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Kinetics and mechanisms of CO substitution of $M_4(CO)_{11}L(M = Co, Ir; L = PPh_3, P^nBu_3, P(OMe)_3, P(OEt)_3)$ with L in the presence of Me_3NO *

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Abstract

Reported are rates of CO substitution by L of $M_4(CO)_{11}L(M = Co, Ir; L = PPh_3, P^nBu_3, P(OMe)_3, P(OEt)_3)$ in the presence of added Me_3NO. The rate law is the same as that found earlier on such reactions, being first-order in the concentrations of metal carbonyl and of Me_3NO but zero-order in ligand concentration. The Ir compounds react from 2 to 7 times faster than do the corresponding Co compounds, and for each the rates of reaction with changes in ligand decrease in the order $P(OMe)_3 > P(OEt)_3 > P^nBu_3$. The results are compared with earlier studies on the $M_3(CO)_{12}$ and $M_3(CO)_{11}L$ (M = Fe, Ru, Os) clusters, where it was found that the reactivities decrease in the order Fe > Ru > Os. That this order differs from that now reported (Co < Ir) for the $M_4(CO)_{11}L$ clusters is discussed in terms of the presumed important contribution of CO bridging to the rates of associative reactions in metal carbonyl clusters.

Introduction

Our previous studies on the kinetics for reactions of $M_3(CO)_{12}$ [1] and of $M_3(CO)_{11}L$ [2] (M = Fe, Ru, Os, L = P donor ligands) clusters with Me_3NO in the presence of another entering ligand have shown that the rates of CO substitution of these metal clusters decrease in the order Fe > Ru > Os. The suggestion was made that the order of reactivity of these clusters decreases with decreasing tendency of bridging CO formation in the transition state for reaction. Since bridging COs are believed to be more electron withdrawing than are terminal COs, the formation of bridging CO in the transition state should better accommodate a developing negative charge in the transition state by nucleophilic attack. This explanation finds support in the results of a kinetic study on substitution of CO by PPh_3 for the mononuclear carbonyls $M(CO)_5$ (M = Fe, Ru, Os) in the presence of Me_3NO [3]. The rates of reaction for $M_3(CO)_{12}$ clusters are much faster than for $M(CO)_5$. For

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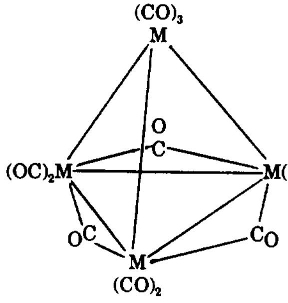
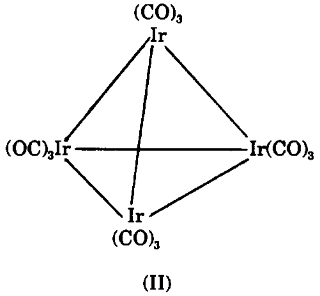
* Dedicated to the memory of Professor Piero Pino.

iron the rate difference is about 2 orders of magnitude, whereas it is approximately 1 order of magnitude for ruthenium, and $Os_3(CO)_{12}$ reacts at about the same rate as does $Os(CO)_5$. That the largest rate difference between $M(CO)_5$ and $M_3(CO)_{12}$ is for iron and the smallest is for osmium was rationalized in terms of formation of bridging carbonyls in the transition state for reaction of the metal carbonyl clusters. This is believed to be the case because it is known that the degree of difficulty in forming bridging COs in $M_3(CO)_{12}$ and in $M_3(CO)_{11}L$ clusters increases in the order Fe < Ru < Os.

The presumed significance of bridging COs in the reactivities of $M_3(CO)_{12}$ prompts an investigation of clusters of the type $M_4(CO)_{12}$ (M = Co, Rh, Ir) which are known to have different structures. The Co and Rh compounds have one bridging CO ligand that spans each M–M bond in a basal plane of the M_4 tetrahedron (I) and the Ir compound has no bridging COs but only three terminal COs on each Ir atom (II). However, the structures of all three of the compounds $M_4(CO)_{11}L$ (L is an appropriate P donor ligand) were characterized in solution and in the solid state as having three bridging COs, one spanning each M–M bond in the basal plane (III) [4–6]. This makes these $M_4(CO)_{11}L$ clusters ideal candidates for a comparative mechanistic study to examine further the importance of the possible CO bridging concept for the reactivities of metal carbonyl clusters. Unfortunately, we have been unable to obtain kinetic data for the reactions of the $Rh_4(CO)_{11}L$ complexes because of their thermal substitution labilities, so reported here are only results for the Co and Ir complexes.



