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LIGAND SUBSTITUTION PROCESSES IN TETRANUCLEAR METAL CARBONYL CLUSTERS

I. $Co_4(CO)_9(\mu_2\text{-}CO)_3$ DERIVATIVES

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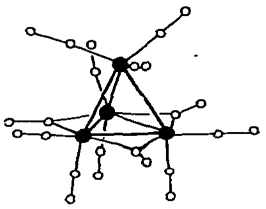
Summary

Kinetic and mechanistic studies of carbon monoxide substitution processes in the tetranuclear metal carbonyl clusters, $Co_4(CO)_{12-n}[P(OMe)_3]_n$ (n = 1, 2), are reported. $Co_4(CO)_{10}[P(OMe)_3]_2$ was found to proceed to $Co_4(CO)_9[P(OMe)_3]_3$ by a two-term rate law (dissociative and ligand-dependent paths) with the CO dissociative process being dominant at low incoming ligand concentrations. On the other hand, the rate of reaction of $Co_4(CO)_{11}[P(OMe)_3]$ with $P(OMe)_3$ to afford $Co_4(CO)_{10}[P(OMe)_3]_2$ was strongly dependent on the concentration of trimethyl phosphite; making it difficult to assess the importance of the CO dissociative process.

Introduction

The need for basic kinetic and mechanistic studies of ligand substitution processes in metal carbonyl cluster derivatives is apparent [1]. In part the exigency for these investigations stems from the interrelationship between heterogeneous and homogeneous catalysis which has resulted in the use of clusters as catalysts in a variety of vital processes [2]. As in many reactions catalyzed by mononuclear metal derivatives, ligand dissociation is a key step to the metal cluster catalytic properties. In this communication we wish to report on carbonyl substitution reactions in the tetranuclear cluster species, $Co_4(CO)_{12-n}[P(OMe)_3]_n$ (n = 1, 2). The tetranuclear cobalt system has been selected for our entry into ligand substitution processes in metal clusters since some knowledge of the solution structures of these derivatives is evident (structures I—IV) [3—5]. Crystallographic investigations of the specific derivatives where L = $P(OMe)_3$ are currently underway [6]. Additionally, some direct comparisons can be made with the previously studied Ir_4 cluster system [7].



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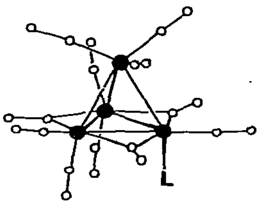

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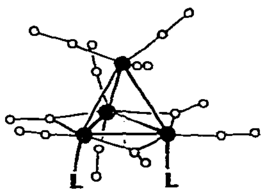

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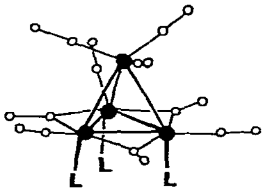

IV

Experimental section

$Co_4(CO)_{12}$ and $P(OMe)_3$ were obtained from Strem Chemicals, Inc. $P(OMe)_3$ was doubtly distilled from sodium metal under nitrogen immediately prior to use. Hexane was distilled from $CaSO_4$ under a nitrogen atmosphere. $Co(CO)_{11}[P(OMe)_3]$ and $Co(CO)_{10}[P(OMe)_3]_2$ were prepared by a modification of the procedures described by Labroue and Poilblanc [8].

$Co_4(CO)_{11}P(OMe)_3$

All manipulations were carried out in an inert atmosphere box (argon) or in Schlenk-ware under a nitrogen atmosphere. $Co_4(CO)_{12}$, 0.241 g (0.421 mmol), was dissolved in approximately 100 ml of olefin-free pentane. In a separate flask 50 μl (0.424 mmol) of freshly distilled (from Na metal) $P(OMe)_3$ was dissolved in 25 ml of pentane. The two flasks were connected via a ground Y-joint. The solutions were cooled to $-77°C$ (acetone/dry ice) and then mixed rapidly. The resulting brown reaction mixture was permitted to warm to 0°C over a period of three hours followed by removal of solvent under vacuum. The residue was dissolved in pentane and chromatographed on silica gel. The first band eluted with pentane was unreacted $Co_4(CO)_{12}$. The next band, $Co_4(CO)_{11}P(OMe)_3$, also brown in color, was eluted with either CH_2Cl_2 or a 10% (v/v) mixture of toluene in hexane. Slow evaporation of the solvent under vacuum afforded a black micro-crystalline product in 20% yield based on $Co_4(CO)_{12}$.

