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Kinetics of some Reactions of $Ru_3(CO)_{10}$(μ-bisdiphenylphosphinomethane)

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Abstract

The kinetics of substitution of $Ru_3(CO)_{10}$(dppm) with several relatively weak nucleophiles to form $Ru_3(CO)_9$(dppm)(L) in benzene have been studied over the temperature range 30–60 °C. At lower temperatures the observed first order rate constants for reaction under N_2 or air are independent of the nature or concentration of the nucleophile but reactions are retarded by CO in a way characteristic of a simple CO dissociative mechanism. It is, however, also possible that the rate determining step is a form of isomerization of the cluster and some possibilities are discussed. In terms of ΔH^* the dppm substituent is found to be more labilizing than two PPh_3 substitutents, possibly because of a greater strain in the cluster caused by the bridging dppm ligand. At higher temperatures another reaction path appears to be available for reaction with PPh_3, and this accounts for *ca.* 30% of the rate at 50 °C. A similar path has been reported for reaction with dppm but some difficulties arise which suggest that the mechanism proposed for that reaction is at least oversimplified.

Introduction

Metal carbonyl clusters that contain bridging ligands are of interest as analogues of polymer supported carbonyl clusters [1]. In spite of this, very few kinetic studies of such complexes have been reported [2–4]. Any stereochemical restraints caused by the presence of the bridging ligands [5] are likely to have effects on the mechanisms and rates of the reactions, as well as possibly on the nature of the products. More information regarding these effects is therefore desirable. We report here the results of a kinetic study of the reactions of $Ru_3(CO)_{10}$(dppm) with a number of relatively weak P- or As-donor nucleophiles to form $Ru_3(CO)_9$(dppm)(L) [6]. The structure of $Ru_3(CO)_{10}$(dppm) has been reported [7] and the dppm ligand is in the plane of the Ru_3 cluster and bridges two of the Ru atoms. A kinetic study of the reaction of $Ru_3(CO)_{10}$(dppm) with dppm has also been reported [3].

Experimental

The cluster $Ru_3(CO_{10}$(dppm) was prepared as described elsewhere [3]. Benzene (BDH, AnalaR) was dried over molecular sieves. PPh_3(BDH), $AsPh_3$ (Aldrich), $P(C_6H_{11})_3(PCy_3)$ and PPh_2Et (Strem), $P(OEt)_3$(BDH), and 1,2-dichloroethane (BDH, Omnisolv) were used as received.

The cluster $Ru_3(CO)_9(dppm)(PPh_3)$ was prepared by reaction of $Ru_3(CO)_{10}$(dppm) (e.g. 37.5 mg, 0.04 mmol) with 1–4 molar equivalents of PPh_3 (10–40 mg) in 1,2-dichloroethane at 50 °C for 1 h. The product was separated by TLC and isolated from $CHCl_3$ solution by evaporation of the solvent.

Anal. Calc. for $Ru_3(CO)_9(dppm)(PPh_3)$: C, 51.96; H, 3.08; P, 7.74. Found: C, 51.9; H, 3.05; P, 8.23%. The IR spectrum in $C_2H_4Cl_2$ showed bands at 2055-(w), 1997(s), 1980(vs), and 1950sh cm^{-1}, and the UV–Vis spectrum in benzene showed a band at 460 nm ($\epsilon = 9.5 \times 10^3$ M^{-1} cm^{-1}). The IR spectra are essentially identical with those in CH_2Cl_2 shown in Fig. 1 of ref. 6.

The kinetics in benzene were followed exactly as described elsewhere [3].

Results

The Course of the Reactions

Reactions with PPh_3 at all concentrations are accompanied by replacement of the band at 420 nm, due to $Ru_3(CO)_{10}$(dppm), by one at 460 nm of slightly higher intensity. Isosbestic points were apparent at *ca.* 400 and 425 nm and the changes were qualitatively exactly the same as those shown for the first stage of reaction with dppm in Fig. 1 of ref. 3. After the maximum intensity at 460 nm is reached the absorbance slowly decreases and the isosbestic points disappear. These further changes were not examined in detail but appear to be slower when reactions were carried out under CO.

