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Reaction Mechanisms of Metal–Metal Bonded Carbonyls. 20.[1] Substitution and Fragmentation Reactions of Undecacarbonyl(triphenylphosphine)triruthenium and Decacarbonylbis(triphenylphosphine)triruthenium

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Kinetic studies are reported of reactions in decalin of the complexes $Ru_3(CO)_{11}(PPh_3)$ and $Ru_3(CO)_{10}(PPh_3)_2$. At moderate temperatures (25–75 °C) they undergo substitution reactions with triphenylphosphine, but only $Ru_3(CO)_{10}(PPh_3)_2$ undergoes simple substitution with carbon monoxide. The retarding effect of CO on reactions with PPh_3 is quantitatively consistent with a simple CO-dissociative mechanism, but the considerable labilization, compared with $Ru_3(CO)_{12}$, caused by the presence of PPh_3 substituents suggests that a more complex mechanism may be operating. Equilibrium constants for the substitution reactions were determined and found to depend very little on temperature. At higher temperatures (130–170 °C) both complexes undergo fragmentation reactions leading to mononuclear complexes at rates that are independent of [CO] and [PPh_3]. The activation enthalpies for fragmentation of $Ru_3(CO)_{12-n}(PPh_3)_n$ (n = 1, 2, or 3) increase dramatically with n with an almost compensating increase in $\Delta S^{\ddagger}$. This trend can be rationalized in terms of steric effects operating in the proposed intermediates $Ru_2(CO)_{8-n}(PPh_3)_n$ (n = 0, 1, or 2).

Introduction

Studies have been reported[2] of the kinetics of substitution reactions of $Ru_3(CO)_9(PPh_3)_3$ with carbon monoxide or tri-n-butylphosphine and of reaction with triphenylphosphine that leads mainly to fragmentation into monoruthenium complexes. The activation parameters for the last reaction, when it occurred at rates independent of both [CO] and [PPh_3], were assigned to fragmentation into $Ru_2(CO)_6(PPh_3)_2$ and diamagnetic $Ru(CO)_3(PPh_3)$. Those for reaction with PPh_3 under argon (under conditions such that rates were independent of [PPh_3]), and with PBu_3 or CO, were assigned to the dissociative loss of CO and PPh_3, respectively, although it was pointed out that dissociation could follow initial reversible formation of a reactive form of the complex. Activation parameters have also been obtained[3] for what is believed to be fragmentation into $Ru_2(CO)_6(PPh_3)_2$ and paramagnetic $Ru(CO)_3(PPh_3)$. In an attempt to obtain a wider base for our mechanistic conclusions, and in order to obtain comparable kinetic parameters for related complexes with different numbers of PPh_3 ligands, we have studied substitution and fragmentation reactions of the incompletely substituted complexes $Ru_3(CO)_{10}(PPh_3)_2$ and $Ru_3(CO)_{11}(PPh_3)$.

Experimental Section

Chemicals were obtained and purified exactly as described in earlier papers in this series.[2,4,5] The complexes $Ru_3(CO)_{11}(PPh_3)$ and $Ru_3(CO)_{10}(PPh_3)_2$ were prepared in situ in decalin by reacting either $Ru_3(CO)_{12}$ or $Ru_3(CO)_9(PPh_3)_3$ in decalin at 80–120 °C under an atmosphere of CO and in the presence of appropriate concentrations of PPh_3. Thus, when decalin solutions that were ca. 10^{-3} M in $Ru_3(CO)_{12}$ and PPh_3 were heated under CO at 120 °C for 5 min, the solution became yellow and showed IR bands characteristic of $Ru_3(CO)_{11}(PPh_3)$ (Table I). The spectrum is closely similar to that reported for isolated $Ru_3(CO)_{11}(PPh_3)$ in cyclohexane,[6] the main difference being the absence, in our samples, of the band of medium intensity at 1986 cm^{-1}. Weak bands characteristic of $Ru_3(CO)_{12}$ and $Ru(CO)_4(PPh_3)$ were also observed but the complex $Ru_3(CO)_{11}(PPh_3)$ was estimated to be ≳95% pure.

