of ether, dark red-brown crystals of the $Fe_3(CO)_{11}^{2-}$ salt were collected by filtration and dried under vacuum.

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Registry No. $[PPN]_2[Fe_3(CO)_{11}]$, 66039-65-4; $[PPN][HFe_3(CO)_{11}]$, 23254-21-9; $[PPN][Fe_3(CO)_{10}(COCH_3)]$, 69421-10-9; $HFe_3(CO)_{10}(COCH_3)$, 55992-19-3; $[PPN][Fe_3(CO)_{10}(COC_2H_5)]$, 69421-12-1; $HFe_3(CO)_{10}(COC_2H_5)$, 69421-13-2; $[PPN][Fe_3(CO)_{10}(COC(=O)CH_3)]$, 69421-15-4; $HFe_3(CO)_{10}(COH)$, 67775-42-2; CH_3SO_3F, 421-20-5; $C_2H_5SO_3F$, 371-69-7; acetyl chloride, 75-36-5; $C_6H_5S^-$, 13133-62-5.

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Reaction Mechanisms of Metal–Metal-Bonded Carbonyls. 22.[1] Fragmentation Reactions of Nonacarbonyltris(tri-*n*-butylphosphine)triruthenium and Nonacarbonyltris(triphenyl phosphite)triruthenium

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The complexes $Ru_3(CO)_9L_3$ (L = P-*n*-Bu_3 and $P(OPh)_3$) undergo thermal fragmentation reactions in decalin to form mononuclear products, and the kinetics of these reactions have been studied. A major path is shown to involve initial rate-determining dissociation of a CO ligand. When L = PPh_3, $P(OPh)_3$, and P-*n*-Bu_3, the activation enthalpies are 33.0 27.4, and 19.4 kcal mol^{-1}, respectively, and this can only be explained by major differences in the bonding within the intermediates $Ru_3(CO)_8L_3$. Some possibilities are discussed. The detailed nature of the kinetics requires that these intermediates are not susceptible to direct attack by L but that they undergo reversible isomerization to a form that is. Fragmentation follows this attack. Assessment of results of these and other kinetic studies of triruthenium clusters suggests that initial ligand dissociation is generally much more facile than cluster fragmentation.

Introduction

Metal carbonyl clusters have been the subject of much intensive study in recent years.[2] Most of the effort has been concentrated on preparative and structural aspects but the growing availability of ^{13}C NMR spectrometers has more recently led to a plethora of investigations into the fluxional behavior of metal carbonyl clusters and their organometallic derivatives. A recent upsurge of interest in the relationship between heterogeneous and homogeneous catalysis[3,4] has resulted in a special effort to determine the general usefulness of clusters as catalysts and to produce especially reactive clusters.[5] In spite of this interest very much less effort has been devoted to basic mechanistic studies of their reactions even though it is not at all clear in many cases that it is the clusters themselves that are the catalysts rather than active mononuclear fragments produced from them.[5] If the latter were the case, then the analogies drawn between surface-active heterogeneous catalysts and metal–cluster catalysts would be misleading.

As part of a quite general interest in the mechanisms of reactions of metal–metal-bonded carbonyls and in the energetics of metal–metal bonds, kinetic studies have been carried out of reactions of $Ru_3(CO)_{12}$ and its P-donor-substituted derivatives.[6-10] It has been established that even the apparently simple formation of $Ru_3(CO)_9(PBu_3)_3$ from $Ru_3(CO)_{12}$ occurs via the formation of mononuclear fragments.[7] $Ru_3(CO)_9(PPh_3)_3$ has been shown to undergo a wide variety of reactions including readily reversible fission at 50 °C into two fragments which are probably $Ru_2(CO)_6(PPh_3)_2$ and paramagnetic $Ru(CO)_3PPh_3$.[9] This fragmentation *and its reverse* must occur ca. 10^4 times for every fragmentation leading to $Ru(CO)_3(PPh_3)_2$ in the perfectly clean formation of the latter in 100% yield from $Ru_3(CO)_9(PPh_3)_3$ and PPh_3 under an atmosphere of CO. Activation parameters for fragmentation of $Ru_3(CO)_{12-n}(PPh_3)_n$ (n = 1–3) have been shown[10] to depend greatly on the value of n and $Ru_3(CO)_{11}(PBu_3)$ must undergo relatively rapid fragmentation, even at 30 °C,[7] whereas $Ru_3(CO)_{12}$[11] and $Ru_3(CO)_9(PBu_3)_3$[7] undergo fragmentation quite slowly at temperatures over 100 °C. The great dependence of the energetics on the number and nature of substituents and the wide range of mechanistic paths followed even by such relatively small clusters have prompted us to extend our studies of substituted triruthenium carbonyl clusters. We report here results of some kinetic studies of

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fragmentation reactions of $Ru_3(CO)_9(PBu_3)_3$ and $Ru_3(CO)_9\{P(OPh)_3\}_3$.