When reactions were carried out at 60 °C in $C_2H_4Cl_2$ the IR spectrum due to $Ru_3(CO)_{10}$(dppm) was replaced over 30 min by one showing bands at 2055w, 1997s, 1980vs, and 1950sh. This spectrum remained essentially unchanged for another 30 min although further changes were evident over a period

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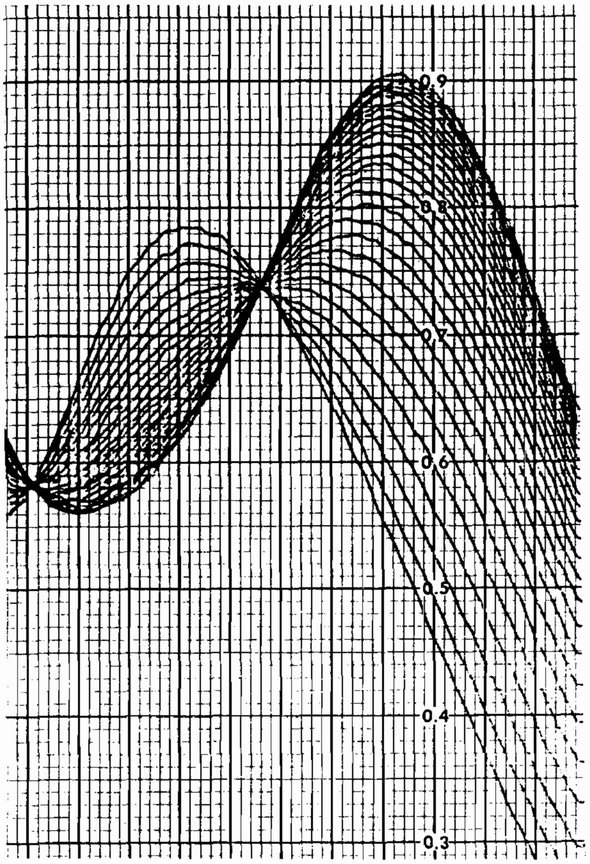


Fig. 1. Spectroscopic changes during reaction of $Ru_3(CO)_{10}$(dppm) with 0.12 M PCy_3 under CO.

of several hours. Isolation of $Ru_3(CO)_9(dppm)(PPh_3)$ after the initial, faster stage of reaction shows that the reaction can be described simply as in eqn. (1) ($L = PPh_3$) in agreement with studies reported elsewhere [6].

$$Ru_3(CO)_{10}(dppm) + L \longrightarrow Ru_3(CO)_9(dppm)(L) + CO \qquad (1)$$

Reactions with PCy_3 and $AsPh_3$ at all concentrations, and with $P(OMe)_3$ or $P(OEt)_3$ at low concentrations, showed similar changes in the UV–Vis spectra with bands growing in at 462, 448, 430, and 430 nm, respectively. Reaction with PPh_2Et at all but very high concentrations ($\gtrsim$ 1 M) showed growth of a band at 452 nm. Figure 1 shows an example of the spectroscopic changes observed for the reaction with PCy_3.

Reactions in $C_2H_4Cl_2$ with $AsPh_3$ and PPh_2Et, and with $P(OEt)_3$ at low concentrations, all showed the growth of IR spectra of essentially the same type as with PPh_3 (*i.e.* with bands at *ca.* 2060m, 2000s, and 1980vs) so it can be concluded that all these reactions are of the type shown in eqn. (1).

TABLE I. Rate Constants for Reaction of $Ru_3(CO)_{10}$(dppm) with several Nucleophiles at 40.6 °C in Deoxygenated Benzene

L	[L] (M)	$10^4 k_{obs}$[a] (s^{-1})	σ (k_{obs})[b] (%)
PPh_3	0.0037–0.0136	2.04 ± 0.05	4.6
PPh_2Et	0.0256–0.205	1.57 ± 0.03	4.2
$P(OMe)_3$	0.0017–0.0085	1.72 ± 0.08	9.7
$AsPh_3$	0.0130–0.104	1.48 ± 0.04	4.6
dppm[c]	0.0264–0.422	1.94 ± 0.04	4.4

[a] The uncertainties are based on the internal consistency of the data for a particular nucleophile. The average value of 10^4 k_{obs} for all the nucleophiles is 1.75 ± 0.11 s^{-1}, the probable error for determination of k_{obs} for an individual nucleophile being *ca.* 14%. [b] The probable error for an individual measurement based on the internal consistency of the results for each nucleophile considered separately. [c] See ref. [3].

