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Substitution and Fragmentation Reactions of $Ru_3(CO)_{12-n}(P\text{-}n\text{-}Bu_3)_n$ (n = 0–2): A Product Yield Study

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The yields of $Ru_3(CO)_9(P\text{-}n\text{-}Bu_3)_3$, $Ru(CO)_4(P\text{-}n\text{-}Bu_3)$, and $Ru(CO)_3(P\text{-}n\text{-}Bu_3)_2$ that result from reactions of P-*n*-Bu_3 with the clusters $Ru_3(CO)_{12}$, $Ru_3(CO)_{11}(P\text{-}n\text{-}Bu_3)$, and $Ru_3(CO)_{10}(P\text{-}n\text{-}Bu_3)_2$ have been studied quantitatively in situ, by spectrophotometric means, as a function of [P-*n*-Bu_3] and temperature. The results show that [P-*n*-Bu_3]-independent paths always lead to substitution (S_N1 paths) whereas [P-*n*-Bu_3]-dependent reactions can lead to substitution (S_N2 paths), fragmentation (F_N2 paths), or both. Estimates of $k(F_N2)/k(S_N2)$ can be made and depend on the particular nature of the complex and on the temperature. Thus the ratio $k(F_N2)/k(S_N2)$ at 25 °C changes along the series $Ru_3(CO)_{11}(P\text{-}n\text{-}Bu_3) \gg Ru_3(CO)_{10}(P\text{-}n\text{-}Bu_3)_2 \approx Ru_3(CO)_{12}$. For $Ru_3(CO)_{12}$ the ratio decreases with increasing temperature, whereas for $Ru_3(CO)_{10}(P\text{-}n\text{-}Bu_3)_2$ it is essentially unaffected by temperature changes.

Introduction

The strength of the metal–metal bonding within a metal carbonyl cluster is often inferred qualitatively from the relative yields of substitution and fragmentation products after reaction with nucleophiles, L[1,2] (which are usually P-donor ligands of various kinds), or from the results of mass spectroscopic studies.[3]

Some years ago it was reported that $Ru_3(CO)_{12}$ reacted with P-*n*-Bu_3 to give mononuclear products unless [P-*n*-Bu_3] was quite low.[4,5] The mole ratio of the products $Ru(CO)_4(P\text{-}n\text{-}Bu_3)$ and $Ru(CO)_3(P\text{-}n\text{-}Bu_3)_2$ was 2:1,[5] and it was concluded that it was the product, $Ru_3(CO)_{11}(P\text{-}n\text{-}Bu_3)$, of the first substitution step that was undergoing fragmentation. Whether fragmentation occurred spontaneously or as a result of attack by P-*n*-Bu_3 was not clear, but it was proposed that overall substitution might occur via aggregation of intermediate $Ru(CO)_3(P\text{-}n\text{-}Bu_3)$ fragments. High concentrations of P-*n*-Bu_3 would prevent this by scavenging the $Ru(CO)_3(P\text{-}n\text{-}Bu_3)$.

We report here a systematic quantitative study of the yields of $Ru_3(CO)_9(P\text{-}n\text{-}Bu_3)_3$, $Ru(CO)_4(P\text{-}n\text{-}Bu_3)$, and $Ru(CO)_3(P\text{-}n\text{-}Bu_3)_2$ formed by reactions of $Ru_3(CO)_{12}$, $Ru_3(CO)_{11}(P\text{-}n\text{-}Bu_3)$, and $Ru_3(CO)_{10}(P\text{-}n\text{-}Bu_3)_2$ with P-*n*-Bu_3.

Experimental Section

Dodecacarbonyltriruthenium (Strem Chemicals) was used as received. Tri-*n*-butylphosphine (Aldrich) was distilled over sodium and stored under argon in a refrigerator. Toluene and dodecane (Aldrich) were dried over molecular sieves, and THF (Aldrich) was distilled over sodium benzophenone.

