Reaction Mechanisms of Metal–Metal-bonded Carbonyls. Part 14.[1] Reactions of 1,1,1,2,2,2,3,3,3-Nonacarbonyl-1,2,3-tris(triphenylphosphine)-*triangulo*-triruthenium

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Some reactions of the complex $[\{Ru(CO)_3(PPh_3)\}_3]$, in decalin between 40 and 150 °C, have been studied and found to proceed by three kinetically distinct paths leading to a variety of products. Reactions with tributylphosphine, carbon mono-oxide, and low concentrations of triphenylphosphine under an atmosphere of argon occur by path A which involves reversible loss of PPh_3 at some stage. The limiting rate at $[PPh_3] = 0$ is governed by the parameters $k_{\text{lim.}}^{A}$ (100 °C) $= 2 \times 10^{-1}\ s^{-1}$, $\Delta H^\ddagger = 122.8 \pm 2.1\ kJ\ mol^{-1}$, and $\Delta S^\ddagger = 68.6 \pm 6.2\ J\ K^{-1}\ mol^{-1}$. Reaction with PPh_3, under an atmosphere of argon and at values of $[PPh_3]$ sufficient to completely suppress path A, occurs by path B which involves reversible loss of CO at some stage. The limiting rate at $[CO] = 0$ is governed by the parameters $k_{\text{lim.}}^{B}$ (100 °C) $= 1.0 \times 10^{-5}\ s^{-1}$, $\Delta H^\ddagger = 137.8 \pm 4.4\ kJ\ mol^{-1}$, and $\Delta S^\ddagger = 27.2 \pm 10.9\ J\ K^{-1}\ mol^{-1}$. Reaction with PPh_3 in the presence of sufficient PPh_3 and CO to completely inhibit reaction by paths A and B proceeds by C for which $k_{\text{lim.}}^{C}$ (at 100° C) $= 5.7 \times 10^{-7}\ s^{-1}$, $\Delta H^\ddagger = 147.9 \pm 3.9\ kJ\ mol^{-1}$, and $\Delta S^\ddagger = 29.6 \pm 9.2\ J\ K^{-1}\ mol^{-1}$. The three paths may simply involve the three distinct primary processes: reversible PPh_3 dissociation (A), reversible CO dissociation (B), and fission into mono- and bi-nuclear fragments (C). It is possible, however, that these three processes are preceded by a common initial step involving reversible fission of a single Ru–Ru bond.

EVIDENCE has been presented that decacarbonyldimanganese and related binuclear complexes having metal–metal bonds undergo reversible homolytic fission as the initial step in many of their thermal reactions.[2,3] Activation parameters for the rate-limiting process have provided, therefore, a quantitative measure of the strength of the metal–metal bonds in a variety of binuclear complexes[4] but no comparable evidence has been adduced for trinuclear metal carbonyls.

The complex $[Ru_3(CO)_{12}]$ undergoes substitution reactions with phosphorus-donor ligands by a mixture of what appear to be simple dissociative and associative processes.[5] However, reaction of tri-n-butylphosphine with low concentrations of the complex leads to formation of mixtures of $[Ru(CO)_3(PBu_3)_2]$ and $[Ru(CO)_4(PBu_3)]$ in the mol ratio 1 : 2 and it was concluded that the intermediate $[Ru_3(CO)_{11}(PBu_3)]$ underwent rapid fission into $[Ru(CO)_4]$ and $[Ru(CO)_3(PBu_3)]$ fragments.[6] No kinetic data were obtained for this process and we have, therefore, begun an investigation of reactions of complexes $[\{Ru(CO)_3L\}_3]$ (L = phosphorus-donor ligand) with particular attention to those that lead to mononuclear products. The complex $[\{Ru(CO)_3(PPh_3)\}_3]$ reacts[7] with triphenylphosphine in isobutyl ketone at 120 °C to form mononuclear $[Ru(CO)_3(PPh_3)_2]$, and we report here some studies of the kinetics of this and related reactions occurring in decalin.

EXPERIMENTAL AND RESULTS

The complex $[\{Ru(CO)_3(PPh_3)\}_3]$ was prepared either *in situ* in decalin or according to the method of Piacenti *et al.*[7] The product showed i.r. bands at 2 045vw, 1 983s, 1 975s, and 1 945(sh) cm^{-1}. Dodecacarbonyl-*triangulo*-trirutheinum (Strem Chemicals) was used as received and triphenylphosphine (B.D.H.) was recrystallised from methanol and dried *in vacuo* before use. Tri-n-butylphosphine (Baker Chemicals) was distilled under reduced pressure (86 °C, 10 mmHg),* and decalin (Baker Analysed Reagent) was dried over molecular sieves. Carbon mono-oxide (C.P grade, 99.5%) and argon (99.998%) were used as received from Union Carbide, and cylinders of gas mixtures ($CO–N_2$) of known composition (±2%) were obtained from Matheson of Canada.