$Co_4(CO)_{10}[P(OMe)_3]_2$

This complex was prepared by two different methods. In the first case tetracobalt dodecacarbonyl was dissolved in degassed hexane (3.2×10^{-3} M) and was titrated under nitrogen with a dilute hexane solution of trimethyl phosphite (3.7×10^{-1} M) to form $Co_4(CO)_{10}[P(OMe)_3]_2$. The product was isolated by removing the solvent under vacuum after filtration through filter-aid. Recrystallization from hexane led to a compound with an infrared spectrum in the ν(CO) region in agreement with that published [8]; however, a slight contamination of trisubstituted $Co_4(CO)_9[P(OMe)_3]_3$ was present. The other procedure was carried out in an inert atmosphere box. A degassed, olefin-free pentane solution of $P(OMe)_3$ was added to a dilute pentane solution of $Co_4(CO)_{12}$ in a 2 : 1 molar ratio. After the reaction mixture had been stirred for 2 to 3 h at ambient temperature, the pentane was removed under vacuum. The solution was chromatographed on a silica gel column; $Co_4(CO)_{12}$ was eluted with pentane, $Co_4(CO)_{11}[P(OCH_3)_3]$ with 10% by volume toluene/pentane, and the major consistent $Co_4(CO)_{10}[P(OMe)_3]_2$ with toluene.

Kinetic measurements

The following set-up was used to study the thermal reactions of the tetranuclear cobalt clusters with trimethyl phosphite. Two 15 X 150 mm heavy-walled pyrex glass test tubes were joined together by a short piece (2 to 3 cm) of 8 mm heavy-walled pyrex glass tubing approximately 3 to 4 cm from their tops. Into one test tube was placed 5 ml of a 3.4—3.8 X 10^{-3} *M* hexane solution of the appropriate cluster compound, and into the other compartment was placed 5 ml of a hexane solution of the $P(OMe)_3$ entering ligand. Both test tube openings were sealed with tightly wired serum caps and the solutions were thoroughly degassed by freeze-pump-thawing cycles followed by charging the tubes with either nitrogen, argon, or carbon monoxide. The tubes were then placed in a Neslab constant temperature bath and equilibrated to the desired temperature prior to being rapidly mixed. The course of the reactions was followed by withdrawing samples with a hypodermic syringe and monitoring their infrared spectra in the $\nu(CO)$ region (vide infra). At all times the samples were protected from room light. During the course of the studied on $Co_4(CO)_{11}[P(OMe)_3]$ it was necessary to constantly purge the system with a slow stream of argon to remove the liberated carbon monoxide.

Infrared measurements

The infrared spectra were recorded on either a Perkin—Elmer 521 or 283 spectrophotometer, both equipped with a linear absorbance potentiometer. The spectra were calibrated against a water vapor spectrum below 2000 cm^{-1} and against a CO spectrum above 2000 cm^{-1}. Matched 0.10 cm sodium chloride cells were used in the measurements.