A similar procedure, but with solutions ca. 5×10^{-3} M in PPh_3, led to mixtures containing ca. 90% of the complex as $Ru_3(CO)_{10}(PPh_3)_2$, as judged by the IR spectrum, together with some $Ru_3(CO)_9(PPh_3)_3$. However, when decalin solutions that were ca. 10^{-3} M in $Ru_3(CO)_{12}$ and 2×10^{-3} M in PPh_3 were heated to 120 °C for 5 min under an atmosphere of CO a mixture of $Ru_3(CO)_{11}(PPh_3)$ and $Ru_3(CO)_{10}(PPh_3)_2$ was obtained. Replacement of the CO atmosphere by one of argon, followed by further heating at 75 °C for 5–10 min, led to solutions showing IR bands (Table I) attributable to $Ru_3(CO)_{10}(PPh_3)_2$ by comparison with spectra of other mono- and bis-substituted triruthenium carbonyls.[4,6,7] $Ru_3(CO)_{10}(PPh_3)_2$ has not yet been isolated and characterized. No bands were observed characteristic of $Ru_3(CO)_{11}(PPh_3)$, $Ru_3(CO)_9(PPh_3)_3$, or any likely mononuclear complexes, and the solutions were therefore judged to contain virtually pure $Ru_3(CO)_{10}(PPh_3)_2$.

Solutions for kinetic studies were prepared as above in Schlenk tubes and sealed with rubber septum caps, and the concentrations of complex and PPh_3 were adjusted as required. The solutions were then degassed by repeated freeze–pump–thaw cycles, and the desired atmosphere was introduced above the solution through stainless steel tubing. The reaction tubes were then wrapped in aluminum foil and placed in a thermostated oil bath (±0.1 °C), and samples were withdrawn at regular intervals through stainless steel tubing by

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Table I. Infrared Spectra[a] of Some Ruthenium Complexes

Complex	Frequencies, cm^{-1} (molar absorption coefficients, mol^{-1} L cm^{-1})	Ref
$Ru_3(CO)_{12}$	2062 (25 000), 2036 (15 000), 2014 (7700)	This work
$Ru_3(CO)_{11}(PPh_3)$[b]	2099 (1700), 2046 (9500), 2016 (15 000)	This work
$Ru_3(CO)_{11}(PPh_3)$[c]	2097 m, 2046 s, 2030 sh, 2023 sh, 2014 s, 1996 sh, 1986 m, 1972 sh, 1960 sh	6
$Ru_3(CO)_{10}(PPh_3)_2$[b]	2078 (1400), 2024 (9000), 1999 (12 000), 1976 sh	This work
$Ru_3(CO)_{10}\{PPh(OMe)_2\}_2$[c]	2080 m, 2029 s, 2005 s, 1984 sh, 1972 sh	6
$Ru_3(CO)_9(PPh_3)_3$	1985 (6800), 1975 (8400)	This work
$Ru_3(CO)_{11}\{P(OPh)_3\}$[c]	2055 s, 2022 s	4
$Ru_3(CO)_{10}\{P(OPh)_3\}_2$[c]	2038 s, 2010 s	4
$Ru_3(CO)_{10}\{P(OPh)_3\}_2$[c]	2089 w, 2038 s, 2018 sh, 2010 s, 1933 sh	7
$Ru(CO)_5$[d]	2035 (ca. 8 × 10^3), 1999 (ca. 10^4)	This work
$Ru(CO)_4(PPh_3)$[e]	2062 (5400), 1986 (3400), 1956 (8000)	This work
$Ru(CO)_3(PPh_3)_2$[e]	1905 (8000)	This work

[a] In decalin unless otherwise indicated. [b] Prepared in situ. [c] In cyclohexane. [d] Prepared by reaction of $Ru(CO)_4(PPh_3)$ with carbon monoxide at 150 °C. Absorption coefficients are very approximate because of correction necessary for formation of $Ru_3(CO)_{12}$ during reaction a and because of volatility of $Ru(CO)_5$. [e] Prepared by reaction of known concentration of $Ru_3(CO)_{12}$ with triphenylphosphine in decalin in sunlight, initial product being a 2:1 mixture of $Ru(CO)_4(PPh_3)$ and $Ru(CO)_3(PPh_3)_2$ which is subsequently converted to pure $Ru(CO)_3(PPh_3)_2$ by thermal reaction with triphenylphosphine at 60 °C.

applying a positive pressure of the appropriate gas or gas mixture. In some cases a continuous stream of the gas was passed through the solution during the reaction. IR spectra were recorded by using a Perkin-Elmer 257 spectrophotometer, the samples being either cooled in ice and stored for later measurements or collected directly in IR cells and their spectra measured immediately. Samples were protected from the light as much as possible.