Kinetic Procedures.—Solutions were generally prepared by adding a solution of known concentration of phosphine ligand in decalin (10 cm^3) to a weighed amount of $[\{Ru(CO)_3(PPh_3)\}_3]$ in a Pyrex Schlenk tube which was then sealed with a rubber septum cap. The solution was degassed by repeated freeze–pump–thaw cycles and the complex was dissolved under CO at 80—90 °C. After dissolution and further freeze–pump–thaw cycles the required atmosphere was introduced above the solution, and the tubes were wrapped in aluminium foil and immersed in a constant-temperature oil-bath (±0.1 °C). Samples were withdrawn through stainless-steel tubing, as required, by applying an appropriate pressure of the gaseous atmosphere, and the extent of reaction was determined by measurement of the i.r. spectrum in the C–O stretching region with a Perkin-Elmer 257 spectrophotometer. In cases where reactions in the presence of very low concentrations of PPh_3 were to be followed, solutions were prepared *in situ* by reaction of $[Ru_3(CO)_{12}]$ with a small excess of PPh_3 under argon. This was necessary because the dissolution of $[\{Ru(CO)_3(PPh_3)\}_3]$ in decalin leads to decomposition in the absence of relatively high concentrations of PPh_3. When similar reactions were being followed the kinetic behaviour did not depend on the mode of preparation of the reactant solutions. In most of the runs where reaction of the complex with $PBu^n{}_3$ was being studied, degassed reaction solutions were introduced through stainless-steel tubing into 1-cm quartz cells sealed with

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* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

[1] Part 13, M. A. Cobb, B. Hungate, and A. J. Poë, *J.C.S. Dalton*, 1976, 2226.

[2] J. P. Fawcett, A. J. Poë, and K. R. Sharma, *J. Amer. Chem. Soc.*, 1976, **98**, 1401.

[3] J. P. Fawcett, A. J. Poë, and R. A. Jackson, *J.C.S. Chem. Comm.*, 1975, 733.

[4] (*a*) J. P. Fawcett and A. J. Poë, *J.C.S. Dalton*, 1976, 2036; (*b*) J. P. Fawcett, A. J. Poë, and M. V. Twigg, *J.C.S. Chem. Comm.*, 1973, 267; (*c*) R. A. Jackson and A. J. Poë, *Proc. 16th Internat. Conf. Co-ordination Chem.*, Dublin, 1974, paper 3.20.

[5] A. J. Poë and M. V. Twigg, *J.C.S. Dalton*, 1974, 1860.

[6] A. J. Poë and M. V. Twigg, *Inorg. Chem.*, 1974, **13**, 2982.

[7] F. Piacenti, M. Bianchi, E. Benedetti, and G. Sbrana, *J. Inorg. Nuclear Chem.*, 1967, **29**, 1389.

rubber septum caps and flushed with argon. The reactions were then followed continuously by monitoring changes in the u.v.–visible absorption of the solutions, the cells being placed in the thermostatted (±0.1 °C) cell holders of a Cary 16K or Perkin-Elmer 402 spectrophotometer.

Reaction with Tri-n-butylphosphine.—As evidenced by the i.r. spectra,[6,7] reaction with PBu^n_3 led to formation of $[\{Ru(CO)_3(PBu_3)\}_3]$, without formation of observable amounts of any mixed-ligand intermediates. The kinetics were generally followed by monitoring the changing absorbance at 390 nm, where the product has a minimum in its absorption spectrum. The absorbance decreased from *ca.* 1.0 to 0.1, and excellent first-order plots, linear to 90% completion of reaction, were obtained. In some cases reactions were monitored by following the decreasing absorbance in the i.r. at 1 975 cm^{-1} when A_∞ was zero. Rate data are shown in the Table. In the presence of 10^{-3} mol dm^{-3} free PPh_3 the reaction is governed by a limiting rate constant, $k_{lim.}^A$, independent of $[PBu_3]$, but addition of free PPh_3 slowed the reactions to an extent dependent on $[PBu_3]$. The activation parameters governing reaction in the presence of negligible amounts of free PPh_3 were estimated by a least-squares analysis of the dependence of log $(k_{lim.}^A/T)$ on $1/T$ and are also given in the Table.

Kinetic data for the reaction in decalin of $[\{Ru(CO)_3(PPh_3)\}_3]$ (4×10^{-4} mol dm^{-3}) with tri-n-butylphosphine

θ_c/°C	$10^3[PPh_3]$/ mol dm^{-3}	$[PBu_3]$/ mol dm^{-3}	$10^5k_{obs.}$/s^{-1}
41.0	1.00	0.10	10.2
	1.00	0.10	10.3
41.7	1.00	0.53	11.0
	1.00	0.68	10.5
47.7	1.00	0.50	23.5
	1.00	0.68	23.2
48.3	1.00	0.05	29.5
	1.00	0.10	32.0
	1.00	0.20	30.0
	1.00	0.50	29.8
	25	0.10	25.0
	58	0.10	20.1
	86	0.10	17.3
	100	0.10	16.4
	154	0.10	13.0
	200	0.10	11.2
	250	0.10	9.6
	320	0.10	7.85
	366	0.10	7.05
	420	0.10	6.25
	466	0.10	5.70
	500	0.10	5.30
	600	0.10	4.66
60.0	1.00	0.10	151
	1.00	0.10	152
62.6	1.00	0.50	215
	1.00	0.70	252
66.3	1.00	0.61	330
	1.00	0.88	322
50.3	1.00	5.7×10^{-3} *	40.0
60.3	1.00	5.6×10^{-3} *	165

$\Delta H^\ddagger = 122.8 \pm 2.1$ kJ mol^{-1}, $\Delta S^\ddagger = 68.6 \pm 6.2$ J K^{-1} mol^{-1}, $\sigma(k_{obs.}) = \pm 8.8\%$, $k_{lim.}^A$ (100 °C) $= 2 \times 10^{-1}$ s^{-1}.