Kinetics

Reactions in benzene were followed by monitoring the growth of the product bands at 430–460 nm. Any subsequent decreases in intensity were relatively quite slow although they were somewhat more pronounced at higher temperatures.

Initial results (Table I) showed that first order rate constants were generally independent of the nature and concentrations of weak nucleophiles, and equal to those for reactions of stronger ones at low concentrations. This indication of a conventional CO dissociative mechanism suggested that reactions with some nucleophiles should be studied in more detail, particularly with respect to the effect of CO on their rates.

Reactions with PPh_3

Rate constants for reactions under 1 atm. CO increased with increasing $[PPh_3]$ towards a limiting value as shown in Fig. 2 for data at 49.8 °C. A plot of $1/k_{obs}$ against $1/[PPh_3]$ was linear and showed that the data are in accord with eqn. (2) ($L = PPh_3$). A linear least-squares analysis was carried out in which each value

$$k_{obs} = \{ak(\lim)_{CO}[L]\}/\{1 + a[L]\} \qquad (2)$$

of $1/k_{obs}$ was assumed to have the same probable error, expressed as a percentage. The analysis led to the values $k(\lim)_{CO} = (4.74 \pm 0.13) \times 10^{-4}$ s^{-1} and $a = 41 \pm 6$ M^{-1} where the uncertainties are standard deviations. The probable error of an individual measurement of k_{obs} was ±10.3%. The continuous line in Fig. 2 was drawn according to these values.

Reactions in the absence of CO also proceed according to good first order kinetics. The rate constants are independent of $[PPh_3]$ and are unaffected by whether reactions are carried out in solutions that

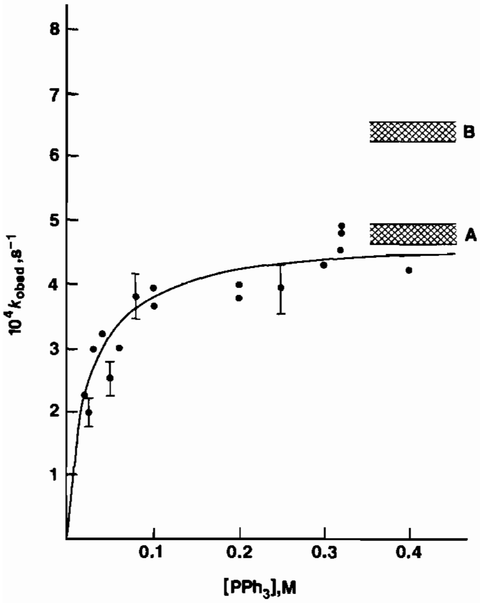


Fig. 2. Dependence of k_{obs} on $[PPh_3]$ for reaction of $Ru_3(CO)_{10}(dppm)$ with PPh_3 in benzene at 49.8 °C under 1 atm. CO. The cross hatching A shows the limiting rate (± its standard deviation), at very high $[PPh_3]$ predicted from a least squares analysis, and the cross hatching B shows the average rate constant found at 49.8 °C for reaction under air or N_2. The continuous line is drawn according to the least squares parameters and the error bars correspond to the derived probable error of ±10.3% for an individual measurement (see text).

have been deoxygenated by bubbling with N_2 or in ones equilibrated with air. A group of 21 rate constants was obtained for reactions with $[PPh_3]$ = 0.0025–0.50 M at 49.0–50.5 °C. Each value was adjusted to what it would have been at 49.8 °C (the temperature at which the reactions under CO were studied) by use of the subsequently determined activation parameters (see below). An average value of $(6.59 \pm 0.13) \times 10^{-4}$ s^{-1} was obtained with $\sigma(k_{obs}) = \pm 8.9\%$.