Results and discussion

The thermal substitution reactions of $Co_4(CO)_{10}[P(OMe)_3]_2$ with $P(OMe)_3$ in hexane (oxygen-free and in the dark) to form $Co_4(CO)_9[P(OMe)_3]_3$ were followed by monitoring the infrared absorbances of both the product and the reactant as a function of time. A decrease in the absorbances of the $\nu(CO)$ bands (2070, 2037, 2017, 1828 and 1814 cm^{-1}) assignable to the $Co_4(CO)_{10}$-$[P(OMe)_3]_2$ species was noted with a concomitant increase in $\nu(CO)$ absorbances at 2052, 1998, 1970 and 1800 cm^{-1} which are all ascribable to the $Co_4(CO)_9$-$[P(OMe)_3]_3$ species. These $\nu(CO)$ assignments were independently made on authentic, purified samples of the corresponding derivatives [8]. The infrared spectrum in the terminal $\nu(CO)$ region for $Co_4(CO)_{10}[P(OMe)_3]_2$ in hexane solution is illustrated in Fig. 1, where the peak employed in rate measurements

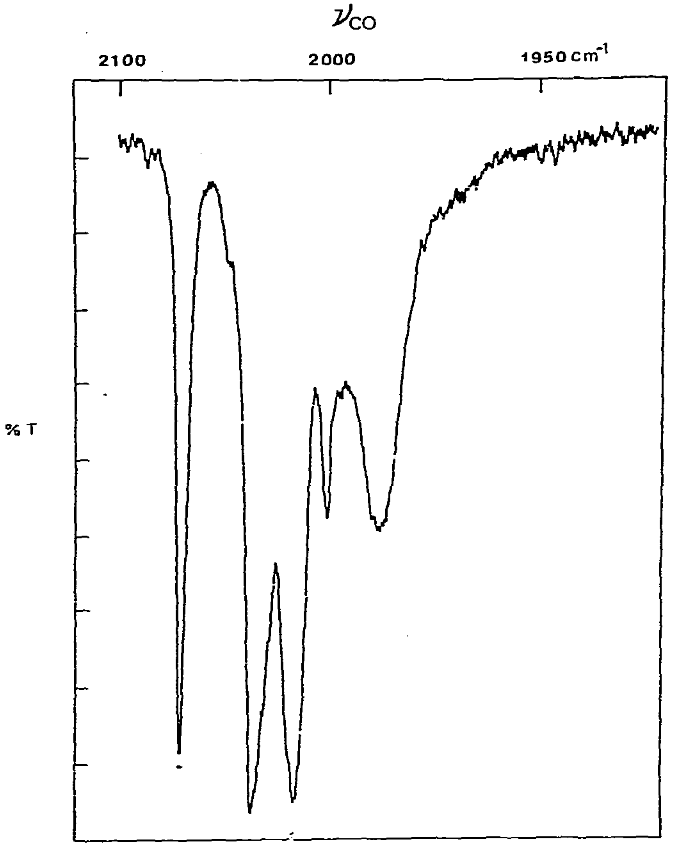

Fig. 1. Infrared spectrum in the terminal ν(CO) region of $Co_4(CO)_{10}[P(OMe)_3]_2$ in hexane solution. 2070 cm^{-1} absorption used in the kinetic measurements indicated with an asterisk.

is indicated by an asterisk. Figure 2 demonstrates the typically observed smooth decrease in the ν(CO) absorbance at 2070 cm^{-1} for the substrate $Co_4(CO)_{10}$-$[P(OMe)_3]_2$ as a function of time, clearly indicating the lack of an induction period. Although the reaction is greatly retarded by the addition of oxygen, the rate of CO substitution was not affected by the presence of the radical scavenger 2,6-di-t-butylphenol. Plots of $\log[C_0/C_t]$, where C_0 and C_t (as determined by the ν(CO) absorption at 2070 cm^{-1}) represent the concentration of $Co_4(CO)_{10}[P(OMe)_3]_2$ at time zero and t, respectively, versus time were linear over at least three half lives. There was no significant dependence of the reaction rate on the concentration of trimethyl phosphite over the range of 0.0042—0.064 M, with the rate being retarded in the presence of carbon monoxide (see Table 1). Such kinetic behavior is indicative of a dissociative process (D).