* Reaction with carbon mono-oxide, $[PBu_3] = 0$.

Some reactions under an atmosphere of CO and in the presence of negligible amounts of free PPh_3 were also followed. The product was almost pure $[Ru_3(CO)_{10}(PPh_3)_2]$, as judged by a comparison of its i.r. spectrum with that of other disubstituted complexes $[Ru_3(CO)_{10}L_2]$,[8,9] and the rate constants are shown in the Table.

Reaction with Triphenylphosphine.—This reaction proceeded under argon at convenient rates between 120 and 150 °C and a large number of i.r. bands were observed to grow. Separation of the products by thin-layer chromatography (t.l.c.) on silica gel indicated the presence of four products, the main one being $[Ru(CO)_3(PPh_3)_2]$ characterised by its i.r. absorption band at 1 905 cm^{-1} in decalin. One of the other three products was clearly characterised as the 'benzyne' complex $[Ru_3(C_6H_4)(CO)_7(PPh_2)_2]$ with i.r. bands at 2 059s, 2 022s, 2 012vs, 2 004s, 1 968s, and 1 956s cm^{-1} in decalin (*cf.* 2 057s, 2 020s, 2 009vs, 1 998s, 1 968s, and 1 955s cm^{-1} in cyclohexane [9]), while the two others had spectra similar to those of $[Ru_2(CO)_6\{P(C_6H_4)Ph_2\}_2]$ [9] and $[Os_3(CO)_9H\{P(C_6H_4)Ph_2\}(PPh_3)]$.[10] No further attempt was made to characterise these products. Analysis of the spectroscopic changes during the reaction showed that the yield of $[Ru(CO)_3(PPh_3)_2]$ rose to *ca.* 85% above $[PPh_3] = 0.5$ mol dm^{-3}. As the concentration of PPh_3 was reduced, more of the 'benzyne' complex was observed. Appearance of bands of low intensity suggested that small amounts of $[Ru(CO)_4(PPh_3)]$ [11] and $[Ru_3(CO)_{10}(PPh_3)_2]$ [8,9] were formed early in the reaction and that small amounts of $[Ru_2(CO)_6\{P(C_6H_4)Ph_2\}_2]$ were formed later in the reaction.

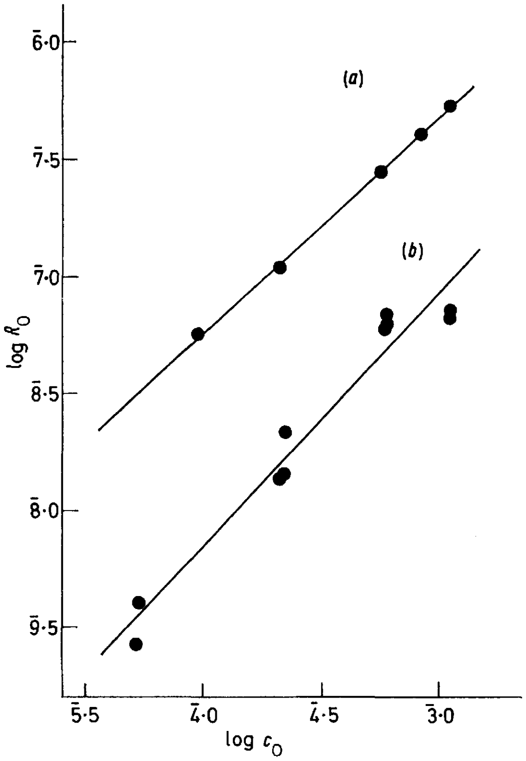

FIGURE 1 Initial rate plots for the reaction of $[\{Ru(CO)_3(PPh_3)\}_3]$ with (*a*) 0.5 mol dm^{-3} PPh_3 under an atmosphere of CO at 160 °C, (*b*) 0.2 mol dm^{-3} PPh_3 under an atmosphere of argon at 120 °C

The kinetics were followed by monitoring the i.r. band of $[\{Ru(CO)_3(PPh_3)\}_3]$ at 1 975 cm^{-1}. The growth of the band at 1 968 cm^{-1} due to the benzyne product and to $[Ru_2(CO)_6$-

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[8] M. I. Bruce, G. Shaw, and F. G. A. Stone, *J.C.S. Dalton*, 1973, 1667.

[9] M. I. Bruce, G. Shaw, and F. G. A. Stone, *J.C.S. Dalton*, 1972, 2094.

[10] C. W. Bradford and R. S. Nyholm, *J.C.S. Dalton*, 1973, 529.

[11] B. F. G. Johnson, J. Lewis, and M. V. Twigg, *J.C.S. Dalton*, 1975, 1876.