The dependence of the rate constants on [CO] was studied with $[PPh_3] \geqslant 0.3$ M. These values of $[PPh_3]$ were sufficient to bring the rate constants virtually up to their limiting values, according to the plot in Fig. 2, for those reactions carried out under atmospheres containing <100% CO. As before, small corrections were applied for the temperature differences (⩽0.7 °C) between sets of runs and the dependence of k_{obs} on [CO] at 50.0 °C is shown in Fig. 3.

The temperature dependence of the rate constants for reactions under air or N_2 and under 100% CO are shown in Table II. The data for reactions under 100% CO were obtained with $[PPh_3] \geqslant 0.3$ M and small corrections (<10%) were applied to provide the limiting values that would have been obtained at very high values of $[PPh_3]$. These corrections were made according to the value of *a* reported above, the same value of *a* being assumed to apply at 40 and 60 °C as was found at 50 °C.

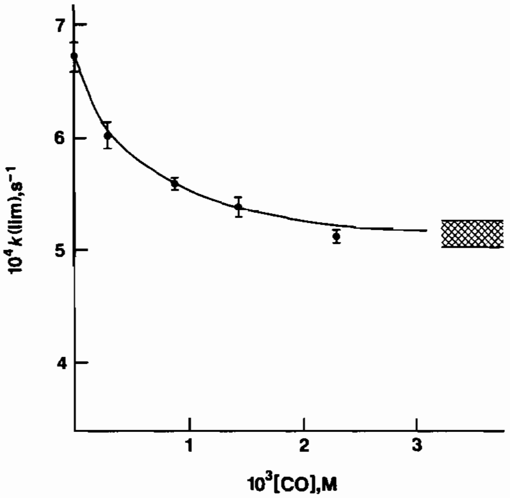


Fig. 3. Dependence of *k*(lim) on [CO] for reaction in benzene at 50 °C. *k*(lim) is the rate constant at $[PPh_3] = \infty$ estimated by averaging several values of k_{obs} with $[PPh_3] \geqslant 0.3$ M and extrapolating to high $[PPh_3]$ (see text). Error bars indicate standard deviations, and the cross hatching indicates the lower limit reached under 1 atm. CO (5.14×10^{-3} M).

TABLE II. Temperature Dependence of Rate Constants for Reaction with PPh_3

T (°C)	$10^4\ k_{obs}\ (s^{-1})$	
	under air or N_2[a]	under 100% CO[a, b]
28.0	0.328 ± 0.016(3)	[0.337]
29.0	0.390 ± 0.025(2)	[0.385]
32.5	0.564 ± 0.036(2)	[0.609]
35.0	0.822 ± 0.042(3)	[0.838]
40.0	1.77 ± 0.11(2)	1.57 ± 0.08(3)
41.5	1.91 ± 0.08(5)	[1.88]
50.0	6.74 ± 0.13(21)	5.14 ± 0.08(9)[c]
58.6	19.1 ± 0.64(7)	13.7(5)

[a] Numbers of individual values averaged to give listed rate constants are given in parentheses. [b] Values calculated according to the temperature dependence between 40 and 58.6 °C are given in brackets. [c] *cf.* 4.83 ± 0.13 from $[PPh_3]$-dependence.

Reactions with PCy_3

Reactions with PCy_3 were also found to be retarded by CO. Two sets of runs, at 49.8 and 50.9 °C, were carried out under CO with $[PCy_3]$ = 0.09–0.56 M, and data for both sets were in excellent accord with eqn. (2). Values of *a* were 17.3 ± 2.3 and 14.6 ± 0.7 M^{-1} for the two temperatures, respectively, values of $k(\text{lim})_{CO}$ being $(5.44 \pm 0.17) \times 10^{-4}$ and $(6.16 \pm 0.09) \times 10^{-4}$ s^{-1}, and values of $\sigma(k_{obs})$ were ±4.2 and ±2.3%. Rate constants for reactions under air or N_2 were $(5.49 \pm 0.12) \times 10^{-4}$ and $(6.38 \pm 0.12) \times 10^{-4}$ s^{-1}, respectively. Adjustment of these rate constants to what they would have been at 50.0 °C leads to the values, $(5.55 \pm 0.18) \times 10^{-4}$, $(5.57 \pm 0.09) \times 10^{-4}$, $(5.60 \pm 0.12) \times 10^{-4}$, $(5.76 \pm 0.12) \times 10^{-4}$ s^{-1}, respectively.