Table I. Spectra[a] of Ruthenium Carbonyls

complex	ν_{CO}, cm^{-1}	λ_{max}, nm
$Ru_3(CO)_{12}$	2062 (25 000), 3036 (m), 2014 (w)[b]	390 (7500)[c]
$Ru_3(CO)_{11}(P\text{-}n\text{-}Bu_3)$	2097 (w), 2044 (s), 2026 (sh), 2014 (14 600), 1999 (sh), 1993 (sh), 1983 (m), 1970 (sh), 1956 (sh)	415 (7250)
$Ru_3(CO)_{11}(P\text{-}n\text{-}Bu_3)_2$	2072 (w), 2013 (sh), 1991 (7850), 1966 (sh), 1946 (sh)	455 (7385)
$Ru_3(CO)_9(P\text{-}n\text{-}Bu_3)_3$	2036 (w), 1966 (10 000), 1932 (sh)	465 (9900)
$Ru(CO)_5$[d]	2035 (s), 1999 (vs)	
$Ru(CO)_4(P\text{-}n\text{-}Bu_3)$[d]	2060 (4600), 1980 (w), 1945 (vs)	... (60)[e]
$Ru(CO)_3(P\text{-}n\text{-}Bu_3)_2$[d]	1888 (8220)	... (54)[e]

[a] In dodecane unless otherwise stated. Numbers in parentheses are molar extinction coefficients (M^{-1} cm^{-1}). [b] In decalin. [c] In toluene. [d] In hexane. [e] No λ_{max} shown. Values are extinction coefficients at 465 nm.

Preparation of $Ru_3(CO)_{11}(P\text{-}n\text{-}Bu_3)$. The cluster $Ru_3(CO)_{11}(P\text{-}n\text{-}Bu_3)$ was prepared by the general method of Bruce et al.[6] $Ru_3(CO)_{12}$ (100 mg, 0.156 mmol) in THF (6 cm^3) was reacted with P-*n*-Bu_3 (0.044 cm^3, 0.18 mmol) in the presence of a few drops of sodium ketyl in THF at 30 °C until the IR band at 2062 cm^{-1} due to $Ru_3(CO)_{12}$ was no longer detectable. Solvent was removed under vacuum, the reddish oily product was dissolved in hexane, and the solution was filtered. The IR spectrum of the clear red filtrate showed bands due (Table I) to $Ru(CO)_4(P\text{-}n\text{-}Bu_3)$ and $Ru(CO)_3(P\text{-}n\text{-}Bu_3)_2$ in addition to those expected for $Ru_3(CO)_{11}(P\text{-}n\text{-}Bu_3)$ by comparison with the spectrum of $Os_3(CO)_{11}(P\text{-}n\text{-}Bu_3)$.[7] The cluster was separated by chromatography on a foil-wrapped 60–100 mesh Fluorosil column. Traces of unreacted $Ru_3(CO)_{12}$ were eluted first with hexane, followed by $Ru_3(CO)_{11}(P\text{-}n\text{-}Bu_3)$, the mononuclear products remaining on the column. The $Ru_3(CO)_{11}(P\text{-}n\text{-}Bu_3)$ was isolated in ca. 40% yield as an orange oil by removal of hexane under vacuum. Attempts to obtain the cluster in crystalline form were unsuccessful. It was characterized by its IR spectrum (Table I), and its purity was demonstrated by means of its ^{31}P NMR spectrum, a single sharp peak being observed at −124.0 ppm relative to $P(OMe)_3$ and decoupled from ^1H. No peaks were observed due to free P-*n*-Bu_3 or to $Ru_3(CO)_{10}(P\text{-}n\text{-}Bu_3)_2$ (see below).

Preparation of $Ru_3(CO)_{10}(P\text{-}n\text{-}Bu_3)_2$. The cluster $Ru_3(CO)_{10}(P\text{-}n\text{-}Bu_3)_2$ was prepared in a way similar to that for the monosubstituted compound but with use of a little over 2 equiv of P-*n*-Bu_3 at 40 °C. Purification by column chromatography was unsuccessful, the cluster decomposing on the column on elution with hexane, dichloromethane, or acetone. However, small amounts of $Ru_3(CO)_{12}$ were separable from a hexane solution by precipitation at 0 °C over 24 h and subsequent filtration. Reduction of the volume of the filtrate by 50% under vacuum, and addition of an equivalent volume of methanol followed by storage for 48 h in the freezer, led to formation of red-purple crystals, which were filtered off and dried (yield ca. 65%). The cluster was characterized by its IR spectrum (Table I), and its purity was demonstrated by the appearance of a single peak at −126.0 ppm in its ^{31}P NMR spectrum.