$\{P(C_6H_4)Ph_2\}_2]$ made it difficult to estimate precisely the value of A_∞, particularly since the latter complex appeared not to be a direct product of the reaction. As a result the first-order rate plots were linear only for *ca.* 1 half-life. The order of the reaction with respect to [complex] was determined by a study of the dependence of the initial rate r_0 on the initial concentration of complex c_0, with $[PPh_3] = 0.2$ mol dm^{-3}. The data are shown in Figure 1 and a least-squares analysis indicates that the order is 1.1 ± 0.1, and the standard deviation of an individual determination of initial rate is $\pm 30\%$. The first-order rate constants depended on $[PPh_3]$ as shown in Figure 2, a low limiting rate constant being obtained above *ca.* 0.05 mol dm^{-3} PPh_3. Exactly the same behaviour was found at 140 °C. This limiting rate was decreased by the presence of CO and a new low limiting rate constant, $k_{lim.}{}^{C}$, was attained when the atmosphere above the solution contained *ca.* $>25\%$ CO. The retardation was accompanied by a simplification of the reaction, the yield of $[Ru(CO)_3(PPh_3)_2]$ being essentially quantitative under a 15% CO atmosphere and in no case was it less than 95%. This markedly improved the quality of the rate plots which were obtained by monitoring the decreasing absorbance either at 1 975 cm^{-1} or at 510 nm. Results of an initial-rate study of the reactions under CO are shown in Figure 1 from which the order of reaction with respect to [complex] is 0.92 ± 0.04, and the standard deviation of an individual measurement of initial rate is $\pm 6\%$. As shown in Figure 2 the rates under CO also attained a limiting rate at higher values of $[PPh_3]$ but increased as $[PPh_3]$ decreased. At *ca.* <0.05 mol dm^{-3} PPh_3, increasing amounts of ' benzyne ' product were observed and the reaction was further complicated, especially under an atmosphere of pure CO, by the rapid formation of $[Ru_3(CO)_{10}(PPh_3)_2]$ and $[Ru_3(CO)_{11}(PPh_3)]$ which then themselves react to form mononuclear products.[12]

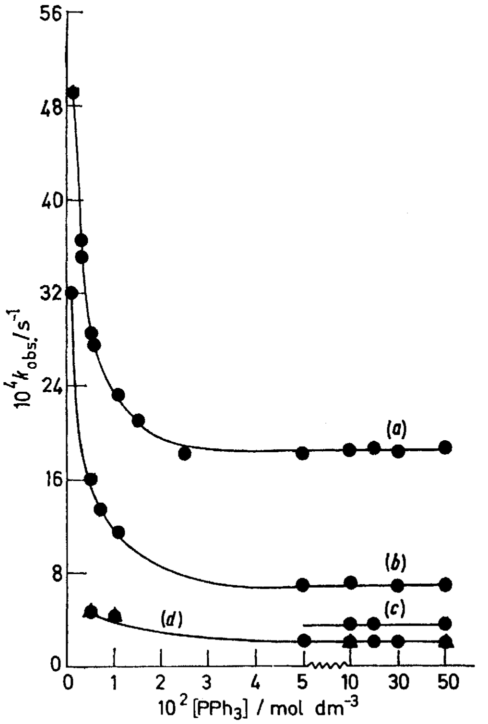

FIGURE 2 Rate constants for reaction with PPh_3 at 150 °C: (*a*) under argon; (*b*) under 4.9% CO; (*c*) under 15.4% CO; (*d*) under 26 (△) and 100% (●) CO

In order to obtain activation parameters for the reaction that is independent of $[PPh_3]$ but inhibited by CO, the values of $k_{lim.}{}^{C}$ were subtracted from the corresponding values of $k_{obs.}$ to give $k_{lim.}{}^{B}$. The Eyring plot is shown in Figure 3 where the uncertainties are standard deviations calculated from a least-squares analysis of the data (at least eight values) at each temperature: $\Delta H^\ddagger = 137.8 \pm 4.4$ kJ mol^{-1}, $\Delta S^\ddagger = 27.2 \pm 9.2$ J K^{-1} mol^{-1}, and $k_{lim.}{}^{B} = 1.0 \times 10^{-5}$ s^{-1} at 100 °C. The Eyring plot for the reaction that is independent both of $[PPh_3]$ and [CO] is also shown, the activation parameters being obtained from a least-squares analysis in which each individual rate constant, $k_{lim.}{}^{C}$, was assumed to have the same standard deviation regardless of the temperature. The points shown are averages of the individual values at each temperature and the total of eight points leads to a value of $\sigma(k_{lim.}{}^{C}) = \pm 9.4\%$ after allowance for the number of degrees of freedom; $\Delta H^\ddagger = 147.9 \pm 3.9$ kJ mol^{-1}, $\Delta S^\ddagger = 29.6 \pm 9.2$ J K^{-1} mol^{-1}, and $k_{lim.}{}^{C} = 5.7 \times 10^{-7}$ s^{-1} at 100 °C. An Eyring plot for the reaction with PBu_3 is also shown in Figure 3 for comparison, some of the points being averages of two or more indistinguishable values. The data for reaction with CO fall exactly on this plot.

