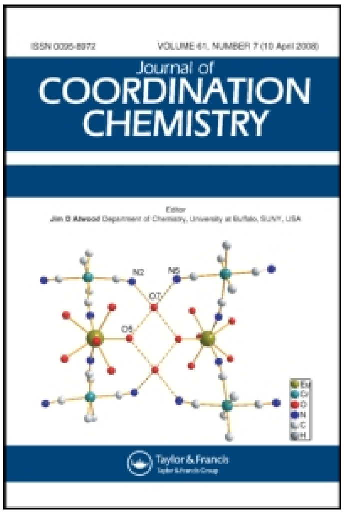

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KINETICS AND MECHANISM OF CO SUBSTITUTION BY PHOSPHITES OF $Co_4(CO)_{12}$

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The otherwise very fast CO substitution of $Co_4(CO)_{12}$ by $P(OMe)_3$ and $P(OEt)_3$ in aprotic solvents, affording phosphite-monosubstituted products was retarded by the use of $CHCl_3$ as solvent. This made it possible to investigate these reactions by conventional methods. Kinetic data were obtained by following changes in IR spectra during reaction. The rates show predominantly a ligand-dependent pathway, with the usual two-term rate law, rate = $(k_1 + k_2[P(OR)_3])[Co_4(CO)_{12}]$. It is suggested that the rates are retarded in protonic solvents by decreasing the nucleophilicity of phosphites due to a hydrogen bonding interaction between the H atom of $CHCl_3$ and the O atoms of the ligands.

Keywords: $Co_4(CO)_{12}$, CO substitution, kinetics, phosphite nucleophiles

INTRODUCTION

Although the kinetics of CO substitution by phosphine and phosphite ligands of $Ir_4(CO)_{12}$ has been investigated in considerable detail,[1] the mechanism of CO substitution in $Co_4(CO)_{12}$[2] and in $Rh_4(CO)_{12}$[3] is less well understood. It appears that the Co and Rh tetranuclear carbonyl clusters are both exceedingly susceptible to nucleophilic attack. Darensbourg and Incorvia[2] studied CO substitution of $Co_4(CO)_{12}$ by the entering ligands PPh_3,$P(OMe)_3$ and ^{13}CO in hexane solution. They found the rates of substitution to be strongly dependent on the nature of the incoming ligand, and that measurable rates by conventional techniques were possible only for the poorest nucleophile, ^{13}CO. The mechanistic results for the rapid CO substitution by PPh_3 in $Co_4(CO)_{12}$ and in $Rh_4(CO)_{12}$ were investigated[3] by using the stopped-flow method. This study showed that the rates of associative CO substitution of the $M_4(CO)_{12}$ clusters vary in the order Co $<<$ Rh $>>>$ Ir. However, detailed kinetic studies, including the determination of activation parameters, were not carried out because of problems with the systems.

EXPERIMENTAL

$Co_4(CO)_{12}$ was obtained from Strem Chemical Co., and used as received. The phosphites $P(OMe)_3$ and $P(OEt)_3$ were distilled over Na under N_2 and stored under N_2. Triphenyl phosphine was purified by recrystallization from ethanol. Chloroform was dried with P_2O_5 and distilled under N_2 prior to use.

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The reactions were followed by IR, with use of a Nicolet-4DX FTIR spectrophotometer and a special, variable temperature IR cell with 0.5-mm CaF_2 windows. Constant temperature was maintained to within ±0.2°C. All the reactions were carried out in oxygen-free chloroform solutions (in the dark) and under conditions where the concentrations of phosphites were at least 10 times greater than that of $Co_4(CO)_{12}$. In a typical experiment, a $CHCl_3$ solution of the appropriate nucleophile was syringed into a flask. After 10 min of temperature preequilibration in a temperature bath, the flask was rigorously shaken, an aliquot was syringed into the special, temperature constant IR cell and sealed with rubber septa. The resultant spectral changes were monitored. The products were characterized by IR spectra.

Plots of $\ln(A_t - A_\infty)$ *vs* time for disappearance of $Co_4(CO)_{12}$ were linear over 2 half-lives (linear correlation coefficient >0.997). The slope of these lines gave values of k_{obsd}.