(I) (M = Co, Rh)



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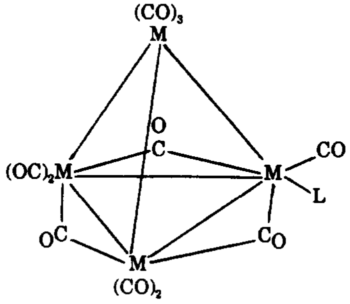


(III) (M = Co, Rh, Ir)

Experimental details

The carbonyl clusters $M_4(CO)_{12}$ (M = Co, Ir) were obtained from the Strem Chemical Co. and used as received. Manipulations involving metal carbonyl clusters were routinely carried out under a N_2 atmosphere by using standard Schlenk techniques. The $P(OR)_3$ compounds (Merck-Schuchardt) were distilled over Na and stored under N_2. P^nBu_3 was provided by the Shanghai Institute of Organic Chemistry. PPh_3 was purified by recrystallization from ethanol. $CHCl_3$ and C_2H_5OH were dried with P_2O_5 and $Mg(OC_2H_5)_2$, respectively, and distilled under N_2 prior to use. Trimethylamine *N*-oxide (Me_3NO) was synthesized and purified by the literature method [7].

The reactions were followed by IR, using a Nicolet-5DX FT-IR spectrophotometer and a special variable temperature IR cell with 0.5 mm CaF_2 windows provided by the Lanzhou Institute of Chemical Physics. Constant temperature was maintained to within $\pm 0.2\,°C$. All the reactions were performed under pseudo-first-order conditions with the concentration of Me_3NO and of ligand being at least 10 times greater than that of $M_4(CO)_4L$, which were obtained in situ.

Plots of $\ln(A_t - A_\infty)$ vs time for disappearance of $M_4(CO)_{11}L$ were linear over two half-lives (linear correlation coefficients > 0.997). The slope of these lines gave values of k_{obsd}.

Results and discussion

Rates for the reaction (eq. 1) of $M_4(CO)_{11}L$ in $CHCl_3$–C_2H_5OH (V/V, 29 : 1)

$$M_4(CO)_{11}L + Me_3NO + L \rightarrow M_4(CO)_{10}L_2 + Me_3N + CO_2 \qquad (1)$$

mixed solvent with entering ligand (L = $P(OMe)_3$, $P(OEt)_3$, and P^nBu_3; and with PPh_3 when M = Ir) in the presence of Me_3NO were monitored by following changes in the IR absorption spectra with time. The reactants $M_4(CO)_{11}L$ were generated from $M_4(CO)_{12}$, and studied *in situ*. Spectral changes for all the reaction mixtures show good isosbestic points (Fig. 1), suggesting stoichiometric reactions affording disubstituted products. The complexes $M_4(CO)_{11}L$ and $M_4(CO)_{10}L_2$ had IR spectra in agreement with spectra reported in literature [8,9].