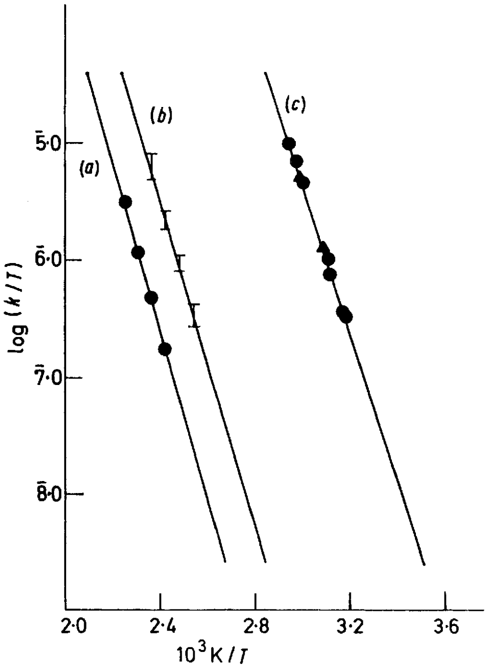

FIGURE 3 Eyring plots for reaction with (*a*) 0.5 mol dm^{-3} PPh_3 under an atmosphere of CO, (*b*) 0.2 mol dm^{-3} PPh_3 under an atmosphere of argon, (*c*) 0.10 mol dm^{-3} PBu_3 in the presence of 10^{-3} mol dm^{-3} PPh_3 (●) or with 6×10^{-3} mol dm^{-3} CO in the presence of 10^{-3} mol dm^{-3} PPh_3 (▲)

DISCUSSION

These kinetic results show that the complex $[\{Ru(CO)_3(PPh_3)\}_3]$ can react by at least three kinetically distinct paths. The fastest reaction (path A) observed here is the replacement of a triphenylphosphine ligand by tributylphosphine or carbon mono-oxide. Replacement of the first PPh_3 ligand by PBu_3 must be the slowest such

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[12] S. K. Malik, unpublished work.

reaction since the only product seen is $[\{Ru(CO)_3(PBu_3)\}_3]$. Replacement of the first PPh_3 by CO is, however, the fastest of the series of reactions with CO.[12] The *inhibition* of the reaction with PBu_3 by free PPh_3 can be expressed by rate equation (1) where $k_{lim.}{}^{A}$ is the

$$k_{obs.} = k_{lim.}{}^{A}(a[PBu_3]/[PPh_3])/(1 + a[PBu_3]/[PPh_3]) \quad (1)$$

rate constant observed at $[PPh_3] = 0$ and a is a constant. A plot of $1/k_{obs.}$ against $[PPh_3]$ at $[PBu_3] = 0.10$ mol dm^{-3} is shown in Figure 4. For a polynuclear carbonyl of this type two main types of mechanism would be in accord with equation (1). The dissociative mechanism shown in equations (2) and (3), with $k_{lim.}{}^{A} = k_2$ and $a = k_3/k_{-2}$, is one and the value $k_3/k_{-2} = 1.1$ found from plot (*b*) in Figure 4 is quite compatible with competition between tributyl- and triphenyl-phosphine for a vacant site in a metal carbonyl.[1,5,13] However, the mechanism shown in equations (4)—(7) (where the asterisks indicate a reactive form of the complex) is also in accord with the data with $k_{lim.}{}^{A} = k_4k_5/(k_{-4} + k_5)$ and $a = [k_6k_7/(k_{-6} + k_7)]/[k_{-4}k_{-5}/(k_{-4} + k_5)]$. In a polynuclear complex such as $[Ru_3(CO)_9(PPh_3)_3]$ a reactive form can reasonably be formulated as (1) resulting from homolytic fission of one Ru–Ru bond, or possibly (2), formed by metal migration. Reactions (5) and (6) can be replaced by (8), a concerted interchange reaction, in which case $k_{lim.}{}^{A} = k_4$ and $a = k_8k_7/k_{-4}k_{-8}$.

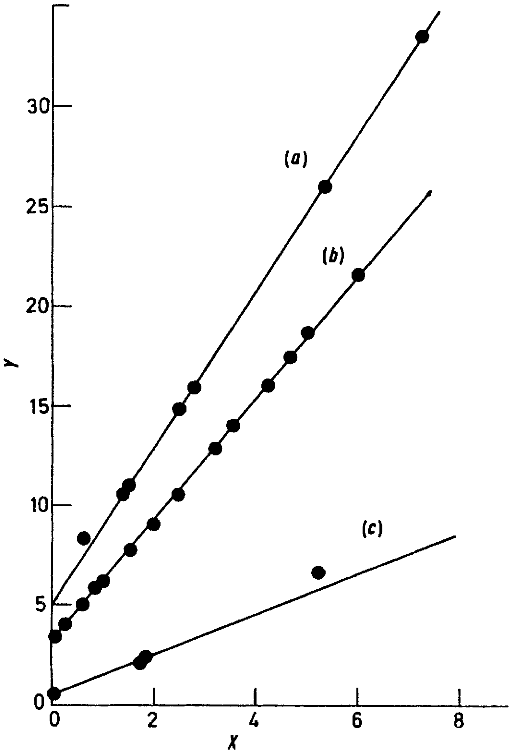

FIGURE 4 Reaction with (*a*) PPh_3 under argon at 150 °C $\{X = 5 \times 10^2[PPh_3]/\text{mol dm}^{-3}, Y = 5 + [10^{-2}/(k_{obs.} - k_{lim.}{}^{B} - k_{lim.}{}^{C})]/\text{s}\}$, (*b*) 0.10 mol dm^{-3} PBu_3 under argon at 48.3 °C $\{X = 10[PPh_3]/\text{mol dm}^{-3}, Y = (10^{-3}/k_{obs.})/\text{s}\}$, (*c*) 0.2 mol dm^{-3} PPh_3 under CO at 150 °C $\{X = 10^4[CO]/\text{mol dm}^{-3}, Y = [(10^{-3})/(k_{obs.} - k_{lim.}{}^{C})]/\text{s}\}$