The first-order rate constant at 31.7°C calculated over this entering ligand concentration range was $1.38 \pm 0.14 \times 10^{-4}$ s^{-1}. At higher ligand concentrations (0.085—0.093 M) a rate enhancement by a factor of ca. 2 was noted (see Table 1). We were initially concerned that this increase in substitutional rate was possibly due to an impurity in the $P(OMe)_3$ (doubly distilled from sodium metal under nitrogen immediately prior to use). For example, trimethyl phosphate

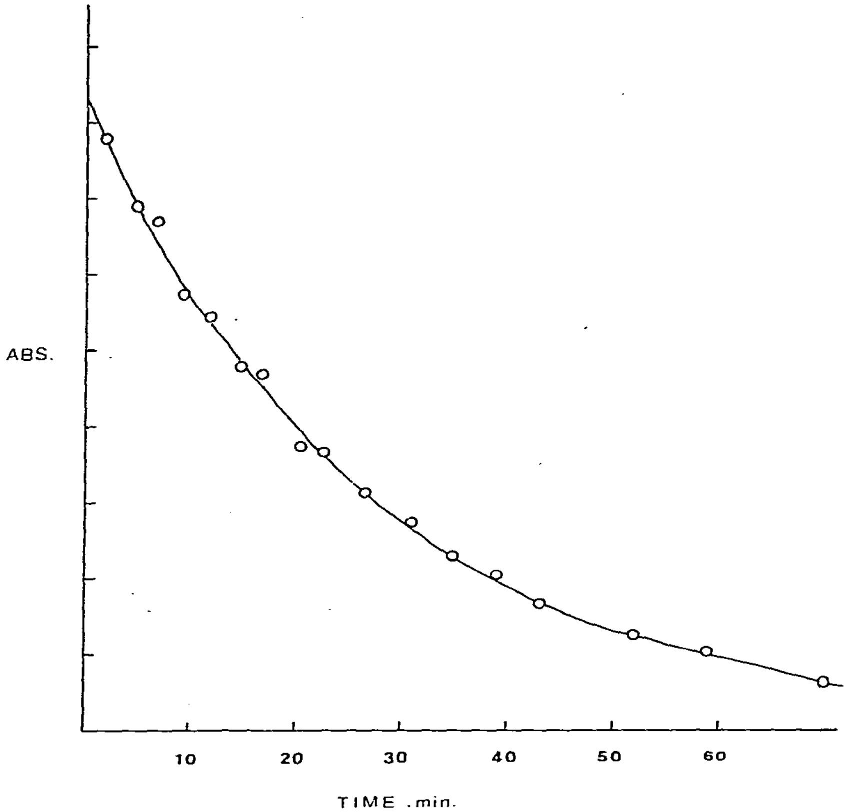

Fig. 2. Variations in the absorbance of the 2070 cm^{-1} band in $Co_4(CO)_{10}[P(OMe)_3]_2$ species with time during the CO substitution reaction at 41.1°C.

was suspected since both n-Bu_3PO [9] and Me_3NO [10] have been observed to enhance greatly the CO substitution rates in metal carbonyl derivatives. However, deliberate addition of sizeable quantities of trimethyl phosphate, up to 9% $O{=}P(OMe)_3$ in $P(OMe)_3$, did not appreciably increase the CO substitution rate (ca. 25% enhancement). Since the enhanced rate was reproducible for different samples of $Co_4(CO)_{10}[P(OMe)_3]_2$ and $P(OMe)_3$, this concentration effect is bona fide. It is quite tempting to asume that this concentration effect is due to the onset of a dissociative interchange process similar to the ligand-dependent rates previously observed in other metal carbonyl cluster species [7,11,12]. However, the transition was rather abrupt (see Table 1), as opposed to the expected smooth increase in k_{obsd} with trimethyl phosphite concentration as dictated by $k_{obsd} = k_1 + k_2$ [L]. No explanation for this observation is presently offered. Nonetheless, we are interested in determining the kinetic parameters associated with the dissociative process, and hence have restricted our studies thus far to low concentrations of incoming ligand.