RESULTS AND DISCUSSION

The reaction under consideration is the substitution of a ligand for CO in $Co_4(CO)_{12}$, (*1*).

$$Co_4(CO)_{12} + L \longrightarrow Co_4(CO)_{11}L + CO \qquad (1)$$
$$(L = P(OCH_3)_3,\ P(OC_2H_5)_3)$$

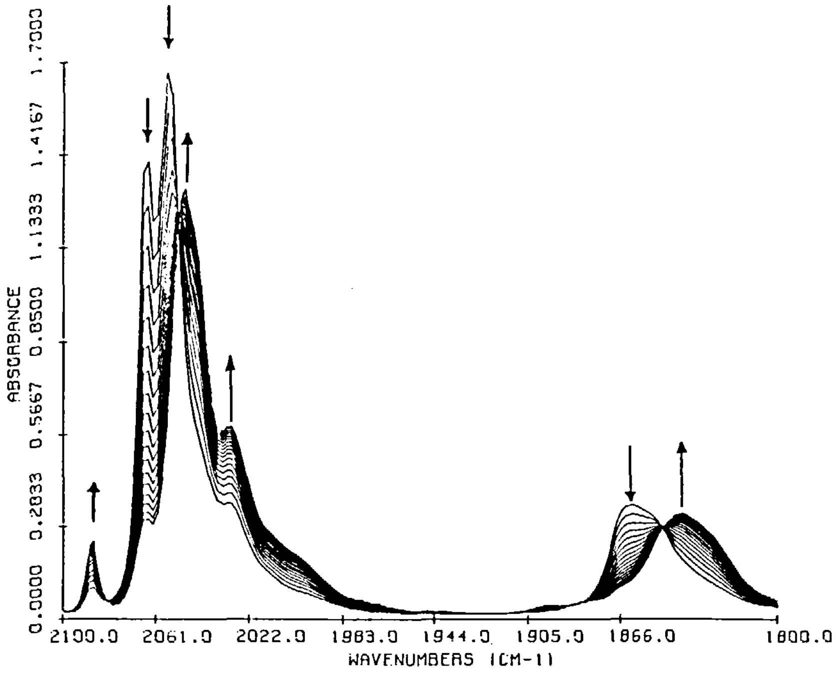

FIGURE 1 IR ν_{CO} absorbance changes *vs* time for the reaction $Co_4(CO)_{12} + P(OMe)_3 \rightarrow Co_4(CO)_{11}P(OMe)_3 + CO$ in $CHCl_3$ at 28.3°C.

TABLE I

Observed rate constants for reactions of $Co_4(CO)_{12}$ with L, (*1*).

L	T, °C	10^3[L], M	10^3 k_{obs}, s^{-1}
$P(OMe)_3$	18.1	4.80	0.782
		8.00	1.18
		11.2	1.60
		14.4	2.02
	23.2	4.80	0.999
		6.40	1.30
		8.00	1.59
		9.60	1.89
	28.2	4.80	1.41
		6.40	1.82
		8.00	2.27
		9.60	2.67
	33.0	4.80	1.76
		6.40	2.29
		8.00	2.86
		9.60	3.46
$P(OEt)_3$	28.2	4.23	1.65
		5.64	2.22
		7.05	2.81
		8.46	3.33

The rates of reaction in $CHCl_3$ solution were monitored by following changes in the IR spectra at 2064 cm^{-1} with time. Spectral changes for a typical reaction mixture show good isosbestic points (Fig. 1), which suggest stoichiometric reaction affording monosubstituted products. The products had IR spectra in agreement with reported spectra of known compounds.[4] $Co_4(CO)_{11}P(OMe)_3$, for example, had bands at 2087.1(m), 2048.4(vs), 2030.9(ms), 2000.4(br), and 1840.4(m) cm^{-1}. Plots of $-\ln(A_t - A_\infty)$ *vs* time for the reactions were linear for 2 half-lives. Observed rate constants, k_{obs}, for different concentrations of entering phosphite are given in Table I, and plots of k_{obsd} *vs* $[P(OMe)_3]$ show a predominantly ligand-dependent pathway with non-zero intercepts, as shown in Figure 2. The second-order rate constants and activation parameters are given in Table II. The $\sim 10^{-4}(s^{-1})$, of magnitude, intercepts could not be measured accurately because of much higher values of the slopes, but the plots did show non-zero intercepts at higher temperature. This kinetic behaviour is consistent with the usual two-term rate law, (*2*).

$$\text{rate} = (k_1 + k_2[L])[Co_4(CO)_{12}] \qquad (2)$$

This rate law suggests parallel pathways of dissociation (k_1) and association (k_2). The associative process is supported by the characteristic low values of ΔH_2^{+} and negative ΔS_2^{+} (Table II).