$$[Ru_3(CO)_9(PPh_3)_3] \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [Ru_3(CO)_9(PPh_3)_2] + PPh_3 \quad (2)$$

$$[Ru_3(CO)_9(PPh_3)_2] + PBu_3 \xrightarrow{k_3} [Ru_3(CO)_9(PBu_3)(PPh_3)_2] \quad (3)$$

$$[Ru_3(CO)_9(PPh_3)_3] \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} [Ru_3(CO)_9(PPh_3)_3]^* \quad (4)$$

$$[Ru_3(CO)_9(PPh_3)_3]^* \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} [Ru_3(CO)_9(PPh_3)_2]^* + PPh_3 \quad (5)$$

$$[Ru_3(CO)_9(PPh_3)_2]^* + PBu_3 \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} [Ru_3(CO)_9(PBu_3)(PPh_3)_2]^* \quad (6)$$

$$[Ru_3(CO)_9(PBu_3)(PPh_3)_2]^* \xrightarrow{k_7} [Ru_3(CO)_9(PBu_3)(PPh_3)_2] \quad (7)$$

$$[Ru_3(CO)_9(PPh_3)_3]^* + PBu_3 \underset{k_{-8}}{\overset{k_8}{\rightleftharpoons}} [Ru_3(CO)_9(PBu_3)(PPh_3)_2]^* + PPh_3 \quad (8)$$

The reaction under argon at low triphenylphosphine concentrations probably also proceeds by the same path as the replacement reaction with PBu_3, being progressively inhibited as $[PPh_3]$ increases until only a reaction path unaffected by PPh_3 is available. The data are consistent with rate equation (9) where b is a constant. A plot of $1/(k_{obs.} - k_{lim.}{}^{B} - k_{lim.}{}^{C})$ against $[PPh_3]$, shown in Figure 4,

$$k_{obs.} - k_{lim.}{}^{B} - k_{lim.}{}^{C} = k_{lim.}{}^{A}(b/[PPh_3])/\{1 + (b/[PPh_3])\} \quad (9)$$

is linear with an intercept indistinguishable from zero, the scale on the ordinate axis being allowed for. This is as expected since the value of $k_{lim.}{}^{A}$ at 150 °C will be very large. According to the activation parameters for the limiting reaction with PBu_3, $k_{lim.}{}^{A} = 23.4$ s^{-1} at 150 °C and a value of $b = 2.2 \times 10^{-7}$ mol dm^{-3} is then obtained from the gradient of the linear plot. These kinetic data are consistent with reaction (2) as an initial step followed by a complex series of intramolecular processes that lead eventually to the 'benzyne', and other, products. Alternatively they are consistent with reactions (4) and (5) followed by intramolecular reaction. The very low value for b is an indication of the much greater tendency of PPh_3 to recombine with a reactive intermediate compared with the tendency of the intermediate to begin the series of reactions leading to complex products.

In the presence of enough PPh_3 to inhibit this path completely, less benzyne product is formed and the major product is $[Ru(CO)_3(PPh_3)_2]$. The reaction is first order in $[Ru_3(CO)_9(PPh_3)_3]$ so that no reversible

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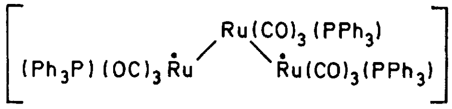
[13] C. L. Hyde and D. J. Darensbourg, *Inorg. Chem.*, 1973, **12**, 1286; D. J. Darensbourg and H. L. Conder, *ibid.*, 1974, **13**, 374.

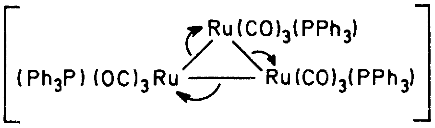


(1)

fragmentation occurs in the rate-determining steps. This reaction is retarded by CO in accordance with rate equation (10), where c is a constant, and the yield of

$$k_{\text{obs.}} - k_{\text{lim.}}^{\text{C}} = k_{\text{lim.}}^{\text{B}}(c/[\text{CO}])/\{1 + (c/[\text{CO}])\} \quad (10)$$

$[Ru(CO)_3(PPh_3)_2]$ rises with increasing [CO]. A plot of $1/(k_{\text{obs.}} - k_{\text{lim.}}^{\text{C}})$ against [CO], shown in Figure 4, is quite a good straight line. (The values of [CO] were estimated from the partial pressures of carbon mono-oxide in the CO–N_2 mixtures above the reacting solutions, the solubility of CO in decalin between 20 and 76 °C,[14] and the changing vapour pressure [15] and molecular volume [16] of decalin with temperature. The enthalpy of dissolution of CO in decalin was taken to be negligible.[14])



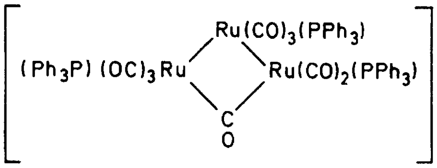
(3)

Again, the kinetic data alone do not distinguish between two possible types of reaction mechanism, namely simple CO dissociation followed mainly by fragmentation and eventual formation of $[Ru(CO)_3(PPh_3)_2]$, or reversible formation of a reactive intermediate followed by CO dissociation [reaction (11)] before fragmentation. In the latter case $k_{\text{lim.}}^{\text{B}} = k_4k_{11}/(k_{-4} + k_{11})$. A

$$[Ru_3(CO)_9(PPh_3)_3]^* \underset{k_{-11}}{\overset{k_{11}}{\rightleftharpoons}} [Ru_3(CO)_8(PPh_3)_3]^* + CO \quad (11)$$

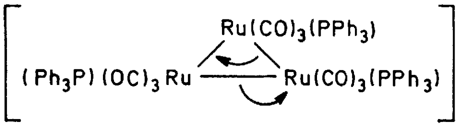
value $c = 3.72 \times 10^{-5}$ mol dm^{-3} is obtained from plot (c) in Figure 4 and shows that addition of CO to a vacant co-ordination site at some stage is highly favoured over whatever further reaction is necessary to form the products.