Results

Substitution Reactions of $Ru_3(CO)_{11}(PPh_3)$ with Triphenylphosphine in Decalin. The kinetics of the reaction between 25 and 50 °C were followed by monitoring the absorbance at 2045 cm^{-1} as it decreased eventually to zero. The initial product was pure $Ru_3(CO)_{10}(PPh_3)_2$ but $Ru_3(CO)_9(PPh_3)_3$ was formed later in the reaction. First-order rate plots were linear for 90–95% reaction and the rate constants are reported in Table II. When [complex] = 4×10^{-4} M and $[PPh_3] \lesssim 5 \times 10^{-3}$ M the rate constants (not given in Table II) were less than the limiting values, k_{lim}, found at higher phosphine concentrations, but when Ar was bubbled vigorously through the reaction mixtures the rate constants increased. Further, when [complex] was reduced to $\leq 10^{-4}$ M, limiting values of the rate constants were obtained down to $[PPh_3] = 1 \times 10^{-4}$ M and the retardation of the rates at higher [complex] must be ascribed to the presence of CO released during the reaction. That the reaction is indeed retarded by CO at lower values of $[PPh_3]$ is shown by the rate constants for reactions carried out under 5.3% CO in CO–N_2 mixtures. As $[PPh_3]$ is increased, these rise to the same limiting values as those found under Ar and an excellent linear plot of $1/k_{obsd}$ against $1/[PPh_3]$ is obtained. The reaction therefore follows the rate equation

$$k_{obsd} = \{k_{lim}a[PPh_3]\}/\{1 + a[PPh_3]\} \qquad (1)$$

and a linear least-squares analysis of the dependence of $1/k_{obsd}$ on $1/[PPh_3]$, in which each value of k_{obsd} is assumed to have the same percent uncertainty, leads to $k_{lim} = (34.2 \pm 1.2) \times 10^{-4}\ s^{-1}$, $a = 580 \pm 30$ L mol^{-1}, and $\sigma(k_{obsd}) = \pm 5.9\%$.

Activation parameters for the reaction occurring at the limiting rate were determined by a least-squares analysis of the dependence of log (k_{lim}/T) on $1/T$ and are reported in Table V, each value of k_{lim} being assumed to have the same percentage uncertainty. The uncertainties are standard deviations corrected for the number of degrees of freedom so that 95% confidence limits can be obtained by doubling the uncertainties.

Substitution Reactions of $Ru_3(CO)_{10}(PPh_3)_2$ with Triphenylphosphine or Carbon Monoxide. Reaction with PPh_3 under argon was followed by monitoring the absorbance of the complex at 2024 cm^{-1} which eventually decreased to zero, the final spectrum being characteristic of $Ru_3(CO)_9(PPh_3)_3$. First-order rate plots were linear for ca. 90% reaction and the rate constants are shown in Table III.

Table II. Kinetic Data for the Reaction

$$Ru_3(CO)_{11}(PPh_3) \xrightarrow{PPh_3} Ru_3(CO)_{10}(PPh_3)_2$$

in Decalin, [Complex] = 4×10^{-4} M

Temp, °C	$10^4 \cdot [PPh_3]$, M	$10^4 \cdot k_{obsd}$, s^{-1}	Temp, °C	$10^4 \cdot [PPh_3]$, M	$10^4 \cdot k_{obsd}$, s^{-1}
50.3	1.00	33.0[a]	33.9	500	3.74
	2.50	35.0[b]		500	3.77
	2.50	34.1[a]		500	3.76
	2.50	33.4[a]	26.0	500	1.20
	2.50	33.6[a]		500	1.20
	5.60	31.5[a]			
	10.0	33.2[a]		Under 5.3% CO[a]	
	50.0	34.1[a]	50.3	5.0	7.28
	100	33.8[a]		5.0	7.30
	109	31.8		8.0	11.2
	200	32.0		8.0	11.7
	369	32.0		10.0	12.6
	500	31.6		15.0	16.0
	500	31.9		20.0	16.7
40.7	500	9.66		20.0	20.0
	500	9.50		30.0	21.9
40.9	500	9.22		40.0	24.0
				50.0	26.0
				500	32.0
				1000	32.8

[a] [Complex] = 1×10^{-4} M. [b] [Complex] = 5×10^{-5} M.

Again, when [complex] = 4×10^{-4} M and $[PPh_3] \lesssim 1 \times 10^{-2}$ M, rate constants (not shown in Table III) less than the limiting values at higher values of $[PPh_3]$ were obtained, but vigorous bubbling of Ar through the reaction mixtures increased these low rate constants. When [complex] = 6×10^{-5} M, limiting values of the rate constants were obtained for $[PPh_3]$ down to 2×10^{-4} M as shown in Table III.