Experimental Section

Chemicals were obtained and purified exactly as described previously.[6,7] The complexes $Ru_3(CO)_9(PBu_3)_3$ and $Ru_3(CO)_9\{P(OPh)_3\}_3$ were prepared by published methods, and their purity was demonstrated by comparison of their IR spectra with published ones.[7,12] For some kinetic runs the complexes were prepared in situ by reaction of a known excess of ligand with $Ru_3(CO)_{12}$ under mild conditions.

Solutions for kinetic runs were prepared in Schlenk tubes by standard methods[8] and samples for analysis were obtained as described previously.[8] Reactions were followed by observing the changes in the IR or UV–visible spectra and rate constants were derived from the change with time of log $(A_t - A_\infty)$. The absorbance A_∞ at "infinite" time was generally quite small compared with initial absorbances but in some cases difficulties caused by uncertainties in the exact (fairly large) values of A_∞ were avoided by making Swinbourne plots.[13]

Results

Reaction of $Ru_3(CO)_9(PBu_3)_3$ with PBu_3. Reaction at $\gtrsim$100 °C in decalin under argon with $[PBu_3]$ ca. 0.1 M led to complete loss of absorbance at 1961 (s) and 1925 (m) cm^{-1} due to the cluster and formation of $Ru(CO)_3(PBu_3)_2$ (IR bands at 1883 (w) and 1879 (s) cm^{-1})[7,12] in ca. 90% yield. Initial results showed an increase to a limiting rate as $[PBu_3]$ was increased to ca. 0.5 M. However, this appears to have been due to the retarding effect of CO released by some decomposition during the reaction. When Ar was bubbled through the solution or, more effectively, when [complex] was reduced by a factor of 10, this retardation did not occur until lower values of $[PBu_3]$. Thus, when [complex] = 2.5×10^{-5}, 5.0×10^{-5}, and 50×10^{-5} M, the values of k_{obsd} for reaction with $[PBu_3]$ = 0.1 M at 120.0 °C under Ar were 18.5×10^{-4}, 12.5×10^{-4}, and 3.1×10^{-4} s^{-1}, respectively. For [complex] = 5.0×10^{-5} M and $[PBu_3]$ = 0.23–1.30 M the average of nine values of k_{obsd} was $(25.3 \pm 0.2) \times 10^{-4}$ s^{-1} with $\sigma(k_{obsd})$ = 2.4%. These uncertainties are estimates of standard deviations adjusted for the number of degrees of freedom so that 95% confidence limits can be obtained by doubling them. When $[PBu_3] \lesssim 0.5$ M, the rate plots were linear for up to 90% completion of reaction, but when $[PBu_3] \gtrsim 0.5$ M, the IR spectrum of the product changed gradually from that of $Ru(CO)_3(PBu_3)_2$, bands growing at 1985, 1952, and 1915 cm^{-1} at a rate that increased with $[PBu_3]$. The appearance of these bands resulted in an uncertain value of A_∞ but application of Swinbourne's method[13] provided rate plots that were linear for 85–90% reaction.

The temperature dependence of the limiting values of k_{obsd} ($[PBu_3] \geq 1.0$ M) was determined from 16 values over the range 89.5–130.1 °C.

Reactions under atmospheres of pure CO or CO–N_2 mixtures in the presence of only ca. 10^{-3} M free PBu_3 led rapidly to $Ru(CO)_4(PBu_3)$[7] with only a little $Ru(CO)_3(PBu_3)_2$. When $[PBu_3] \gtrsim 10^{-2}$ M, the reaction led to $Ru(CO)_3(PBu_3)_2$ in almost 100% yield and its further reaction was almost completely inhibited by the CO. Reactions under CO were much slower than those under Ar. Values of k_{obsd} increased to a limiting value with increasing $[PBu_3]$ as shown in Table I but the limiting values obtained when $[PBu_3] \gtrsim 1.0$ M decreased with increasing [CO]. The temperature dependence of the limiting rate constants obtained under atmospheres of pure CO was determined from 13 measurements over the range 130.0–166.3 °C.