The temperature dependence of the rate of the reaction was obtained (see Table 2). The energy of activation calculated from an Arrhenius plot is 27.7 ± 1.1 kcal mol^{-1} with a ΔH^* value of 27.1 ± 1.1 kcal mol^{-1} (113.4 kJ mol^{-1}) and a ΔS^* value of 10.7 ± 3.7 kcal mol^{-1}/deg (44.8 J mol^{-1}/deg). The average value

TABLE 1

OBSERVED RATE CONSTANTS FOR THE REACTION OF $Co_4(CO)_{10}[P(OMe)_3]_2$ WITH $P(OMe)_3$ AT 31.7° IN HEXANE [a]

$10^2[P(OMe)_3]$ (*M*)	$10^4\,k$ [b] (s^{-1})	
	N_2 atmosphere	CO atmosphere [c]
0.424	1.35 ± 0.02	0.153 ± 0.051
	1.18 ± 0.05	
0.594	1.30 ± 0.04	0.241 ± 0.026
0.848	1.49 ± 0.05	0.556 ± 0.025
	1.28 ± 0.44	0.572 ± 0.035
1.27		0.757 ± 0.038
2.97	1.54 ± 0.06	0.833 ± 0.051
4.24	1.57 ± 0.04	1.21 ± 0.08
5.94	1.51 ± 0.07	1.07 ± 0.04
6.36	1.24 ± 0.24	
8.48	2.50 ± 0.13	
	2.50 ± 0.06	
	2.84 ± 0.22	
9.33	2.59 ± 0.17	

[a] The concentration of substrate, $Co_4(CO)_{10}[P(OMe)_3]_2$, was 1.71×10^{-3} *M*. [b] Duplicate runs at the same incoming ligand concentration provide a measure of reproducibility of these parameters. [c] Concentration of CO at one atmosphere pressure in hexane ca. 0.0116 *M*.

of a Co—Co bond energy is 32.5 kcal mol^{-1} (136 kJ mol^{-1}) according to Connor [13]. Thus the activation parameters, i.e., the magnitude of ΔH^* and positive ΔS^*, are consistent with a dissociative process.

Competition studies between carbon monoxide and trimethyl phosphite for the intermediate resulting from CO loss were performed at 31.7°C. Using the reaction scheme below, the competition ratio between CO and $P(OMe)_3$ for the intermediate [M] is defined by k_{-1}/k_2. The competition ratio calculated over a CO to $P(OMe)_3$ molar ratio of 0.14 to 1.4 was ca. 1.2 with a somewhat larger

$$[MCO] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [M] + CO \underset{L}{\overset{k_2}{\rightarrow}} [ML] \qquad (1)$$

k_{-1}/k_2 value (ca. 3) being observed at greater $[CO]/[P(OMe)_3]$ ratios. Therefore, the $[Co_4(CO)_9[P(OMe)_3]_2]$ intermediate is fairly nondiscriminating, exhibiting only a slight preference for carbon monoxide over $P(OMe)_3$.

TABLE 2

TEMPERATURE DEPENDENCE OF RATE OF REACTION OF $Co_4(CO)_{10}[P(OMe)_3]_2$ WITH TRIMETHYL PHOSPHITE [a]

Temp. (°C)	$k \times 10^4$ (s^{-1})
25.0	0.504 ± 0.006
31.7	1.48 ± 0.03
41.1	5.89 ± 0.40
48.4	13.9 ± 0.90

[a] Reaction studied under conditions of zero-order dependence on entering ligand concentration in hexane solution.