The reaction was also followed under 5.3% carbon monoxide when the reactions did not proceed quite to completion. Rate constants were obtained from initial slopes of first-order rate plots made by assuming $A_\infty = 0$, and these increased with increasing $[PPh_3]$, the same limiting value being obtained at sufficiently high values of $[PPh_3]$. A good linear plot of $1/k_{obsd}$ against $1/[PPh_3]$ was obtained and a least-squares analysis, identical with that used for the corresponding reactions of $Ru_3(CO)_{11}(PPh_3)$, led to the values $k_{lim} = (23.3 \pm 1.3) \times 10^{-4}$ s^{-1}, $a = 215 \pm 20$ L mol^{-1}, and $\sigma(k_{obsd}) = \pm 10.2\%$. Under atmospheres of pure CO no reaction occurred at all until $[PPh_3] \gtrsim 0.04$ M after which the rate constants increased rapidly with $[PPh_3]$ to the limiting rate. The reactions did

Table III. Kinetic Data for the Reaction

$$Ru_3(CO)_{10}(PPh_3)_2 \xrightarrow{PPh_3} Ru_3(CO)_9(PPh_3)_3$$

in Decalin, [Complex] = 4 × 10^{-4} M

Temp, °C	10^4·[PPh$_3$], M	10^4·k_{obsd}, s^{-1}	Temp, °C	10^4·[PPh$_3$], M	10^4·k_{obsd}, s^{-1}
50.3	1.8	22.3[a]	33.9	1000	2.12
	2.0	22.1[a]		1000	2.10
	4.0	22.2[a]		1000	2.10
	10.0	22.8[a]	26.0	1000	0.62
	18.0	23.4[a]		1000	0.60
	140	21.8			
	200	22.4	Under 5.3% CO		
	500	22.8	50.3	9.50	4.10
	500	22.8		18.0	6.76
	1000	23.0		29.0	9.60
	1000	22.7		60.0	11.0
	1000	22.4		60.0	12.5
	1000	23.0		90.0	13.4
	2000	22.8		100	15.5
	2000	23.0		154	19.4
40.7	1000	6.53		238	18.6
	1000	6.40		507	22.8
	1000	6.10		1000	23.4

[a] [Complex] = 6 × 10^{-5} M.

Table IV. Kinetic Data for the Reaction

$$Ru_3(CO)_{10}(PPh_3)_2 \xrightarrow{CO^a} Ru_3(CO)_{11}(PPh_3)$$

in Decalin, [Complex] = 4.5 × 10^{-4} M

Temp, °C	10^4k_{obsd}, s^{-1}	Temp, °C	10^4k_{obsd}, s^{-1}
60.3	2.50	72.2	11.00
	2.65		10.70
			10.80
65.5	5.60		
	5.75	75.6	16.2
	5.50		17.0
			16.5

[a] Reaction under pure CO.

not go to completion until [PPh$_3$] ≳ 0.2 M. Equilibrium mixtures were studied over the range 50–150 °C, 10^3[PPh$_3$] = 5–10 M and 10^4[CO] = 3–50 M,[8] and values for K = [Ru$_3$(CO)$_9$(PPh$_3$)$_3$][CO]/[Ru$_3$(CO)$_{10}$(PPh$_3$)$_2$][PPh$_3$] were obtained. No significant variation with temperature was evident and the mean of ten measurements was 0.33 with a mean deviation of 0.09. The activation parameters in Table V were derived as described above, all the limiting values of the rate constants being used.

Reaction of Ru$_3$(CO)$_{10}$(PPh$_3$)$_2$ under an atmosphere of pure CO, and in the initial absence of any free PPh$_3$, was followed in a similar way and led to equilibrium mixtures containing about 20% unreacted complex. Knowing the total concentration of complex (4.5 × 10^{-4} M) the concentration of PPh$_3$ released could be calculated for each solution and a value of K = [Ru$_3$(CO)$_{10}$(PPh$_3$)$_2$][CO]/[Ru$_3$(CO)$_{11}$(PPh$_3$)][PPh$_3$] obtained. Two values each were obtained at temperatures of 65, 72, and 76 °C and no trend with temperature was observed, the average value being 8.0 with a mean deviation of ±1.0. Rate constants for approach to equilibrium were identical when measured by loss of reactant or growth of product. The constants quoted in Table IV, however, were obtained from initial slopes of first-order rate plots for loss of reactant with $A_\infty = 0$.