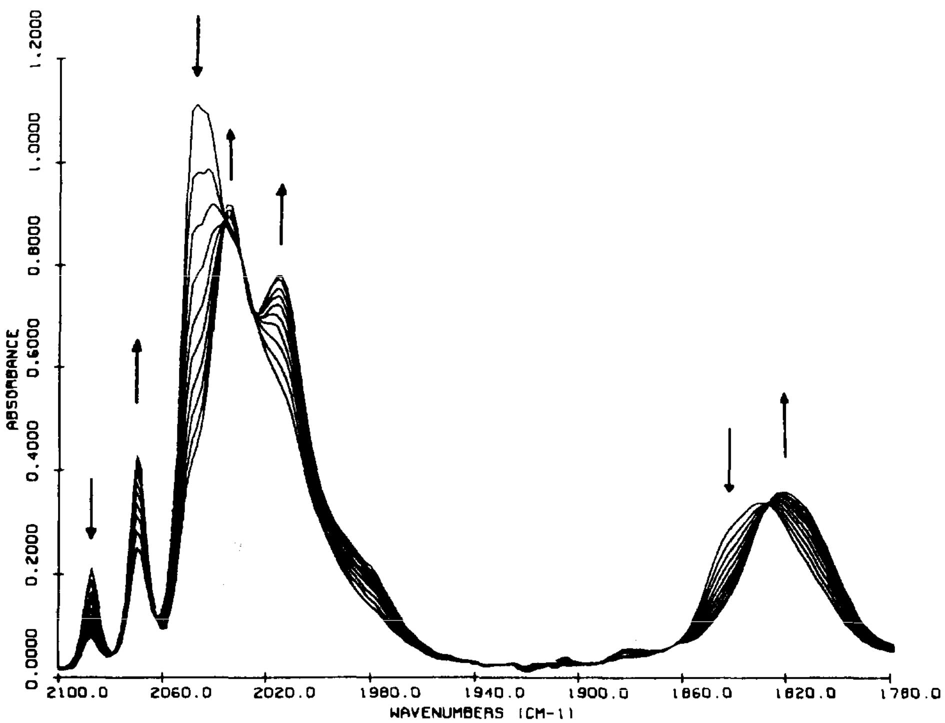


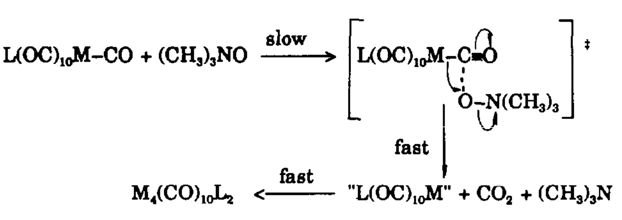
Fig. 1. IR ν(CO) absorbance changes vs. time for the reaction $Co_4(CO)_{11}P(OMe)_3 + Me_3NO + P(OMe)_3 \rightarrow Co_4(CO)_{10}[P(OMe)_3]_2 + Me_3N + CO_2$ in $CHCl_3$-EtOH (V/V 29:1) at 26.6°C.

Plots of k_{obsd} vs Me_3NO concentration show a first order dependence on trimethylamine *N*-oxide concentration (Fig. 2), and the rates of reaction are zero order in entering ligand concentration (Table 1). Thus, CO substitution obeys the second-order rate law given by eq. 2:

$$\text{rate} = k_2[M_4(CO)_{11}L][Me_3NO] \qquad (2)$$

This rate law and kinetic behavior is the same as the reported earlier [1–3] for the corresponding reactions of $M_3(CO)_{12}$ and of $M(CO)_5$ carbonyls of the iron triad, and thus provides a common basis for comparison. The mechanism proposed earlier [1] is consistent with the kinetic data obtained on these systems (Scheme 1).

Although the C-atom of which CO in the cluster is attacked by the O-atom of $(CH_3)_3NO$ is not known, we agree with one of the referees that it could occur on one of the COs at the apical $M(CO)_3$ center. This seems plausible, because these



Scheme 1.