Reactions with $AsPh_3$ and PPh_2Et

Reactions with $[AsPh_3] = 0.03$–0.149 M under air at 49.7 °C gave a rate constant of $(6.25 \pm 0.14) \times 10^{-4}$ s^{-1} as the average of 9 measurements, and 7 reactions under 100% CO with $[AsPh_3] = 0.40$–0.70 M gave an average value, independent of $[AsPh_3]$, of $(5.75 \pm 0.15) \times 10^{-4}$ s^{-1}, $\sigma(k_{obs})$ for all these reactions being ±6.9%. Seven reactions with $[PPh_2Et] = 0.0122$–0.220 M at 40.6 °C under air gave a rate constant of $(1.87 \pm 0.06) \times 10^{-4}$ s^{-1} ($\sigma(k_{obs}) = \pm 9.4\%$). There does, however, appear to be a very slight increase of k_{obs} with $[PPh_2Et]$. A least-squares analysis according to eqn. (3)

$$k_{obs} = k_1 + k_2[PPh_2Et] \tag{3}$$

gave $k_1 = (1.73 \pm 0.04) \times 10^{-4}$ s^{-1} and $k_2 = (1.51 \pm 0.47) \times 10^{-4}$ M^{-1} s^{-1} with $\sigma(k_{obs}) = 4.6\%$.

Discussion

The nature of the spectroscopic changes for reactions with a variety of relatively weak nucleophiles suggest strongly that the initial reaction is always a simple substitution reaction as shown in eqn. (1) and as previously demonstrated for $L = PPh_3$ and $PPh_2(CH_2)_2Si(OMe)_3$ [6]. This substitution occurs at the unsubstituted Ru atom in The $Ru(CO)_4$ moiety to form a trisubstituted cluster with one P-donor substituent atom on each Ru atom. No evidence exists for disubstitution by P-donor ligands on one Ru atom in a Ru_3 cluster unless both the other Ru atoms are singly substituted.

Although there seem to be relatively large systematic differences between results for different nucleophiles (Table I) the internal consistency of data for the same nucleophile is excellent, even for data obtained with different samples of complex, at widely different times and, after adjustment to a constant temperature, at slightly different temperatures. This applies to reactions carried out under air or N_2 as well as under various partial pressures of CO. The reasons for the systematic differences between results for different nucleophiles may lie in problems with determining values for A_∞. Rate constants obtained from reactions showing an increase of absorbance are extremely sensitive to the values chosen for A_∞ and even small systematic uncertainties caused by small amounts of a subsequent reaction can have quite significant effects. This will tend not to affect the internal consistency (*i.e.* precision) for a given nucleophile because the effect will be constant for a group of runs done under similar conditions. It will, however, affect the accuracy of the results.

The results in Table I immediately suggest that reaction occurs via the classic CO dissociative path shown in eqns. (4) and (5)

$$Ru_3(CO)_{10}(dppm) \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} Ru_3(CO)_9(dppm) + CO \tag{4}$$

$$Ru_3(CO)_9(dppm) + L \xrightarrow{k_5} Ru_3(CO)_9(dppm)(L) \tag{5}$$

for which rate eqn. (6) applies. In the absence of CO

$$k_{obs} = (k_4(k_5/k_{-4})\{[L]/[CO]\}) / \{1 + (k_5/k_{-4})[L]/[CO]\} \tag{6}$$

$k_{obs} = k_4$, but under an atmosphere of CO values of k_{obs} should increase with [L] as shown in Fig. 2. In this case $k(\text{lim})_{CO}$ and a in eqn. (2) correspond to k_4 and $k_5/k_{-4}[CO]$, respectively. Taking $[CO] = 5.4 \times 10^{-3}$ M in benzene under 1 atm CO [3] we obtain $k_5/k_{-4} = 0.22 \pm 0.03$ for $L = PPh_3$ and 0.080 ± 0.004 for $L = PCy_3$ (obtained from the weighted average, 14.8 M^{-1}, of the two values of a reported above). These can be compared with the value of 0.124 ± 0.005 obtained for dppm [3] and they are all quite compatible with corresponding competition ratios for other coordinatively unsaturated metal carbonyls, both mononuclear and polynuclear [8, 9].