Preparation of $Ru_3(CO)_9(P\text{-}n\text{-}Bu_3)_3$, $Ru(CO)_4(P\text{-}n\text{-}Bu_3)$, and $Ru(CO)_3(P\text{-}n\text{-}Bu_3)_2$. The cluster $Ru_3(CO)_9(P\text{-}n\text{-}Bu_3)_3$ was prepared by a published method,[8] characterized by its IR spectrum, and shown to be pure by its single ^{31}P NMR peak at −127.2 ppm.

The mononuclear carbonyl $Ru(CO)_4(P\text{-}n\text{-}Bu_3)$ was prepared in situ by reaction of $Ru(CO)_5$ in hexane at 40 °C with 1 equiv of P-*n*-Bu_3, completion of the reaction being established by IR spectroscopy. The $Ru(CO)_5$ was itself prepared quantitatively in situ by photolysis[9] of a

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(1) Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds. *Comprehensive Organometallic Chemistry*; Pergamon: Oxford, England, 1982; Vol. 4 and 5.

(2) Grant, S. M.; Manning, A. R. *Inorg. Chim. Acta* **1978**, *31*, 41–48.

(3) Lewis, J.; Johnson, B. F. G. *Acc. Chem. Res.* **1968**, *1*, 245–256. Ferrari, R. P.; Vaglio, G. A.; Valle, M. *J. Chem. Soc., Dalton Trans.* **1978**, 1164–1166.

(4) Candlin, J. P.; Shortland, A. C. *J. Organomet. Chem.* **1969**, *16*, 289–299.

(5) Poë, A. J.; Twigg, M. V. *Inorg. Chem.* **1974**, *13*, 2982–2985.

(6) Bruce, M. I.; Hambley, T. W.; Nicholson, B. K.; Snow, M. R. *J. Organomet. Chem.* **1982**, *235*, 83–91. Bruce, M. I.; Kehoe, D. C.; Matisons, J. G.; Nicholson, B. K.; Rieger, P. H.; Williams, M. L. *J. Chem. Soc., Chem. Commun.* **1982**, 442–444. Bruce, M. I.; Matisons, J. G.; Nicholson, B. K. *J. Organomet. Chem.* **1983**, *247*, 321–343.

(7) Poë, A. J.; Sekhar, V. C. *Inorg. Chem.* **1985**, *24*, 4376–4380.

(8) Piacenti, F.; Bianchi, M.; Benedetti, E.; Sbrana, G. *J. Inorg. Nucl. Chem.* **1967**, *29*, 1389–1391.

(9) Johnson, B. F. G.; Lewis, J.; Twigg, M. V. *J. Organomet. Chem.* **1974**, *67*, C75–C76; *J. Chem. Soc., Dalton Trans.* **1975**, 1876–1879.

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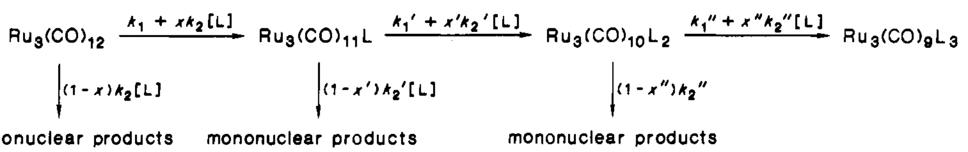
Scheme I[a]



[a] L = P-*n*-Bu$_3$.

known concentration of $Ru_3(CO)_{12}$ under CO in hexane and removal of unreacted CO by purging with argon. The complex $Ru(CO)_3(P\text{-}n\text{-}Bu_3)_2$ was prepared in situ by reaction of $Ru(CO)_4(P\text{-}n\text{-}Bu_3)$ in hexane at 60 °C with 1 molar equiv of P-*n*-Bu$_3$ until all IR bands due to $Ru(CO)_4(P\text{-}n\text{-}Bu_3)$ had disappeared.