Table I. Kinetic Data for Reactions of $Ru_3(CO)_9(PBu_3)_3$[a] in Decalin under CO–N_2 Mixtures at 149.9 °C

10^4[CO],[b] M	$[PBu_3]$, M	10^4k_{obsd}, s^{-1}	10^4k_{calcd},[c] s^{-1}	100Δ[d]
0	1.0	205[e]	186	−10.2
1.84	0.080	22.3	22.5	0.9
	0.110	24.5	25.7	4.8
	0.160	29.8	29.6	−0.6
	0.250	36.5	34.0	−7.4
	0.440	39.8	38.7	−2.8
	0.72	40.2	41.7	3.8
	1.00	39.2	43.3	9.5
		40.0	43.3	7.7
5.36		21.6	20.9	−3.3
		21.7	20.9	−3.8
9.33		15.7	15.0	−4.4
		16.0	15.0	−6.3
34.8	0.80	8.65	8.78	1.5
	1.00	8.60	8.86	2.9
	1.30	8.70	8.94	2.6

[a] Initial [complex] = 5×10^{-4} M. [b] Estimated from data for CO solubility as described in ref 8, p 237. [c] Calculated as described in the text. [d] $100(k_{calcd} - k_{obsd})/k_{calcd}$. [e] Calculated from the temperature dependence of values of k_{obsd} under Ar with $[PBu_3] \geqslant 1.0$ M.

Reaction of $Ru_3(CO)_9\{P(OPh)_3\}_3$ with $P(OPh)_3$. When the complex was heated at 150 °C alone in decalin under Ar, a rapid reaction occurred accompanied by the appearance of a large number of IR bands. The strongest bands were at 2080, 2064, 2048, 2028, 2006, and 1595 cm^{-1}. After a few minutes a mixture of a white and a yellow solid compound was deposited. Separation was effected by column chromatography, and the white product, which was soluble in CH_2Cl_2, showed strong IR bands at 2064 and 2028 cm^{-1} that are characteristic of one or both of the isomers of $Ru(CO)_2\{P(OC_6H_4)(OPh)_2\}_2$.[14] The yellow product showed strong bands at 2080, 2065, 2048, and 2012 cm^{-1} which can be assigned[14] to a mixture of the complexes $H_4Ru_4(CO)_9\{P(OPh)_3\}_3$ and $Ru_2H(CO)_3\{P(OC_6H_4)(OPh)_2\}_2\{OP(OPh)_2\}$. The band at 1595 cm^{-1} is also known in orthometalated complexes.[15] The qualitative nature of the product IR bands was unaffected by the presence of 0.01–0.05 M $P(OPh)_3$ but their rate of appearance was very much slower. The product bands did not all appear at the same rate which shows that a complex series of reactions was probably occurring. When reactions were carried out under atmospheres of CO, a product band at 1932 cm^{-1} was also apparent. Reaction of a decalin solution of $Ru_3(CO)_{12}$ with 0.1 M $P(OPh)_3$ in sunlight under CO gave product bands at 2058 (s), 1975 (m), and 1931 (vs) cm^{-1} which can probably be assigned to $Ru(CO)_4\{P(OPh)_3\}$, a very similar pattern being shown by $Ru(CO)_4(PBu_3)$, etc.[7,12] Reaction with ca. 1.0 M $P(OPh)_3$, even under an atmosphere of CO, led to products with complex IR spectra characteristic of the various orthometalated and other species. A weak band at 1918 cm^{-1}, assignable to $Ru(CO)_3\{P(OPh)_3\}_2$, also appeared together with bands attributable to $Ru(CO)_4\{P(OPh)_3\}$.

The kinetics of reactions in the presence of free $P(OPh)_3$ were followed by monitoring the decreasing absorbance of the complex at 2002 or 1982 cm^{-1}. At low $[P(OPh)_3]$ the kinetics were complicated by product bands with frequencies close to those of the reactants and with uncertain intensities. Even the Swinbourne method[13] failed to give good rate plots, and only rather approximate rate constants were obtained. However, as $[P(OPh)_3]$ was increased, this interference became less important, A_∞ became negligible, and first-order rate plots were linear for up to 90% reaction. Dilute solutions of complex (5×10^{-5} M) were used in the kinetic studies and no retardation by released CO was observed at low $[P(OPh)_3]$ for reactions under Ar. Thus the mean of 20 measurements of k_{obsd} ($[P(OPh)_3]$ = 0.05–1.00 M; 150.0 °C) was $(12.4 \pm 0.2) \times 10^{-4}$ s^{-1} with $\sigma(k_{obsd})$ = 7.6%. The temperature dependence of the rate constants was determined from 29 measurements over the range 130.0–160.0 °C.

Reaction under various partial pressures of CO showed (Table II) that k_{obsd} increased to limiting values with increasing $[P(OPh)_3]$ and that the limiting values decreased with increasing [CO]. The temperature dependence of the limiting values under an atmosphere of pure CO was determined over the range 140.2–170.4 °C.