The fact that earlier studies[2] showed the rate for CO exchange with $Co_4(CO)_{12}$ is much slower than that of CO substitution by phosphorus donor ligands, also

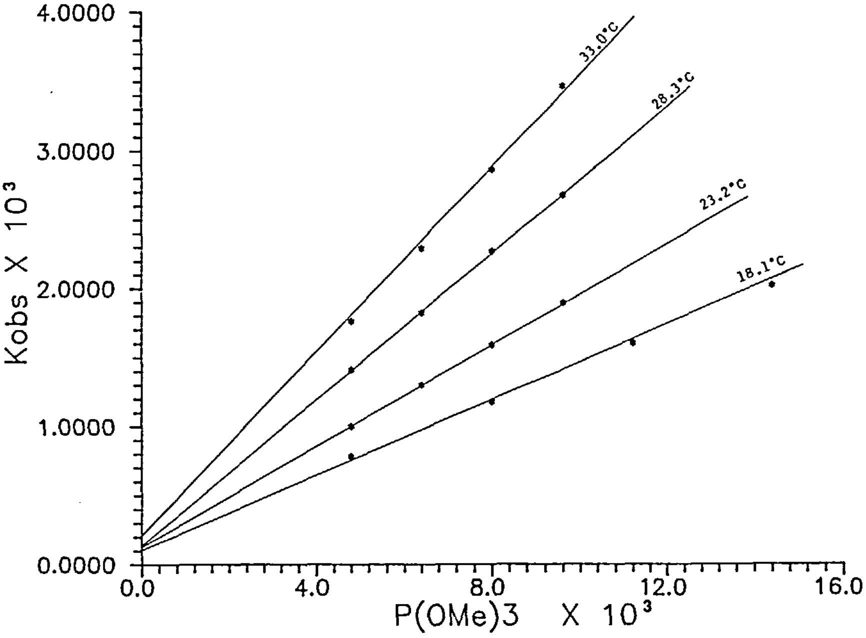

FIGURE 2 Plots of k_{obs} *vs* [P(OMe)$_3$] at different temperatures for the reaction $Co_4(CO)_{12}$ + P(OMe)$_3$ → $Co_4(CO)_{11}$P(OMe)$_3$ + CO in $CHCl_3$.

TABLE II

Second-order rate constants and activation parameters of $Co_4(CO)_{12}$ with P(OMe)$_3$, (*1*).

L	T, °C	k_2, $M^{-1}s^{-1}$	$\Delta H_2^\ddagger$ kcal/mol	$\Delta S_2^\ddagger$ cal/mol.deg.
P(OMe)$_3$	18.1	0.129	11.5 ± 0.27	−23.2 ± 0.91
	23.2	0.185		
	28.3	0.264		
	33.0	0.354		
P(OEt)$_3$	28.2	0.399		

strongly suggests the existence of an associative process in the rate-determining step. It was proposed that formation of adducts such as $Co_4(CO)_{12}[P(OMe)_3]$[2] and $Ir_4(CO)_{12}L$[1] by nucleophilic attack at the metal centre is the first step of the reaction, accompanied by a synchronous bond-breaking process. The first comparison[3] of the rates of these parent tetranuclear clusters gave an order for the associative process of Rh > > Co > Ir. Kinetic studies[5] for the $M_4(CO)_9[HC(PPh_2)_3]$ (M = Co, Rh, Ir) cluster family show the same order. The results reported here are consistent with earlier findings that the rates of associative substitution of $M_4(CO)_{12}$ decrease in the order Co > Ir (Table III). The higher reactivity of the cobalt cluster may be attributed in part to the lower average bond enthalpy of the Co–Co bond (19.8 kcal/mol)* compared with that of the Ir–Ir bond (31.1 kcal/mol),[6] in accord with a synchronous M–M bond cleavage.

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* Here, 1 cal = 4.184J.