Studies of the reaction of $Co_4(CO)_{11}[P(OMe)_3]$ with $P(OMe)_3$ to afford $Co_4(CO)_{10}[P(OMe)_3]_2$ indicate this CO substitution process to be more facile than CO loss in the $Co_4(CO)_{10}[P(OMe)_3]_2$ derivative under similar conditions. This process was observed, however, to be extremely dependent on the concentration of the incoming ligand, $P(OMe)_3$, with a second-order rate constant (k_2) of $0.197 \pm 0.010\ M^{-1}\ s^{-1}$ at 20.6°C. Unfortunately, due to the magnitude of k_2, it is not possible to assess the k_1 value very accurately (e.g., at $[P(OMe)_3] = 2.12 \times 10^{-2}\ M$, the first-order process contributes <5% to the measured rate). Nevertheless, we have been able to set an upper limit to k_1 of $8.5 \times 10^{-5}\ s^{-1}$ at 20.6°C; whereas the comparable first-order rate constant in the $Co_4(CO)_{10}[P(OMe)_3]_2$ species (extrapolated from the Arrhenius plot) is $2.75 \times 10^{-5}\ s^{-1}$. There was no dramatic increase in rate upon the addition of small quantities of trimethyl phosphate. Again, the rate of substitution of CO was unaffected by the presence of the radical scavanger 2,6-di-t-butylphenol.

Although this substitution process appears to be associative in nature it was greatly retarded by the presence of CO, indeed much more so than in the dissociative process involving $Co_4(CO)_{10}[P(OMe)_3]_2$ (vide supra). It was necessary to provide a means for carbon monoxide removal by an argon sweep in order to accurately measure the rate of CO substitution in eq. 2.

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

This rather surprising result suggests the presence of an unsaturated intermediate during this process which shows a preference for coordination of CO over $P(OMe)_3$. Plans are to investigate reaction (2) in the presence of ^{13}CO to provide information regarding CO incorporation into the starting material promoted by the attendance of $P(OMe)_3$. Albeit we have not detected products derived from cluster disruption during these facile substitution processes, it will be necessary to consider intermediates involving metal—metal bond cleavage with formation of $Co_4(CO)_{13-n}[P(OMe)_3]_n$ ($n = 2, 3$) as proposed for the reaction of $Co_4(CO)_{12}$ with CO to afford $Co_2(CO)_8$ [14].

Thus, the incoming ligand $P(OMe)_3$ greatly accelerates the loss of the CO ligand in $Co_4(CO)_{11}[P(OMe)_3]$, thereby making it difficult ro measure the dissociative rate constant for CO loss in the absence of $P(OMe)_3$ interactions. Hopefully, an accurate assessment of this kinetic parameter will be obtainable employing other incoming ligands which are less nucleophilic and sterically more demanding (e.g., PPh_3) *. At this point our results do not allow for an accurate comparison of the first-order rate constants in the reaction sequences (eqs. 3, 4) involving CO substitution in the tetranuclear clusters of the cobalt family [7].

$$Ir_4(CO)_{11}[PPh_3] \xrightarrow{75^\circ C} Ir_4(CO)_{10}[PPh_3]_2 \xrightarrow{75^\circ C} Ir_4(CO)_9[PPh_3]_3 \qquad (3)$$

$$Co_4(CO)_{11}[P(OMe)_3] \xrightarrow{20^\circ C} Co_4(CO)_{10}[P(OMe)_3]_2 \xrightarrow{20^\circ C} Co_4(CO)_9[P(OMe)_3]_3 \qquad (4)$$

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* *Note added in proof.* The rate constant for CO dissociation in $Co_4(CO)_{11}P(OMe)_3$ in the presence of PPh_3 to afford $Co_4(CO)_{10}[P(OMe)_3]PPh_3$ has been determined to be $4 \times 10^{-4}\ s^{-1}$ at 40°C, i.e. comparable to the constant observed for CO loss in $Co_4(CO)_{10}[P(OMe)_3]_2$ in the absence of consideration of statistical factors.

Continuing studies on these and related mixed-metal complexes are currently underway to extensively probe the importance of interactions among metal atoms in clusters on substitutional properties. Initial results on the kinetics of CO substitution with PEt_3 in $HFeCo_3(CO)_{10}[PEt_3]_2$ to afford $HFeCo_3(CO)_9[PEt_3]_3$ reveal this process to be significantly decelerated in the presence of the radical scavenger 2,6-di-t-butylphenol, suggesting a radical-chain mechanism in this instance.

Acknowledgments

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