Although the data are quite consistent with a simple CO dissociative mechanism it has been pointed out [10] that the same kinetic behaviour could be obtained if the rate determining step were reversible isomerization to form a reactive isomer capable of reversibly substituting an L for a CO. This has to be borne in mind when the kinetic parameters are discussed.

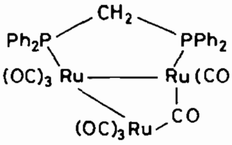
The data in Table II for the limiting rates under CO at 40–60 °C lead to the parameters $\Delta H^{\neq} = 23.4 \pm 0.1$ kcal mol^{-1} and $\Delta S^{\neq} = -1.4 \pm 0.4$ cal K^{-1} mol^{-1}. Limiting rates at ⩽35 °C can be calculated by using these values and are found to be essentially identical with limiting rates under air or N_2 over this temperature range. The activation parameters were therefore recalculated from the data for reactions under CO from 40–60 °C combined with those for reactions under air or N_2 at ⩽35 °C. The results are given in Table III together with activation parameters for all the data under air or N_2. The only other available parameters for comparable Ru_3 clusters are also included. Even if the slightly different parameters for reactions of $Ru_3(CO)_{10}(dppm)$ under air or N_2 are considered it is evident that the dppm

TABLE III. Activation Parameters for [Nucleophile]-independent Reactions of some Ru_3 Clusters

	$\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ (cal K^{-1} mol^{-1})	$10^5 k$ (50 °C) (s^{-1})	Reference
$Ru_3(CO)_{12}$	31.81 ± 0.19	+20.2 ± 0.6	55	8a
$Ru_3(CO)_{10}(dppm)^a$	23.56 ± 0.22	−0.84 ± 0.69	51	this work
$Ru_3(CO)_{10}(dppm)^b$	25.85 ± 0.45	+6.7 ± 1.4	66	this work
$Ru_3(CO)_{10}(dppm)^c$	24.96 ± 0.51	+4.2 ± 1.7	82	3
$Ru_3(CO)_{10}(PPh_3)_2$	27.9 ± 0.2	+15.5 ± 0.6	220	11

[a]From limiting rates of reaction with PPh_3 under CO (⩾40 °C) and rates under air or N_2 (<40 °C). [b]From limiting rates of reaction with PPh_3 under air or N_2. [c]From limiting rates under air or N_2 with dppm.

substituent is labilizing, as are two PPh_3 ligands [11]. The dppm is less labilizing in terms of rate constants but more labilizing in terms of $\Delta H^{\ddagger}$. This is because of the relatively unfavourable entropy effect for $Ru_3(CO)_{10}(dppm)$. The very small value of $\Delta S^{\ddagger}$ for this cluster is not unusual for [nucleophile]-independent reactions of metal carbonyl clusters [3, 4a, 4b, 12, 13] and is not necessarily inconsistent with a simple CO dissociative mechanism [12, 13]. The formally unsaturated intermediates formed by CO dissociation from clusters have several ways of relieving the unsaturation, e.g. by formation of CO bridges [12, 13], and these lead to strengthening of the bonding within the intermediates, a lowering of their enthalpies, and a compensating decrease in their entropies. Whether this process is energetically worthwhile will probably depend on the nature of any substituents present and the detailed balance between enthalpic and entropic effects [13]. Similar rationalizations might, however, be possible for other mechanisms for the [nucleophile]-independent paths. The structure of $Ru_3(CO)_{10}(dppm)$ [7] shows evidence of strain in the molecule caused by the dppm ligand, and this strain might be removed by CO loss or, alternatively, and possibly more likely, by some form of isomerization. Formation of **I** or **II** could well involve such a decrease in strain through opening up of the Ru_3 cluster. One of the $Ru(CO)_3$ moieties in **I** has a vacant coordination site at which rapid addition of a nucleophile could occur [14] whereas **II** contains a 17-electron $Ru(CO)_4$ radical species at which rapid associative substitution [15–18] could occur in competition with the reformation of $Ru_3(CO)_{10}(dppm)$ in its more stable form. Neither of these intermediates is necessarily unstable towards fragmentation. It must be emphasized that, although bridging ligands can stabilize a cluster towards total fragmentation, it does not follow that breaking metal–metal bonds to form intermediates such as **I** or **II** is made more difficult by bridging ligands, possibly quite the reverse. Formation of **II** might be expected to lead to quite positive values of $\Delta S^{\ddagger}$ whereas insertion of a terminal CO into a Ru–Ru bond to form **I** might well involve more restricted atomic movements and a consequently unfavorable $\Delta S^{\ddagger}$. Isomerization to **I** is, therefore, more compatible with the data than isomerization to **II**. The absence of reaction with a chlorinated solvent also suggests that the metal centred diradical **II** is a less likely intermediate than **I**. Substitution at the $Ru(CO)_3$ radical moiety in **II** might also be possible and this would lead to a different product from that actually observed. Since the structure of $Ru_3(CO)_{10}(PPh_3)_2$ has not been reported we do not know if similar arguments in terms of strain in that cluster are possible. It does seem likely that the two PPh_3 substituents would lead to some degree of strain even if, as is most probable, the positions of the substituents are different from the necessarily *cis* positions of the two P atoms in $Ru_3(CO)_{10}(dppm)$ [7].



