor nucleophile [13]CO reported herein is believed not to be proceeding through this intermediate since the reaction was carried out at atmospheric CO pressure;[38] nevertheless, a more persuasive argument must await the determination of activation parameters for this CO-exchange process.

It appears that there is a need for much more kinetic data on substitutional processes in metal-cluster species before definitive statements regarding cooperativity between metal

centers can be made. Clearly, studies should involve not only changes in metal centers but also variations in the steric and electronic nature of the substituent ligands. Work in progress includes kinetic measurements on [13]CO-exchange reactions with a variety of metal carbonyl cluster species, as well as phosphine and phosphite substitution processes with $Ir_4(CO)_{12}$ in hydrocarbon or other inert solvents.

Note Added in Proof. We have completed recently X-ray structure determinations on two substituted cobalt species, $Co_4(CO)_{11}[P(C_6H_5)_3]$ and $Co_4(CO)_{10}[P(OCH_3)_3]_2$. The phosphine and phosphite ligands occupy axial coordination sites in these clusters.

Registry No. $Co_4(CO)_{11}[P(C_6H_5)_3]$, 12336-57-1; $Co_4(CO)_{10}[P-(OCH_3)_3][P(C_6H_5)_3]$, 73953-20-5; $Co_4(CO)_{11}[P(OCH_3)_3]$, 56277-17-9; $Co_4(CO)_{12}$, 17786-31-1; $Co_4(CO)_{11}(^{13}CO)$, 73953-21-6; Co_4-$(CO)_{10}(^{13}CO)_2$, 73953-21-6; $Co_4(CO)_9(^{13}CO)_3$, 73953-22-7; $Co_4(C-O)_{10}[P(OCH_3)_3]_2$, 11067-01-9.

(37) Bor, G.; Dietler, U. K.; Pino, P.; Poë, A. *J. Organomet. Chem.* **1978,** *154,* 301.

(38) The reaction studied in ref 37 involved CO pressures between 5 and 120 bar.

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Reactions of Tin(II) Halides with Complexes Containing Two Transition Metal–Halogen Bonds, [Co(η-dienyl)(L)Y₂] and [Fe(CO)₃(PPh₃)Y₂], and with [Co(η-dienyl)(CO)(C₃F₇)I] (Dienyl = C₅H₅ or MeC₅H₄; L = CO or PPh₃; Y = Br or I). A Novel Intramolecular Halogen Migration

JOHN FORTUNE and A. R. MANNING*

Tin(II) halides, SnX_2 (X = Cl, Br, or I), react with an equimolar amount of $[Co(\eta\text{-dienyl})(CO)Y_2]$, $[Co(\eta\text{-dienyl})(PPh_3)Y_2]$, or $[Co(\eta\text{-dienyl})(CO)(C_3F_7)I]$ (dienyl = C_5H_5 or MeC_5H_4; Y = Br or I) in tetrahydrofuran solution at room temperature to give, in most instances, $[Co(\eta\text{-dienyl})(CO)(Y)(SnX_2Y)]$, $[Co(\eta\text{-dienyl})(PPh_3)(Y)(SnX_2Y)]$, or $[Co(\eta\text{-dienyl})-(CO)(C_3F_7)(SnX_2I)]$. On the basis of the frequencies of the $\nu(CO)$ modes of the first series of compounds, it is concluded that during the $[Co(\eta\text{-dienyl})(CO)Br_2]/SnI_2$ reactions a novel halogen rearrangement occurs to give $[Co(\eta\text{-dienyl})-(CO)(I)(SnBr_2I)]$ in which one of the less electronegative halogen atoms, I, migrates from tin to cobalt and both of the more electronegative bromine atoms migrate from cobalt to tin. $[Fe(CO)_3(PPh_3)Y_2]$ and SnX_2 generally give $[Fe-(CO)_3(PPh_3)(Y)(SnX_2Y)]$, but when X = I and Y = Br, the only isolated product is $[Fe(CO)_3(PPh_3)I_2]$, and when Y = Br and X = Cl, some $[Fe(CO)_3(PPh_3)_2]$ is also formed. This last compound is the only product when an excess of triphenylphosphine is present, and the reaction is a rare example of a reductive elimination of a tin(IV) halide from a transition-metal complex. There is no evidence for the formation of SnX_3 derivatives or for complexes where SnX_2 inserts into both M–Y bonds under these conditions. It is suggested that a Lewis acid–Lewis base interaction between the SnX_2Y ligand and the Y ligand cis to it deactivates the second M–Y bond toward attack by tin(II) halides. A plausible reaction scheme is proposed which accounts for all of the above experimental observations.

Previously we showed that tin(II) halides, SnX_2 (X = Cl, Br, or I), reacted under mild conditions with a variety of compounds containing a single transition metal, M, to halogen, Y, bond, M–Y, to give $M–SnX_2Y$ derivatives as the initial products in most instances.[1,2] As a continuation of this work we have investigated the interaction of tin(II) halides with transition-metal complexes containing two halogen ligands. We anticipated that, as well as similarities between the two series of reactions, significant differences would be observed. This has proved to be the case. Our studies have been limited to the readily accessible derivatives of the first-row elements having the general formulas $[Fe(L)_nY_2]$ and $[Co(\eta\text{-dienyl})-(L)Y_2]$ (L = CO, PPh_3, or CNMe; dienyl = C_5H_5 or MeC_5H_4; Y = Cl, Br, or I), but, recognizing the possibility of insertion into the $Co–C_3F_7$ bond, we also extended them to include $[Co(\eta\text{-dienyl})(CO)(C_3F_7)I]$.

Most of the previous work in this field has been devoted to the interaction of tin(II) chloride with the chlorides of the heavier metals and their coordination compounds. For example, Pregosin and Sze showed that various $[Pt(PR_3)_2Cl_2]$ and $SnCl_2$ react rapidly at room temperature to form $[Pt-(PR_3)_2(Cl)(SnCl_3)]$ and then $[Pt(PR_3)_2(SnCl_3)_2]$.[3] However, of direct relevance to our work is that of Powell and Mays, who found that at room temperature in chloroform solution $[Co(\eta\text{-}C_5H_5)(CNC_6H_4OMe\text{-}p)I_2]$ and $SnCl_2$ gave only $[Co-(\eta\text{-}C_5H_5)(CNC_6H_4OMe\text{-}p)(SnCl_3)_2]$.[4]

Experimental Section

Literature methods were used to synthesize $[Co(\eta\text{-}C_5H_5)(CO)_2]$[5] and $[Co(\eta\text{-}C_5H_5)(CO)Y_2]$ (Y = Br[6] or I[7]), their ($\eta\text{-MeC}_5H_4$) counterparts,[5–7] $[Co(\eta\text{-MeC}_5H_4)(PPh_3)I_2]$,[7] $[Co(\eta\text{-}C_5H_5)\text{-}$

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