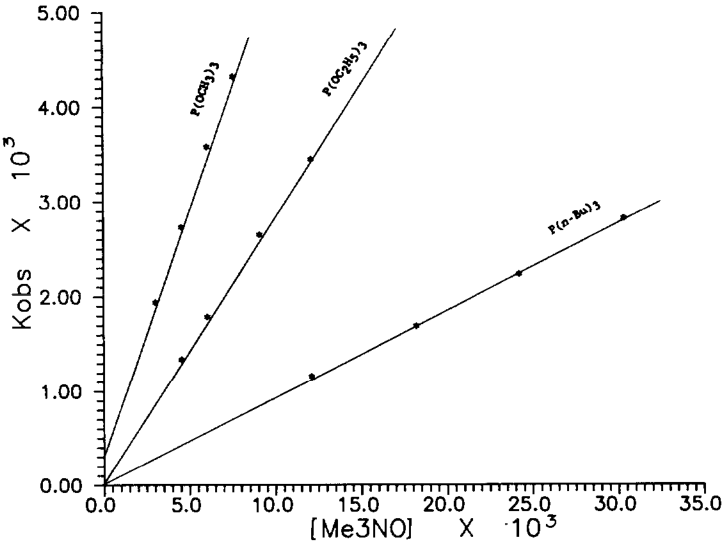


Fig. 2. Plot of k_{obsd} vs [Me_3NO] for the reaction $Co_4(CO)_{11}L + Me_3NO + L \rightarrow Co_4(CO)_{10}L_2 + Me_3N + CO_2$ in $CHCl_3$–EtOH (V/V 29:1) at 26.6°C.

COs are the ones most positively charged in the cluster, and this can be followed by rearrangement to give the final product.

The second order rate constants are given in Table 2. The rates for the reactions of $Co_4(CO)_{11}L$ with Me_3NO for changes in L decrease in the order $P(OMe)_3 > P(OEt)_3 > P^nBu_3$, consistent with what was observed in $Mo(CO)_5L$ [10] and in $M_3(CO)_{11}L$(M = Fe, Ru, Os) [2]. These phosphorus ligands are better σ-donors and poorer π-acceptors than is the π-acid CO ligand. The substitution of a CO ligand with a phosphorus ligand increases the π-back bonding from metal to the other COs, which then increases the electron density on the carbonyl carbon atoms and retards nucleophilic attack of the O-atom at carbonyl carbon. This electronic effect of the phosphorus ligands observed with $Co_4(CO)_{11}L$ appears not to be so strong for the reaction of $Ir_4(CO)_{11}L$ with Me_3NO. The electron density which is expected to be mainly transferred through the chemical bonds between the L–M–M–CO groups [2] of the clusters is perhaps transferred less efficiently in $Ir_4(CO)_{11}L$ than in $Co_4(CO)_{11}L$ because $Ir_4(CO)_{11}L$ has longer M–M bonds than does $Co_4(CO)_{11}L$.

Table 1

Observed rate constants for reactions (eq. 1) of $M_4(CO)_{11}L$ with L in presence of Me_3NO at 26.6°C in $CHCl_3$–EtOH (V/V 29:1)

Compound	L	10^3 [L] *M*	10^3 k_{obsd} (s^{-1})
$Co_4(CO)_{11}P(OEt)_3$ [a]	$P(OEt)_3$	3.23	2.65
		6.45	2.67
		9.68	2.79
$Ir_4(CO)_{11}PPh_3$ [b]	PPh_3	1.02	2.53
		3.08	2.71
		6.16	2.61

[a] [Me_3NO] = 9.08×10^{-3} *M*. [b] [Me_3NO] = 2.29×10^{-3} *M*.

Table 2

Second-order rate constants for the reactions (eq. 1) of $M_4(CO)_{11}L$ with L in the presence of Me_3NO at 26.6 °C $CHCl_3$–EtOH (V/V, 29 : 1)

M	L[a]	ΔHNP (mv)	θ[b] (deg)	k_2 (M^{-1} s^{-1})
Co	$P(OMe)_3$	580	109	0.528
	$P(OEt)_3$	520	109	0.279
	P^nBu_3	131	132	0.091
Ir	$P(OMe)_3$	580	109	0.998
	$P(OEt)_3$	52	109	0.851
	P^nBu_3	131	132	0.676
	PPh_3	573	145	1.28

[a] Difference in half neutralization potentials of ligands L from that of *N,N'*-diphenylguanidine as a standard. See C.A. Streuli *Anal. Chem.*, 32 (1960) 985; R.C. Bush, and R.J. Angelici, *Inorg. Chem.*, 27 (1988) 681. [b] Cone angle of ligands L. See C.A. Tolman, *J. Am. Chem. Soc.*, 92 (1970) 2956.