TABLE III
Second-order rate constants and activation parameters of $Co_4(CO)_{12}$ with $Ir_4(CO)_{12}$ with $P(OEt)_3$ at 28.2°C.

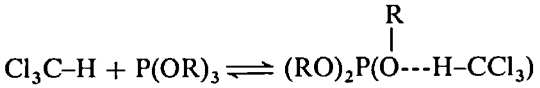
Complex	L	k_2, $M^{-1}s^{-1}$
$Co_4(CO)_{12}$[a]	$P(OEt)_3$	3.39×10^{-1}
$Ir_4(CO)_{12}$[b]	$P(OEt)_3$	2.74×10^{-3}

[a] This work, in $CHCl_3$. [b] In C_2Cl_4, estimated from ref. 1b.

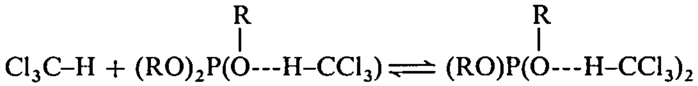
The reactions of $Co_4(CO)_{12}$ with phosphines and phosphites in hexane are too fast to follow using conventional methods.[2] However, we observed that phosphines continue to react rapidly in protonic solvents, but the reactions of phosphites are markedly retarded when $CHCl_3$ is used as a solvent. This strong solvent effect may be caused by a hydrogen bonding interaction between $CHCl_3$ and the phosphite ligands. There can be two types of hydrogen bonding interaction in the $CHCl_3$ solutions. One is between the H atom of $CHCl_3$ and a P atom, (*3*).

$$Cl_3CH + P(OR)_3 \rightleftharpoons Cl_3C\text{-}H\text{---}P(OR)_3 \tag{3}$$

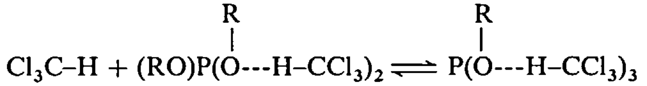
Hydrogen bonding may also take place between the H atom of $CHCl_3$ and the O atoms of the phosphite ligands, (*4*)-(*6*).



$$Cl_3C\text{-}H + P(OR)_3 \rightleftharpoons (RO)_2P(\overset{R}{\overset{|}{O}}\text{---}H\text{-}CCl_3) \tag{4}$$



$$Cl_3C\text{-}H + (RO)_2P(\overset{R}{\overset{|}{O}}\text{---}H\text{-}CCl_3) \rightleftharpoons (RO)P(\overset{R}{\overset{|}{O}}\text{---}H\text{-}CCl_3)_2 \tag{5}$$



$$Cl_3C\text{-}H + (RO)P(\overset{R}{\overset{|}{O}}\text{---}H\text{-}CCl_3)_2 \rightleftharpoons P(\overset{R}{\overset{|}{O}}\text{---}H\text{-}CCl_3)_3 \tag{6}$$

Both types of hydrogen bonding, to P (*3*) and to O (*4–6*), are expected to retard the rates of nucleophilic attack by phosphite ligands. Hydrogen bonding to P would decrease the concentration of free $:P(OR)_3$, with its available Lewis base electron pair needed for nucleophilic attack at the metal. However, hydrogen bonding at P is also expected to take place to much the same extent with phosphines of similar proton basicities as phosphites. Yet, experiments show that the rate of reaction of PPh_3 with $Co_4(CO)_{12}$ is not markedly retarded in $CHCl_3$ compared with hexane as solvent. Since the basicity[7] of PPh_3 is similar to that of $P(OMe)_3$ and of $P(OEt)_3$, it is believed that retardation in rates of reaction observed for the phosphites is a result of hydrogen bonding to O (*4–6*). This hydrogen bonding tends to remove electron density from the O atom, and inductively from the P atom. The inductive effect is to decrease the Lewis basicity, or nucleophilic strength, of the P atom of the phosphite ligand. The result of this is a marked decrease in the rates of reaction of $Co_4(CO)_{12}$ with phosphites in $CHCl_3$ compared to other aprotic solvents. That hydrogen bonding in phosphites seems to prefer the O atoms to the P atom is to be expectec knowing full well that the first row elements (N, O, F) form the strongest hydroge bonds.

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