Table V. Kinetic Parameters for Dissociative Substitution Reactions of Ru$_3$(CO)$_{12-n}$(PPh$_3$)$_n$ in Decalin

Dissociating ligand	n	$\Delta H^\ddagger$, kcal mol^{-1}	$\Delta S^\ddagger$, cal deg^{-1} mol^{-1}	10^5k (50 °C), s^{-1}	$\sigma(k_{obsd})$, %
CO	0[b]	31.81 ± 0.19[a]	20.2 ± 0.6[a]	5.6	2.3
CO	1	25.59 ± 0.17[a]	9.06 ± 0.52[a]	340	3.4
CO	2	27.90 ± 0.18[a]	15.48 ± 0.57[a]	220	3.8
PPh$_3$	3[c]	29.35 ± 0.48	16.5 ± 1.5	40	8.8
PPh$_3$	2	26.42 ± 0.96	4.19 ± 2.80	7	8.0
PPh$_3$	1[d]			<0.2	

[a] From rate constants independent of [PPh$_3$]. [b] From ref 4. [c] From ref 2. [d] Simple substitution not observed. Limit for 10^5k (50 °C) obtained by extrapolation of data in Table VI.

Table VI. Rate Data for Fragmentation Reactions of Ru$_3$(CO)$_{12-n}$(PPh$_3$)$_n$ in Decalin,[a] [Complex] = 4 × 10^{-4} M

$n = 1$			$n = 2$		
Temp, °C	10^4·[PPh$_3$], M	10^4·k_{obsd}, s^{-1}	Temp, °C	10^4·[PPh$_3$], M	10^5·k_{obsd}, s^{-1}
170.0	0.00	39.5	170.0	90	115
	0.00	39.8		90	116
	0.00	39.9		90	116
160.0	0.00	21.5	160.0	90	50.0
	0.00	21.5		90	49.5
	0.00	21.6		90	48.0
150.0	0.00	12.0[b]	150.0	4.0	55.5
	0.00	12.1[b]		4.5	65.0
	0.00	12.1		6.0	59.0
	0.00	12.1		6.0	54.0
	0.00	12.0		9.0	39.0
	0.80	11.0		13.0	34.5
	0.80	10.4		25.8	25.0[b]
	0.80	10.6		28.0	25.2[b]
	1.50	8.0		30.0	29.4
	1.50	7.8		50.0	25.8
	5.00	3.9		60.0	25.5
	6.00	3.9		80.0	25.0
	6.50	3.7		80.0	24.0
	10.0	2.6		90.0	25.0
	15.0	2.8		90.0	25.3
	30.0	2.6		90.0	24.8
140.6	0.00	7.10		100	25.3
	0.00	7.20		100	22.0
	0.00	7.29		100	21.0
130.0	0.00	3.30	140.0	90.0	8.0
	0.00	3.40		90.0	8.3
	0.00	3.39		90.0	9.3

[a] Under atomospheres of 100% carbon monoxide except where indicated. [b] Under 26.8% carbon monoxide (in CO–N$_2$ mixture).

Table VII. Kinetic Parameters for Fragmentation Reactions of Ru$_3$(CO)$_{12-n}$(PPh$_3$)$_n$ in Decalin[a]

n	$\Delta H^\ddagger$, kcal mol^{-1}	$\Delta S^\ddagger$, cal deg^{-1} mol^{-1}	10^7k (100 °C), s^{-1}	$\sigma(k_{obsd})$, %
1	20.66 ± 0.22	−23.7 ± 0.5	500	3.4
2	29.68 ± 0.85	−5.7 ± 2.0	50	9.5
3[b]	35.3 ± 1.2	+7.1 ± 2.7	5	9.4

[a] Under conditions such that rates are independent of [CO] and [PPh$_3$]. [b] From ref 2.

Fragmentation Reactions of Ru$_3$(CO)$_{11}$(PPh$_3$). Reaction of Ru$_3$(CO)$_{11}$(PPh$_3$) under an atmosphere of pure CO did not occur until temperatures were raised considerably above the 25–75 °C sufficient for the substitution reactions described above to proceed quite rapidly. At 150 °C and [complex] = 4 × 10^{-4} M the products in the absence of more than traces of PPh$_3$ were Ru$_3$(CO)$_{12}$ (58%), Ru(CO)$_5$ (8%), and Ru(CO)$_4$(PPh$_3$) (34%), the yields in parentheses being based on what would have been obtained if the particular species had been the only product. The reactions at 130–170 °C were followed by monitoring the absorbance at 2046 cm^{-1} which decreased eventually to zero. First-order rate plots were linear to 80–90% reaction. Rate constants (Table VI) for reactions under 27% CO were identical with those for reactions under pure carbon monoxide.

Activation parameters (Table VII) were obtained from all the rate constants obtained in the absence of added PPh_3, the effect of which was to diminish the rates.