Discussion

Reaction of $Ru_3(CO)_9(PBu_3)_3$ with PBu_3 leads to the formation of simple, well-defined mononuclear complexes in very high yields. Reaction of $Ru_3(CO)_9\{P(OPh)_3\}_3$ with $P(OPh)_3$, however, leads to a complicated mixture of products owing to the pronounced tendency of $P(OPh)_3$ as a ligand to undergo orthometalation. In spite of these differences in the overall reactions, the kinetic behavior of the two complexes, as measured by their rate of disappearance, is very similar and closely related to that of $Ru_3(CO)_9(PPh_3)_3$.[8] This complex reacts to form mononuclear products by three paths (A, B, and C). Paths A and B involve rate-determining PPh_3 and CO dissociation, respectively, while path C involves rate-determining fragmentation at rates independent of [CO] and $[PPh_3]$. The relative rate constants for the three paths are in the order $k_A \gg k_B > k_C$. $Ru_3(CO)_9(PBu_3)_3$ and $Ru_3(CO)_9\{P(OPh)_3\}_3$ both undergo rapid fragmentation at ca. 160 °C under CO in the absence of the free ligands PBu_3 or $P(OPh)_3$, respectively, but the reaction is very strongly inhibited by the presence of quite small amounts of free ligand. Path A therefore appears also to be available for these complexes but it was not investigated quantitatively.

Reaction with larger amounts of free ligand L under Ar proceeds at rates independent of [L]. Under an atmosphere of mixed CO and N_2 rates rise to limiting values with increasing [L] but the limiting values decrease with increasing [CO]. This rise to a limiting rate is not observed[8] in the reactions of $Ru_3(CO)_9(PPh_3)_3$ because, at lower values of $[PPh_3]$, the rates actually increase owing to the greater relative importance of path A for that complex. The limiting rates at high $[PPh_3]$ do, however, decrease as [CO] is increased. All three complexes can therefore react by path B.

The rate of reaction of $Ru_3(CO)_9(PPh_3)_3$ with PPh_3 reaches a clearly defined lower limit as [CO] is increased so that path C is well established. Although the limiting rates of reaction of $Ru_3(CO)_9L_3$ {L = PBu_3 or $P(OPh)_3$} with L are also reduced by CO, it is not so clear that a lower limit is reached under 1 atm of CO, and path C is not so well defined for these complexes (see below).

The simplest mechanism for path B that fits with the observed qualitative behavior is shown in eq 1–3. $Ru_3(CO)_8L_3{}^*$

$$Ru_3(CO)_9L_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ru_3(CO)_8L_3 + CO \quad (1)$$

$$Ru_3(CO)_8L_3 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Ru_3(CO)_8L_3{}^* \quad (2)$$

$$Ru_3(CO)_8L_3{}^* + L \xrightarrow{k_3} \text{various possible intermediates} \rightarrow \text{fragmentation} \quad (3)$$

is an isomeric form of $Ru_3(CO)_8L_3$ that can be attacked directly by L. $Ru_3(CO)_8L_3$ itself cannot be attacked by L or the rates would increase with [L] to the same limiting rates (governed by k_1) irrespective of [CO]. The mechanism shown in eq 4–6 is impossible for the same reason. A similar

$$Ru_3(CO)_9L_3 \rightleftharpoons Ru_3(CO)_9L_3{}^* \quad (4)$$

$$Ru_3(CO)_9L_3{}^* \rightleftharpoons Ru_3(CO)_8L_3 + CO \quad (5)$$

$$Ru_3(CO)_8L_3 \xrightarrow{L} \text{intermediates} \rightarrow \text{fragmentation} \quad (6)$$

mechanism (but with the rate of reaction 6 being independent of [L]) was proposed[8] for reaction of $Ru_3(CO)_9(PPh_3)_3$ for which no rise to a limiting rate with increasing $[PPh_3]$ could be detected. This would clearly not be consistent with the data for L = PBu_3 or $P(OPh)_3$, and $Ru_3(CO)_9(PPh_3)_3$ may, therefore, also react by the mechanism shown in (1)–(3) rather than (4)–(6).