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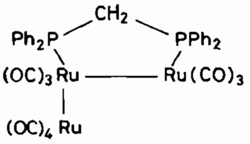
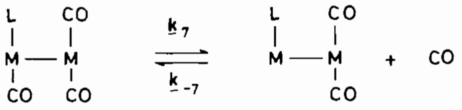


II

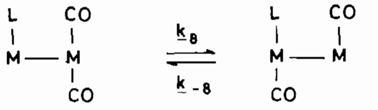
Some strain, apparently located in the tripod ligand $HC(PPh_2)_3$, is also shown in $Co_4(CO)_9(tripod)$ [4a]. In this case the tripod substituent is a very slightly deactivating ligand and a limited range of P-donor substituents ($HC(PPh_2)_3$, $P(OR)_3$, PEt_3) have rather small effects on the rates of unimolecular CO displacement in these Co_4 clusters. This is not general for all substituents since $SbPh_3$ and $AsPh_3$ in $Co_4(CO)_{11}(L)$ are substantially deactivating, and $Co_4(CO)_9\{P(OMe)_3\}_3$ also reacts much more slowly than $Co_4(CO)_{12-n}\{P(OMe)_3\}_n$ ($n = 0$–2) [19].

The mechanistic ambiguity at the basis of any explanation of substituent effects in such metal carbonyl clusters, even for an apparently simple CO-retarded reaction path, shows that more kinetic and structural work is necessary before the effects can be fully understood.

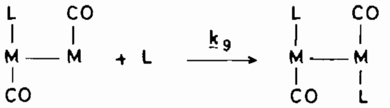
In addition to the reaction path discussed above there appears to be another one that is significant for reactions at ⩾40 °C. As indicated in Fig. 3, this path is retarded by CO but it is independent of [PPh_3] when [PPh_3] is large. A similar path was observed for reaction with dppm and a possible explanation was given [3] in terms of a mechanism proposed by Atwood *et al.* [20]. This supposes that, in a substituted di- or poly-nuclear metal carbonyl, reversible CO dissociation occurs from an already substituted metal atom. Although the vacant site can be attacked by any free CO present, attack by another P-donor ligand is slow because of steric effects. In the absence of free CO the coordinative unsaturation at the substituted metal atom is relieved by transfer of a CO ligand from an unsubstituted metal. Coordinative unsaturation is thereby transferred to the unsubstituted metal atom where attack by a P-donor can occur. This mechanism is outlined schematically in eqns. (7)–(9) (no stereochemical details being implied). The rate equation