Fragmentation Reactions of $Ru_3(CO)_{10}(PPh_3)_2$. Reaction of this complex under CO and in the presence of varying amounts of PPh_3 led to $Ru(CO)_3(PPh_3)_2$ as the major product. Increasing but relatively small amounts of $Ru(CO)_4(PPh_3)$ were formed when $[PPh_3]$ was decreased below ca. 4×10^{-3} M, and the rates increased as well. Excellent first-order rate plots were obtained by monitoring loss of reactant. The rate constants are shown in Table VI, the activation parameters (Table VII) being estimated from data for reactions under pure CO and with $[PPh_3] = (5–10) \times 10^{-3}$ M.

Discussion

The Substitution Reactions. Substitution reactions of $Ru_3(CO)_{12}$ are believed to proceed via two paths; an associative path most probably involving nucleophilic attack at a ruthenium atom and a simple CO-dissociative path.[4] Studies of the thermal reaction of tri-*n*-butylphosphine with $Ru_3(CO)_{12}$, however, suggested that the complex $Ru_3(CO)_{11}(PBu_3)$ underwent a fission reaction leading to one $Ru(CO)_3(PBu_3)$ and two $Ru(CO)_4$ fragments in preference to further simple substitution.[5] Whether a mixture of the mononuclear products $Ru(CO)_4(PBu_3)$ and $Ru(CO)_3(PBu_3)_2$ or the trinuclear cluster complex $Ru_3(CO)_9(PBu_3)_3$ was formed eventually depended on the concentrations of $Ru_3(CO)_{12}$ and PBu_3, high $[Ru_3(CO)_{12}]$ and low $[PBu_3]$ favoring formation of the cluster product. These results suggest that substitution reactions of trinuclear ruthenium carbonyl complexes, particularly those with phosphine substituents, should not necessarily be assumed to proceed via simple paths. It has been pointed out[2] that the kinetic data for replacement of PPh_3 in $Ru_3(CO)_9(PPh_3)_3$ by PBu_3 are as consistent with a mechanism that involves reversible formation of an activated form of the complex prior to dissociative ligand interchange as with one that involves simple dissociative interchange at the intact cluster. The exact nature of the reactive form cannot be defined but one formed by homolytic fission of one Ru–Ru bond was suggested as a possibility.

The form of the kinetic data reported here does not provide direct evidence to distinguish between these mechanisms, the rate equation followed being consistent with either.[2] The data can, therefore, be explained in terms of the mechanism shown in eq 2 and 3 according to which the terms k_{lim} and a in eq 1 are equal to k_1 and k_2/k_{-1} [CO], respectively, when the reaction goes to completion.

$$Ru_3(CO)_{12-n}(PPh_3)_n \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ru_3(CO)_{11-n}(PPh_3)_n + CO \qquad (2)$$

$$Ru_3(CO)_{11-n}(PPh_3)_n + PPh_3 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Ru_3(CO)_{11-n}(PPh_3)_{n+1} \qquad (3)$$

Since, under the conditions used, $[CO] = 3.0 \times 10^{-4}$ M,[8] $k_2/k_{-1} = 0.18 \pm 0.02$ and 0.065 ± 0.010 at 50 °C for $n = 1$ and 2, respectively. The rate constants, k_{-2}, for reaction with CO at 50 °C are 7.3×10^{-5} and 40×10^{-5} s^{-1} when $n = 2$ and 3,[2] respectively, so that equilibrium constants for displacement of CO by PPh_3 are 8.4 ± 0.8 and 0.38 ± 0.06 for $n = 1$ and 2, respectively. These are in excellent agreement with those found from direct measurements of solutions at equilibrium (see above).

The data in Table V show that the introduction of one PPh_3 substituent into $Ru_3(CO)_{12}$ increases the lability toward further dissociative substitution by a factor of ca. 60 while introduction of a second increases it by a further 30%, after allowing for statistical factors. The effects on the enthalpies of activation are also pronounced, the introduction of the first substituent decreasing $\Delta H^{\ddagger}$ by ca. 6 kcal mol^{-1}, while the second results in a 2 kcal mol^{-1} increase. The activation parameters fall on a reasonably good isokinetic plot. The rather large effect of a substituent on one Ru atom on the ease of substitution at another Ru atom is surprising for a simple dissociative mechanism and may support the more complicated mechanism proposed earlier.[2] A related study[9] of the successive substitution of PPh_3 into $Ir_4(CO)_{12}$ does not provide exactly comparable information because of structural changes caused by the introduction of the first substituent.