Table II. Kinetic Data for Reaction of $Ru_3(CO)_9\{P(OPh)_3\}_3{}^a$ with $P(OPh)_3$ in Decalin under CO–N_2 Mixtures at 150.0 °C

$10^4[CO]$,[b] M	$[P(OPh)_3]$, M	10^4k_{obsd}, s^{-1}
0	≥0.05	12.4 ± 0.2[c]
1.84	0.20	7.80, 8.00
	0.30	9.20, 9.50
	0.50	9.70, 9.80, 10.2
	0.70	9.10, 9.50, 9.20
5.36	0.10	3.90, 4.10
	0.20	5.50, 5.80
	0.30	6.30, 6.93, 6.50
	0.40	6.98, 7.10, 7.50
	0.50	7.50, 7.80
	0.70	8.00, 8.10
	0.90	7.40, 7.90
	1.00	8.20
9.33		5.00, 4.90
34.8	0.20	1.41
	0.60	1.49
	0.80	1.56
	1.00	1.58, 1.55

[a] Initial [complex] = 5 × 10^{-5} M. [b] See footnote *b*, Table I. [c] Mean of 20 values.

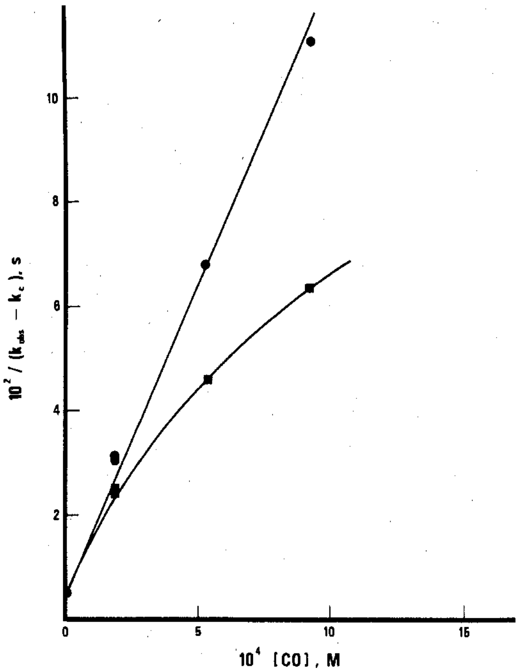


Figure 1. Dependence of k_B ($=k_{obsd} - k_C$) on [CO] for reaction of $Ru_3(CO)_9(PBu_3)_3$ with PBu_3 at 150 °C: (■) k_C taken as zero; (●) k_C taken as 7.0 × 10^{-4} s^{-1}. $[PBu_3]$ = 1.0 M.

The rate equation for the mechanism proposed for path B is shown in eq 7. Under the conditions used in our studies

$$k_B = k_1k_2k_3[L]/\{k_{-1}k_{-2}[CO] + k_2k_3[L] + k_{-1}k_3[CO][L]\} \quad (7)$$

$k_{obsd} = k_B + k_C$ so that (7) can be rearranged to (8). A plot

$$1/(k_{obsd} - k_C) = 1/k_1 + k_{-1}[CO]/k_1k_2 + k_{-1}k_{-2}[CO]/k_1k_2k_3[L] \quad (8)$$

of $1/(k_{obsd} - k_C)$ against [CO] at constant [L] should therefore be linear. Such plots for L = PBu_3 are shown in Figure 1 for k_C = 0 and 7 × 10^{-4} s^{-1}. The plots show clearly that k_C has to be finite and that a value of ca. 7 × 10^{-4} s^{-1} is satisfactory. A plot of $1/(k_{obsd} - k_C)$ against $1/[PBu_3]$ at constant [CO] is shown in Figure 2 to be satisfactorily linear as required by eq 8. The gradient of this plot provides a value of 1.6 × 10^5 s for $k_{-1}k_{-2}/k_1k_2k_3$ and the combination of this value with the gradient of the plot in Figure 1 for k_C = 7 × 10^{-4} s^{-1} leads

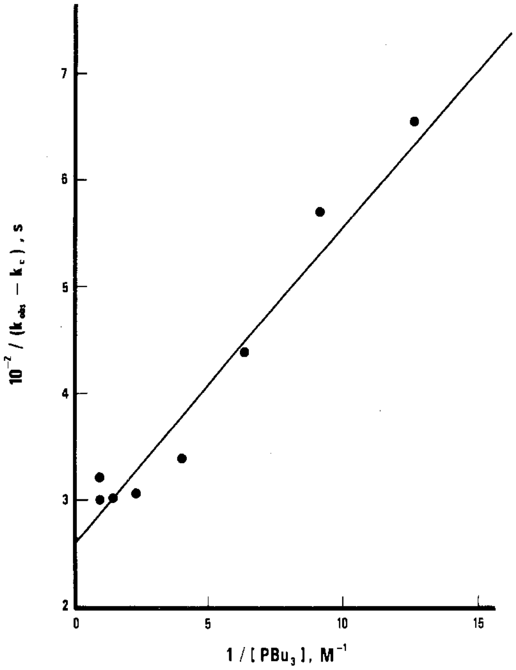


Figure 2. Dependence of k_B on $[PBu_3]$ for reaction of $Ru_3(CO)_9(PBu_3)_3$ with PBu_3 at 150 °C. k_C was taken as 7×10^{-4} s^{-1}. [CO] = 1.84×10^{-4} M.