The slowest reaction is that in the presence of sufficient PPh_3 and CO to inhibit completely the first two paths. The reaction then leads to $[Ru(CO)_3(PPh_3)_2]$ as virtually the only product, the rate being essentially first order in [complex]. The rate-determining step must, therefore, involve some degree of loosening of the Ru_3 cluster in the transition state and irreversible formation of an intermediate, or intermediates, that react rapidly with PPh_3. At one extreme this loosening would involve fission of all the Ru–Ru bonds to form three $[Ru(CO)_3(PPh_3)]$ fragments as shown in (3). This, however, is unlikely since the reverse process would involve a trimolecular reaction.



(2)

Although the reverse step does not occur under the conditions used here, it is known that four-co-ordinate d^8 ruthenium(0) species such as $[Ru(CO)_4]$ [11,17] or $[Ru(CO)_3(PBu_3)]$ [6] do readily trimerise, and a two-step process involving $[Ru_2(CO)_6L_2]$ (L = CO or PBu_3) is more probable. It follows that fragmentation of $[\{Ru(CO)_3(PPh_3)\}_3]$ could form $[Ru(CO)_3(PPh_3)]$ and $[Ru_2(CO)_6(PPh_3)_2]$ in the primary step. The complex $[Ru_2(CO)_6(PPh_3)_2]$ is probably best formulated with a Ru=Ru double bond so that the breaking of two Ru–Ru single bonds as a $[Ru(CO)_3(PPh_3)]$ fragment breaks away is accompanied by compensating formation of the double bond in the residual binuclear fragment as shown in (4). {An analogous species $[Fe_2(CO)_8]$ has been proposed [18] to explain some reactions of $[Fe(CO)_4]$; Fe=Fe double bonds are now quite well known [19] although none, so far, appears to have been characterised that does not have bridging groups of some kind.} This compensation would have to be quite effective since the value $\Delta H^{\ddagger} = 148$ kJ mol^{-1} is only slightly greater than the 138.0 ± 2.2 kJ mol^{-1} that has been assigned to homolytic fission of the one Tc–Tc bond in $[\{Tc(CO)_4(PPh_3)\}_2]$.[4a]



(4)

Although this mechanism is quite reasonable, a mechanism involving reaction (4) as the initial step followed by fragmentation [equation (12)] without loss of

$$[Ru_3(CO)_9(PPh_3)_3]^* \longrightarrow [(Ph_3P)(OC)_3Ru{=}Ru(CO)_3(PPh_3)] + [Ru(CO)_3(PPh_3)] \quad (12)$$

CO or PPh_3 could also explain the data with $k_{\text{lim.}}^{\text{C}} = k_4k_{12}/(k_{-4} + k_{12})$. It is, therefore, possible to describe all three reactions either according to the unified Scheme shown below or by $[Ru_3(CO)_9(PPh_3)_3]$ itself undergoing

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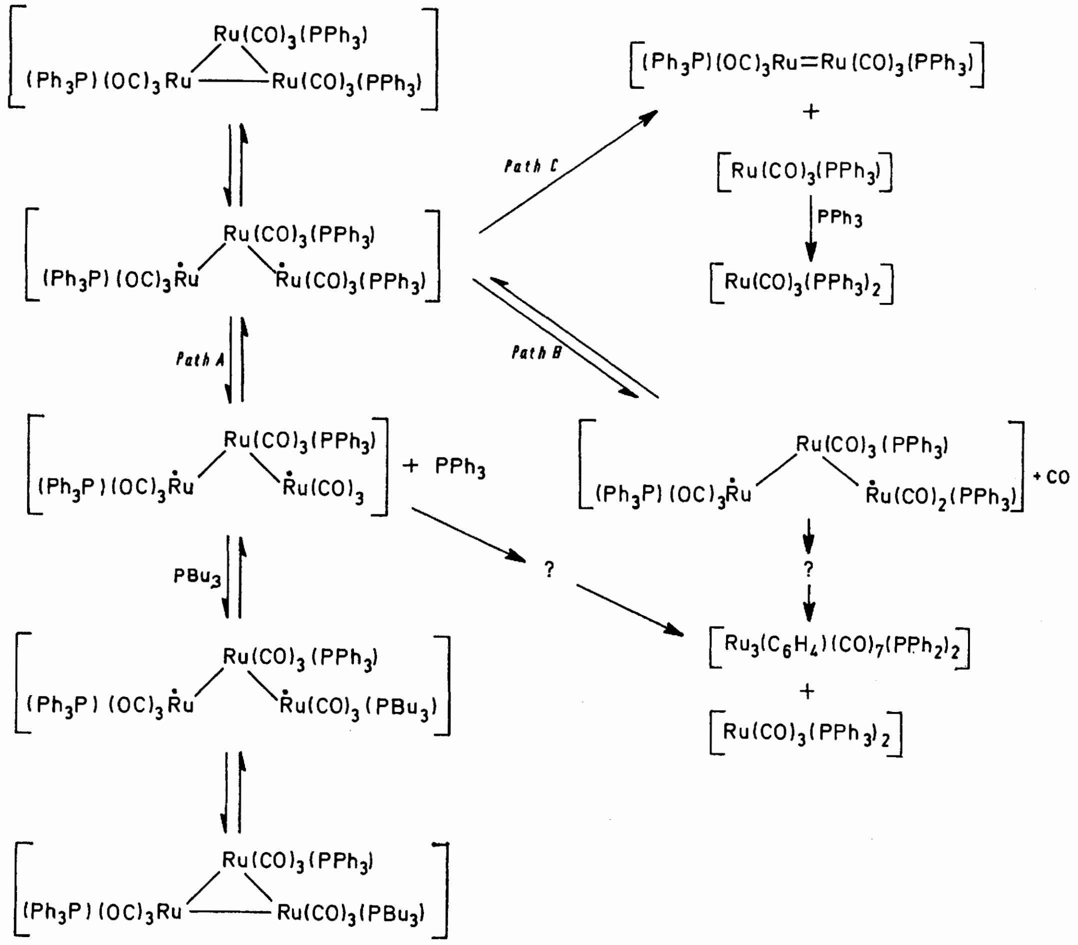
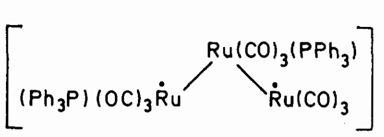