Although the substituted ruthenium complexes appear not to undergo associative reaction with PPh_3, in contrast to $Ru_3(CO)_{12}$ itself, the increased rate of dissociative substitution in the former complexes could be accompanied by at least as fast an associative process as occurs with $Ru_3(CO)_{12}$ without it being detectable. It has, however, been shown[10] that the presence of a phosphine substituent on one metal atom can greatly decrease the tendency for associative reaction at another metal (joined to the first by a metal–metal bond), without any structural changes having been caused by the first substituent.

The values of k_2/k_{-1} at 50 °C do not vary very much with n, being 0.2, 0.18, and 0.07 for $n = 0$, 1, and 2, respectively. This suggests that the reactive centers at which the competition occurs are quite similar. The corresponding equilibrium constants are >6, 8, and 0.4.

Fragmentation Reactions. The rate of fragmentation of $Ru_3(CO)_9(PPh_3)_3$, in decalin from 140 to 170 °C and leading eventually to $Ru(CO)_3(PPh_3)_2$ in 100% yields, has been shown to be independent of [CO] and $[PPh_3]$ over certain ranges.[2] The rate-determining step was postulated to be the formation of $(PPh_3)(OC)_3Ru{=}Ru(CO)_3(PPh_3)$ and $Ru(CO)_3(PPh_3)$, further fragmentation of the dinuclear complex being rapid under these conditions. The fragmentation of $Ru_3(CO)_{11}(PPh_3)$ is also independent of [CO] ($(1–4) \times 10^{-3}$ M) but appears to be inhibited by PPh_3 (Table VI). Fragmentation of $Ru_3(CO)_{10}(PPh_3)_2$ appears to become faster when $[PPh_3]$ is decreased below 5×10^{-3} M. This behavior can be attributed, not to a dependence of the rate of fragmentation of either complex on $[PPh_3]$ but to the rapid establishment of an equilibrium mixture of the two complexes under those particular conditions. In this case the observed pseudo-first-order rate constants for fragmentation will be given by

$$k_{\text{obsd}} = \{k_{\text{fr}}' + k_{\text{fr}}''K[PPh_3]/[CO]\}\{1 + K[PPh_3]/[CO]\} \qquad (4)$$

irrespective of whether the decrease of $[Ru_3(CO)_{11}(PPh_3)]$ or $[Ru_3(CO)_{10}(PPh_3)_2]$ is monitored. (k_{fr}' and d_{fr}'' are [CO]- and $[PPh_3]$-independent rate constants for fragmentation of the mono- and bis(phosphine) complexes, respectively, and $K = [Ru_3(CO)_{10}(PPh_3)_2][CO]/[Ru_3(CO)_{11}(PPh_3)][PPh_3]$.)

The smooth line in Figure 1 was calculated with $k_{\text{fr}}' = 1.25 \times 10^{-3}$ s^{-1}, $k_{\text{fr}}'' = 2.2 \times 10^{-4}$ s^{-1}, $K = 15$, and $[CO] = 3.8 \times 10^{-3}$ M.[8] These values provide calculated values of the rate constants whose deviations from the observed rate constants (Table VI, $10^4[PPh_3] = 0.8–30$ M) lead to a value of $\sigma(k_{\text{obsd}})$ of ca. ±10%. Only those values of k_{obsd} obtained by monitoring the major constituent of the equilibrium mixture were plotted in Figure 1. These parameters also provide calculated values of 10^5k_{obsd} for reactions under 26.8% CO and $10^4[PPh_3] = 25.8$ and 28.0 M of 24.9 and 25.1 s^{-1} in excellent agreement with the measured values shown in Table VI. This confirms that eq 4 adequately describes the dependence of k_{obsd} on [CO] and that fragmentation of $Ru_3(CO)_{10}(PPh_3)_2$ also occurs by a process that is independent of [CO] as well as of $[PPh_3]$. The value of $K = 15$ at 150 °C is to be compared with the average value of 8 obtained from analysis of the equilibria over the temperature range 65–76 °C and is consistent with a fairly