to a value of 1.2×10^6 L mol^{-1} s for k_{-1}/k_1k_2. The intercept of the plot in Figure 1 provides a value of 2×10^{-2} s^{-1} for k_1. These values for the constants, together with $k_C = 7 \times 10^{-4}$ s^{-1}, were used in a computer program that calculated $\sum\Delta^2$ $\{\Delta = (k_{calcd} - k_{obsd})/k_{calcd}\}$ and made small systematic variations in the constants until $\sum\Delta^2$ was minimized. All of the data in Table I were used. The best values for k_C, k_1, k_{-1}/k_1k_2, and $k_{-1}k_{-2}/k_1k_2k_3$ were 5.4×10^{-4} s, 1.86×10^{-2} s^{-1}, 1.03×10^6 L mol^{-1} s, and 1.67×10^5 s, respectively. The corresponding value of $\sigma(k_{obsd}) = \{\sum(\Delta^2/(N-4)\}^{1/2}t_{95}/1.96$ (N is the number of values of k_{obsd} and t_{95} is the t factor appropriate to the number of degrees of freedom, $N - 4$, that is required to give 95% confidence limits) was 5.9% as compared with 8.5% for the initial set of constants.

These constants show that, under 1 atm of CO, $k_B = 2.75 \times 10^{-4}$ s^{-1} and $k_C = 5.4 \times 10^{-4}$ s^{-1} so that path B is not completely suppressed. The temperature dependence of k_{obsd} under 1 atm of CO and with $[PBu_3] \geq 1$ M leads to $\Delta H^{\ddagger} = 31.7$ kcal mol^{-1} and $\Delta S^{\ddagger} = 1.7$ cal deg^{-1} mol^{-1}. k_C is only ca. 2.7% of the limiting value of k_B under Ar at 149.9 °C and $\Delta H_B^{\ddagger}$ and $\Delta S_B^{\ddagger}$ can therefore be obtained from the temperature dependence of the limiting values of k_{obsd} found for reactions under Ar. These values were analyzed by a least-squares program weighted according to the assumption that the percent uncertainty in k_{obsd} is the same irrespective of the temperature. The activation parameters are shown in Table III. Those calculated above for reaction under 1 atm of CO are clearly not exact measurements of $\Delta H_C^{\ddagger}$ and $\Delta S_C^{\ddagger}$ since path B is not completely suppressed. However, the increase in the activation enthalpy from 19 to 32 kcal mol^{-1} when [CO] is changed from 0 to 3.48×10^{-3} M shows that $\Delta H_C^{\ddagger}$ must be greater than 32 kcal mol^{-1}. Similarly $\Delta S_C^{\ddagger} > 2$ cal deg^{-1} mol^{-1}.

The data for L = $P(OPh)_3$ can be analyzed in a similar way. No satisfactory fit was found unless k_C was taken as zero (i.e., it was negligible compared to k_B even under 1 atm of CO). The data in Table II lead to a good linear plot of $1/k_{obsd}$ against $1/[P(OPh)_3]$ when [CO] = 5.36×10^{-4} M (Figure 3). The gradient of 139 mol L^{-1} leads to $k_{-1}k_{-2}/k_1k_2k_3 = 2.6 \times 10^5$ s, and with the intercept of 1.07×10^3 s a value of $\sigma(k_{obsd}) = 4.5\%$ is obtained. This value of $k_{-1}k_{-2}/k_1k_2k_3$ can be used to plot $(1/k_{obsd}) - (k_{-1}k_{-2}[CO]/k_1k_2k_3[L])$ against [CO]. The plot is a reasonably good straight line although the scatter is worse than in the other plots and some systematic errors appear to be indicated. This is not surprising in view of the complexity of the reaction and the wide range of concentrations. A value of 1.3×10^6 L mol^{-1} s is obtained for k_{-1}/k_1k_2. Activation parameters for path B were obtained from values of k_{obsd} under Ar and are shown in Table III. Activation parameters for some related reactions are also included in Table III.