SCHEME

the three distinct processes of PPh$_3$ dissociation (path A), CO dissociation (path B), and fragmentation (path C).

The two possibilities for path C differ only in that one involves sequential breaking, and the other concerted breaking, of two Ru–Ru bonds. When the bonds are broken sequentially the second step is assisted by the incipient formation of a Ru=Ru bond in one fragment.



(5)

If an activation enthalpy of 148 kJ mol^{-1} is sufficient to break two Ru–Ru bonds in this way it seems highly probable that the 138 (path B) and 123 kJ mol^{-1} (path A) will be sufficient to break one. This is supported by the fact that 138 kJ mol^{-1} is sufficient to break a Tc–Tc bond. For the simple dissociative mechanisms to apply to paths A and B the energy would have to be largely concentrated in the Ru–PPh$_3$ and Ru–CO bonds without enough being distributed elsewhere in the molecule to break a Ru–Ru bond. We consider this unlikely. Further, path A seems more likely to lead to the observed benzyne product *via* an intermediate such as (5) since one simple vacant co-ordination site on a ruthenium atom in an intact Ru$_3$ cluster does not seem sufficiently reactive to enable the quite complex intramolecular reactions, leading to the benzyne product, to occur.

If the reactions do proceed as shown in the Scheme, then $k_{\mathrm{lim.}}{}^{\mathrm{A}}$, $k_{\mathrm{lim.}}{}^{\mathrm{B}}$, and $k_{\mathrm{lim.}}{}^{\mathrm{C}}$ will be $k_4k_5/(k_{-4} + k_5)$, $k_4k_{11}/(k_{-4} + k_{11})$, and $k_4k_{\mathrm{fr}}/(k_{-4} + k_{\mathrm{fr}})$, respectively, where k_{fr} is the rate constant for fragmentation of the reactive intermediate. At 100 °C the limiting rate constants have the values 2×10^{-1}, 1×10^{-5}, and 6×10^{-7} s^{-1}, respectively, so that $k_5 \gg k_{11} > k_{\mathrm{fr}}$. If these constants are all much less then k_{-4}, then $k_{\mathrm{lim.}}{}^{\mathrm{A}} = k_4k_5/k_{-4}$, $k_{\mathrm{lim.}}{}^{\mathrm{B}} = k_4k_{11}/k_{-4}$, and $k_{\mathrm{lim.}}{}^{\mathrm{C}} = k_4k_{\mathrm{fr}}/k_{-4}$ so that $k_5 : k_{11} : k_{\mathrm{fr}}$ are in the ratio $1 : 5 \times 10^{-5} : 3 \times 10^{-6}$. If, on the other hand, $k_5/k_{-4} \gtrsim 10$ then $k_{\mathrm{lim.}}{}^{\mathrm{A}} = k_4 = 2 \times 10^{-1}$ s^{-1}, $k_{11}/k_{-4} = 5 \times 10^{-5}$, and $k_{\mathrm{fr}}/k_{-4} = 3 \times 10^{-6}$. In this case the activation enthalpy for path A (123 kJ mol^{-1}) is that for simple ring opening with fission of one Ru–Ru bond. In the former case it is the sum of $\Delta H_4{}^{\ominus}$ (reversible fission of one Ru–Ru bond) and $\Delta H_5{}^{\ddagger}$ (loss of phosphine from the intermediate), *i.e.* $\Delta H_4{}^{\ominus} < 123$ kJ mol^{-1}.

Although making a distinction between the various mechanisms discussed involves decisions about the detailed way in which the overall enthalpy of activation is distributed around the molecule, we tend to favour the more complex mechanism outlined in the Scheme since it seems to us intrinsically more likely that the enthalpy will be more rather than less widely distributed and that, therefore, more complex mechanisms will be followed.

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