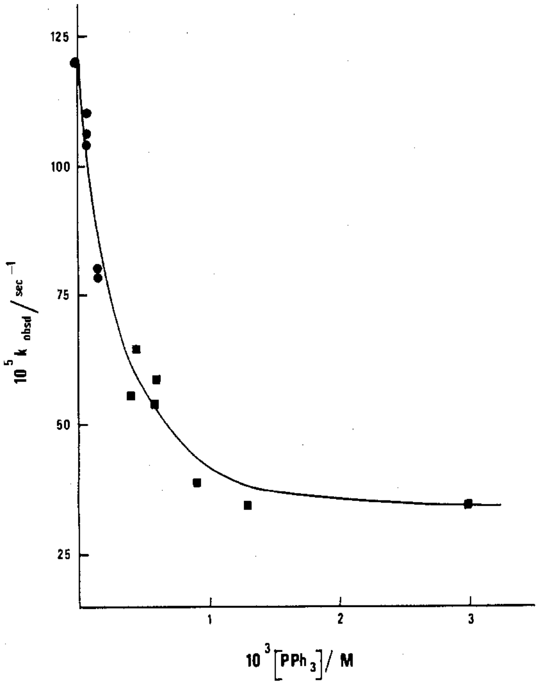

Figure 1. Dependence of rate constants for fragmentation of equilibrium mixtures of $Ru_3(CO)_{12-n}(PPh_3)_n$ (n = 1 and 2) on $[PPh_3]$ at 150 °C, measured by following loss of $Ru_3(CO)_{11}(PPh_3)$ (●) or $Ru_3(CO)_{10}(PPh_3)_2$ (■) under an atmosphere of pure CO.

small value of $\Delta H°$ for the equilibrium.

A plot of $\Delta H^{\ddagger}$ against $\Delta S^{\ddagger}$ as a function of n gives an excellently linear isokinetic plot with an isokinetic temperature of ca. 200 °C. The fact that the products of reaction of $Ru_3(CO)_{11}(PPh_3)$ with carbon monoxide include substantial amounts of $Ru_3(CO)_{12}$ does not imply that direct replacement of triphenylphosphine occurs since $Ru_3(CO)_{12}$ and $Ru(CO)_5$ are in quite labile equilibrium under these conditions, the equilibrium being in favor of $Ru_3(CO)_{12}$. Although the isokinetic plot indicates that the three reactions are occurring by very similar processes, the very wide and compensating variations of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ suggest that the transition states must lie at substantially different positions along the reaction coordinate. It must also be significant that successive substitution in the cluster makes the fragmentation progressively much harder in terms of $\Delta H^{\ddagger}$. A rationalization in terms of steric effects can be formulated. Because of the shortness expected for a fully formed Ru=Ru double bond in the $Ru_2(CO)_{8-n}(PPh_3)_n$ intermediates (n = 0, 1, or 2), we suggest that steric repulsions within the dinuclear complexes will be large so that n is kept as small as possible; i.e., the mononuclear intermediate is always $Ru(CO)_3(PPh_3)$. The two PPh_3 ligands in $[Mn(CO)_4(PPh_3)]_2$ have been shown[12] to destabilize the complex to a considerable extent due to ligand–ligand repulsion, and $[Ru(CO)_3(PPh_3)]_2$ with a short Ru=Ru bond could, therefore, also be significantly destabilized. The monotonic and substantial increase of $\Delta H^{\ddagger}$ with increasing substitution can therefore be ascribed to the increasing steric repulsion in the intermediates $Ru_2(CO)_8$, $Ru_2(CO)_7(PPh_3)$, and $Ru_2(CO)_6(PPh_3)_2$. This steric repulsion probably tends to diminish the extent of Ru=Ru double bond formation. This would account for the pronounced changes in $\Delta S^{\ddagger}$. The large negative value of $\Delta S^{\ddagger}$ (and the small value of $\Delta H^{\ddagger}$) for formation of $Ru_2(CO)_8$ and $Ru(CO)_4(PPh_3)$ is accounted for by substantial Ru=Ru double bonding and a very tightly bonded dinuclear intermediate, so that the transition state has a relatively low entropy. The positive value of $\Delta S^{\ddagger}$ (and high value of $\Delta H^{\ddagger}$) for formation of $Ru_2(CO)_6(PPh_3)_2$ and $Ru(CO)_3(PPh_3)$ implies that far less Ru=Ru double bonding has occurred in the transition state, the $Ru_2(CO)_6(PPh_3)_2$ having much less tight bonding and a corresponding high entropy. These steric effects must be much greater than any tending to destabilize the trinuclear reactant complexes.

However, whatever the detailed nature of the mechanisms, it is clear that substituents have a considerable effect on the rates of reactions of these complexes and that the effects are quite different for the different reactions.

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Registry No. $Ru_3(CO)_{12}$, 15243-33-1; $Ru_3(CO)_{11}(PPh_3)$, 38686-52-1; $Ru_3(CO)_{10}(PPh_3)_2$, 66172-60-9; $Ru_3(CO)_9(PPh_3)_3$, 15453-53-9; $Ru(CO)_5$, 16406-48-7; $Ru(CO)_4(PPh_3)$, 21192-23-4; $Ru(CO)_3(PPh_3)_2$, 14741-36-7.

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