Table III. Activation Parameters for Fragmentation Reactions of $Ru_3(CO)_{12-n}L_n$ [a]

L	n	$\Delta H_B^{\ddagger}$,[a] kcal mol^{-1}	$\Delta S_B^{\ddagger}$,[a] cal deg^{-1} mol^{-1}	$\Delta H_C^{\ddagger}$,[b] kcal mol^{-1}	$\Delta S_C^{\ddagger}$,[b] cal deg^{-1} mol^{-1}
PPh_3	1	25.6 ± 0.2[c]	9.06 ± 0.52[c]	20.7 ± 0.2	−23.7 ± 0.5
PPh_3	2	27.9 ± 0.2[c]	15.5 ± 0.6[c]	29.7 ± 0.9	−5.7 ± 2.0
PPh_3	3	33.0 ± 1.1	6.5 ± 2.6	35.3 ± 1.2	+7.1 ± 2.7
$P(OPh)_3$	3	27.4 ± 0.7[d]	−7.8 ± 1.6[d]		
PBu_3	3	19.5 ± 0.4[e]	−21.2 ± 1.0[e]	>32	>2

[a] Path B involves initial rate-determining CO dissociation. [b] Path C involves rate-determining fragmentation of Ru_3 cluster.[8,10] [c] These parameters[10] pertain to CO dissociation from $Ru(CO)_4$ moieties followed by addition of PPh_3 (i.e., overall substitution) rather than fragmentation. [d] $\sigma(k_{obsd}) = 8.0\%$. [e] $\sigma(k_{obsd}) = 7.6\%$.

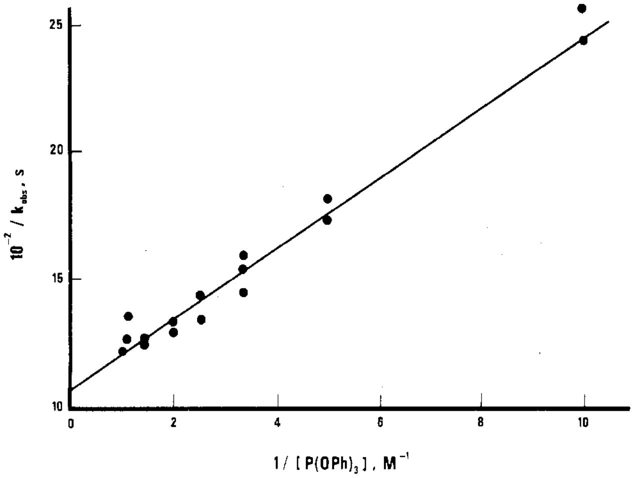
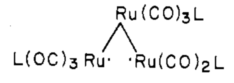
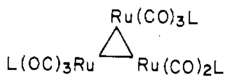


Figure 3. Dependence of k_B on $[P(OPh)_3]$ for reaction of $Ru_3(CO)_9\{P(OPh)_3\}_3$ with $P(OPh)_3$ at 150 °C. [CO] = 5.36×10^{-4} M. k_C was taken as zero (i.e., $k_B = k_{obsd}$).

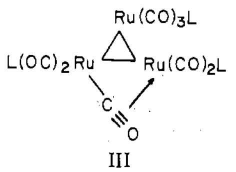
The activation parameters $\Delta H_B^{\ddagger}$ and $\Delta S_B^{\ddagger}$ are very strikingly dependent on the nature of L in $Ru_3(CO)_9L_3$. Changes in $\Delta H_B^{\ddagger}$ are almost balanced by compensating changes in $\Delta S_B^{\ddagger}$ as shown by an isokinetic plot of $\Delta H_B^{\ddagger}$ against $\Delta S_B^{\ddagger}$. These pronounced changes suggest that the structures of the intermediates $Ru_3(CO)_8L_3$ formed by CO dissociation must change appreciably with L. Changes only in the extent of basically rather similar processes would be unlikely to allow for such large variations. The scope for structural speculation in reactive clusters of this kind is large but we consider that species I to IV are quite reasonable possibilities. Dissociation



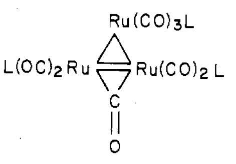
I



II



III



IV

of one CO to form I is likely to be the highest enthalpy path available and would involve the most positive $\Delta S^{\ddagger}$. However, there seems to be no reason why the four-coordinate Ru atom that it contains should not be directly attackable by L to form a further intermediate that eventually leads to complete fragmentation. The kinetics, however, do not allow for this direct competition between CO and L, and intermediate I seems unlikely to be formed directly. Formation of II would be the next highest enthalpy process. It is quite possible that direct attack by L could be slow (e.g., when L = PPh_3) for steric reasons and that rearrangement to some other form (e.g., I) would have to precede attack by L.