$$\begin{array}{cc} L & CO \\ | & | \\ M - & M \\ | & | \\ CO & CO \end{array} \underset{k_{-7}}{\overset{k_7}{\rightleftharpoons}} \begin{array}{cc} L & CO \\ | & | \\ M - & M \\ & | \\ & CO \end{array} + CO \qquad (7)$$



$$\begin{array}{cc} L & CO \\ | & | \\ M - & M \\ & | \\ & CO \end{array} \underset{k_{-8}}{\overset{k_8}{\rightleftharpoons}} \begin{array}{cc} L & CO \\ | & | \\ M - & M \\ | & \\ CO & \end{array} \qquad (8)$$



$$\begin{array}{cc} L & CO \\ | & | \\ M - & M \\ | & \\ CO & \end{array} + L \xrightarrow{k_9} \begin{array}{cc} L & CO \\ | & | \\ M - & M \\ | & | \\ CO & L \end{array} \qquad (9)$$

that corresponds to this mechanism when $k_9[L] \gg k_{-8}$ is shown in eqn. (10) so that the observed rate constant

$$k_{obs} = k_7 k_8/(k_{-7}[CO] + k_8) \qquad (10)$$

for this path should decrease with [CO]. When $k_{-7}[CO] \gg k_8$ k_{obs} will be very small so the reaction should be completely inhibited by sufficiently high [CO] (see Fig. 3). The difference between the rate constants obtained under air or N_2 and the limiting values found under CO should correspond to the rate constant for dissociation of CO from the substituted metal atom, *i.e.* k_7 in eqn. (7).

The differences observed in reactions with dppm [3] and PPh_3 at 50 °C are $(1.7 \pm 0.2) \times 10^{-4}$ and $(1.8 \pm 0.2) \times 10^{-4}$ s^{-1}, respectively, but there are some difficulties to offset this satisfactory agreement. The difference appeared to be independent of temperature for dppm but the data in Table II show that it is clearly temperature dependent for PPh_3. In addition the difference is only $(0.5 \pm 0.2) \times 10^{-4}$ s^{-1} for reaction with $AsPh_3$ and negligibly small for reaction with PCy_3. As implied in eqn. (10) the difference should be the same for all ligands. The latter two ligands show very little further reaction after formation of $Ru_3(CO)_9(dppm)(L)$ whereas both $Ru_3(CO)_9(dppm)PPh_3$ and $Ru_3(CO)_9(\mu\text{-dppm})(\eta^1\text{-dppm})$ undergo further reaction, albeit quite slowly. This might lower the A_∞ for the initial substitution to an extent that decreases with [CO], and this would lead to a decrease in the apparent rate constant with increasing [CO]. However, no such systematic decrease in the A_∞ values is apparent and, unless there is some other systematic source of error, the effect does not appear to be an artifact. Even if it is not an artifact, the mechanism in eqns. (7)–(9) is obviously over-simplified and cannot explain the dependence of the effect on the nature of the nucleophile. It should be noted, however, that a similar, and much larger, effect is found in the chelate ring closure reaction of $Ru_3(CO)_9(\mu\text{-dppm})(\eta^1\text{-dppm})$ to form the very stable $Ru_3(CO)_8(\mu\text{-dppm})_2$ for which there is no problem at all with subsequent reactions and the A_∞ values. An even larger effect was observed in the CO-inhibited fragmentation reaction of $Ru_3(CO)_9(P\text{–n-Bu}_3)_3$. The limiting rates under CO at high [$P\text{–n-Bu}_3$] depend strongly on [CO] and an isomerization of the $Ru_3(CO)_8(P\text{–n-Bu}_3)_3$ formed by CO dissociation was thought to be necessary before attack by $P\text{-n-Bu}_3$ could occur. This type of behaviour is, therefore, quite well established but how general it might be can only be ascertained by careful studies of the precise nature of the effects of CO. It is interesting that unimolecular replacement of CO ligands attached to a ligated apical CO atom in $Co_4(CO)_7(tripod)(dppm)$ is only *ca.* 5 times slower than replacement of a CO from the unligated apical Co atom in $Co_4(CO)_9(tripod)$ [4b]. This implies that CO dissociation from an already ligated metal atom could indeed be significant compared with replacement of CO from an unligated metal atom, although there is no evidence that it is the preponderant path.

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