It should be noted that Darensbourg and Incorvia [9] have investigated the kinetics of CO substitution of $Co_4(CO)_{10}[P(OCH_3)_3]$. They find the thermal substitution reaction to be slower than the reaction in the presence of Me_3NO, thus removing any doubt of a competitive thermal reaction between $P(OCH_3)_3$ and $Co_4(CO)_{10}[P(OCH_3)_3]$.

The most interesting observation of this study is that $Ir_4(CO)_{11}L$ reacts faster than does $Co_4(CO)_{11}L$ for all the corresponding compounds studied. The complexes, $Co_4(CO)_{11}PPh_3$ [4] and $Ir_4(CO)_{11}PPh_3$ [5] have been characterized by single crystal structure and IR, respectively. The results show that both of the complexes have three bridging carbonyl groups spanning each M–M bond in the basal plane, and the PPh_3 ligand occupying an axial coordination site in the clusters (see structure III). The IR band patterns in the ν(co) region of $Co_4(CO)_{11}L$ and of $Ir_4(CO)_{11}L$ (L = $P(OMe)_3$, $P(OEt)_3$, P^nBu_3) are very similar with respect to number of peaks and the relative intensities of their PPh_3-substituted analogs, thus these reactants are assumed to be isostructural. With such analogous structures, it is expected that effects of bridging carbonyl groups in the clusters on the reaction transition states may not differ significantly. Consequently the relative stabilities of the transition states due to bridging COs would have about the same effect on the rates of the reactions of $Co_4(CO)_{11}L$ and of $Ir_4(CO)_{11}L$. Therefore, the ground states may predominate in determining the order of reactivity. This is contrary to what was observed for the iron triad metal clusters where the CO bridging differs and the relative reactivities decrease in the order Fe > Ru > Os [1,2].

Table 3

Rate constants (k_2, M^{-1} s^{-1}) for O-atom transfer reactions of $Os_3(CO)_{11}L$ and of $Ir_4(CO)_{11}L$ with Me_3NO

L	$Ir_4(CO)_{11}L$[a]	$Os_3(CO)_{11}L$[b]
CO	1.72	0.784
PPh_3	1.28	0.018

[a] At 26.6 °C in $CHCl_3$–EtOH (V/V 29 : 1), kinetic data were collected for reaction of $Ir_4(CO)_{12}$ with PPh_3 in the presence of Me_3NO by monitoring UV-Vis spectral changes. [b] At 4.5 °C in $CHCl_3$. Data from ref. 2.

Further evidence supporting the suggestion that the ground state stability may dominate the reactivities of the $M_4(CO)_{12}$ clusters, whereas the transition state stabilities may dominate the reactivities of the $M_3(CO)_{12}$ clusters can be cited. Although the reaction rates of $Ir_4(CO)_{12}$ and of $Ir_4(CO)_{11}PPh_3$ with Me_3NO are about the same, $Os_3(CO)_{12}$ reacts with Me_3NO 45 times faster than does $Os_3(CO)_{11}PPh_3$ [2] (Table 3). Since neither of the osmium compounds have bridging COs, the difference in their rates of reaction is believed largely due to the PPh_3 electronic effect on their ground states. Much the same ground state effect is expected to be experienced by the corresponding $Ir_4(CO)_{12}$ versus $Ir_4(CO)_{11}PPh_3$ clusters, but these react at about the same rates. One clear difference between the Os_3 and the Ir_4 cluster is that neither of the Os compounds have bridging COs, whereas $Ir_4(CO)_{12}$ does not and $Ir_4(CO)_{11}PPh_3$ does have bridging COs. Since the bridging CO groups in $Ir_4(CO)_{11}PPh_3$ may stabilize the transition state by delocalizing the increased electron density, imposed on the system by the attacking nucleophile, greater stability of the transition state results in a rate enhancement that compensates for the rate retardation caused by the PPh_3 ligand electronic effect in the ground state. The net result is then the experimental observation that $Ir_4(CO)_{12}$ and $Ir_4(CO)_{11}PPh_3$ react at similar rates with Me_3NO.

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Supplementary material available. A table (Table 4) of observed rate constants, k_{obsd} s^{-1}, for reactions of $M_4(CO)_{11}L$ at different concentrations of $(CH_3)_3NO$ is available from the authors.

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