III involves a form of bridging by CO that has been detected[16] in a substituted dimanganese carbonyl. This extra bonding could further reduce $\Delta H_B^{\ddagger}$ and would necessarily decrease $\Delta S_B^{\ddagger}$ as well. IV is the most highly bonded of the proposed intermediates and would involve the lowest value of $\Delta H_B^{\ddagger}$ and the least favorable value of $\Delta S_B^{\ddagger}$. It obeys the 18-electron rule (formally one Ru can be regarded as being six-coordinate d^6 and the other two as seven-coordinate d^4) and is by no means intrinsically improbable. A spectrum of intermediates with greatly different bonding enthalpies and entropies is therefore easily formulated in a way consistent with the scale of the observed trend. However, a complete rationalization of how a given ligand L controls the nature of the particular intermediate formed is not yet obvious. The nature of the intermediates $Ru_3(CO)_8L_3{}^*$ may depend on the particular structures of their $Ru_3(CO)_8L_3$ precursors but they could possibly all have the structure shown by I.

The dependence on n of $\Delta H_C^{\ddagger}$ and $\Delta S_C^{\ddagger}$ for $Ru_3(CO)_{12-n}(PPh_3)_n$ also shows isokinetic behavior and this has been rationalized[10] in terms of steric effects. The only additional values are the lower limiting ones for $Ru_3(CO)_9(PBu_3)_3$ and these suggest that the ease of unimolecular fragmentation of this complex is unlikely to be very different from that of $Ru_3(CO)_9(PPh_3)_3$. More investigation of the effect of the nature of L on the [L] and [CO] independent fragmentation of $Ru_3(CO)_9L_3$ is therefore required. Some indication of a dependence on n of the ease of fragmentation of $Ru_3(CO)_{12-n}(PBu_3)_n$ is given by the fact that $Ru_3(CO)_{11}(PBu_3)$ appears to undergo fission under Ar with a rate constant of $\gtrsim 2 \times 10^{-2}\ s^{-1}$ at 50 °C (no $Ru_3(CO)_{11}(PBu_3)$ is observed[7] as an intermediate in the reaction $Ru_3(CO)_{12} \xrightarrow{PBu_3} 2Ru(CO)_4(PBu_3) + Ru(CO)_3(PBu_3)_2$) whereas $Ru_3(CO)_9(PBu_3)_3$ would undergo fragmentation at that temperature with a rate constant of ca. $2 \times 10^{-5}\ s^{-1}$.

Summary

The kinetic studies made so far of reactions of $Ru_3(CO)_{12-n}L_n$ show the following features:

(i) When $n = 3$ and L = PPh_3, PBu_3, and $P(OPh)_3$, dissociation of L is much faster than dissociation of CO. However, when L = PPh_3 and $n = 2$, CO dissociation is faster than L dissociation and, when $n = 1$, it is much faster than L dissociation.

(ii) When L = PPh_3 and n = 0–3 and when L = PBu_3 or $P(OPh)_3$ and $n = 3$, fragmentation to give well-defined mononuclear complexes is much slower than simple ligand dissociation. This is so in spite of the low values estimated for the Ru–Ru bond strengths from thermochemical[17] or other[18] data. For L = PPh_3 and $n = 3$ there is, in addition, a facile and reversible fragmentation[9] process that can be detected by reaction with O_2 but that does not eventually lead to simple mononuclear products. This fragmentation has not yet been observed for other complexes of this type.

(iii) These observations must be contrasted with the behavior of a substantial number of dinuclear carbonyls of the group 7B metals for which homolytic fission of the metal–metal bonds is the fastest rate-determining process, being used even for simple substitution reactions.[19,20]

(iv) Activation parameters for the CO-dissociation process can vary greatly with the nature of L and, to a lesser extent, with the value of n.

(v) Activation parameters for rate-determining fragmentation vary greatly with n when L = PPh_3.

(vi) These variations can only be interpreted by supposing there to be quite major differences in the bonding of the various intermediates formed.

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Registry No. $Ru_3(CO)_{11}PPh_3$, 38686-52-1; $Ru_3(CO)_{10}(PPh_3)_2$, 66172-60-9; $Ru_3(CO)_9(PPh_3)_3$, 15453-53-9; $Ru_3(CO)_9(P(OPh)_3)_3$, 50661-53-5; $Ru_3(CO)_9(PBu_3)_3$, 12258-07-0.

Supplementary Material Available: Tables of additional kinetic data and a figure showing the analysis of the [CO] dependence of the reaction of $Ru_3(CO)_9\{P(OPh)_3\}_3$ (5 pages). Ordering information is given on any masthead page.

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