Spectrometric Measurements. UV–vis spectra were recorded in 10-mm silica cells placed in a thermostated cell holder in a Cary 2300 spectrophotometer. Temperatures of the solutions were measured with an iron–constantan thermocouple combined with a digital multimeter. IR spectra were measured with a Nicolet 10DX FTIR spectrophotometer, and ^{31}P NMR spectra with a Varian XL-200 spectrometer.

Product Yield Studies. Solutions of $Ru_3(CO)_{12}$ in toluene were prepared by weighing and their concentrations confirmed by means of their absorbance values at 390 nm coupled with the independently determined molar extinction coefficient (Table I). Samples (2.7 cm^3) were thermostated (±0.1 °C) in silica cells in the cell holder of the UV–visible spectrophotometer. Toluene solutions (0.3 cm^3) of P-*n*-Bu$_3$ in various known concentrations were added, and the cells were stoppered and shaken vigorously before replacement in the cell holder. The course of each reaction was monitored by measurement of UV–visible spectra until no further change occurred.

The yields, Y_0, of the stable[5,10] product $Ru_3(CO)_9(P\text{-}n\text{-}Bu_3)_3$ were calculated from eq 1, where A_{obsd} is the measured absorbance at 465 nm

$$Y_0 = (A_{obsd} - A_0)/(A_{100} - A_0) \qquad (1)$$

(λ_{max} for $Ru_3(CO)_9(P\text{-}n\text{-}Bu_3)_3$) and A_{100} and A_0 are the absorbances at 465 nm that would have been obtained if the yield of trisubstituted product had been 100% and 0% respectively. Absorbances were normalized to what they would have been for solutions of cluster of exactly 10^{-4} M concentration so that values of 10^4A are the corresponding molar extinction coefficients. 10^4A_0 is given by the sum of the products of the respective molar extinction coefficients at 465 nm and the concentrations of $Ru(CO)_4(P\text{-}n\text{-}Bu_3)$ and $Ru(CO)_3(P\text{-}n\text{-}Bu_3)_2$ that would have been present if 100% fragmentation had occurred. Measurement of the intensities of the IR bands at 2060 cm^{-1} ($Ru(CO)_4(P\text{-}n\text{-}Bu_3)$) and 1888 cm^{-1} ($Ru(CO)_3(P\text{-}n\text{-}Bu_3)_2$) showed that these two complexes were formed in the mole ratio 2.1 ± 0.1 at 25 °C in agreement with previous work.[5] Since their molar extinction coefficients at 465 nm are small and close, the value of A_0 can be taken as $3 \times 10^{-4}\epsilon_{Ru} = 0.017$, where ϵ_{Ru} is the weighted average of the extinction coefficients of the two mononuclear products.

Several groups of measurements were performed at different values of [P-*n*-Bu$_3$] and at temperatures close to 25, 40, 50, and 60 °C. The absorbances were corrected to what they would have been at exactly these temperatures by taking into account the temperature dependence of the yields. These corrections were always small (≤10%).

Similar procedures were followed to obtain the yields, Y_1 and Y_2, of $Ru_3(CO)_9(P\text{-}n\text{-}Bu_3)_3$ from $Ru_3(CO)_{11}(P\text{-}n\text{-}Bu_3)$ and $Ru_3(CO)_{10}(P\text{-}n\text{-}Bu_3)_2$, respectively, but in these cases reactions were carried out in dodecane. Since $Ru_3(CO)_{11}(P\text{-}n\text{-}Bu_3)$ was obtainable only as an oil, its initial concentration was estimated from the sum of the concentrations of the products, those of the mononuclears being obtained from the IR spectra and that of $Ru_3(CO)_9(P\text{-}n\text{-}Bu_3)_3$ being estimated from the absorbance at 465 nm, corrected for that part of the absorbance due to the mononuclears. The yield of fragmentation products from $Ru_3(CO)_{10}(P\text{-}n\text{-}Bu_3)_2$ was quite small, but the $Ru(CO)_4(P\text{-}n\text{-}Bu_3)$ and $Ru(CO)_3(P\text{-}n\text{-}Bu_3)_2$ complexes were formed in the mole ratio of ca. 1:2.3 for 10% fragmentation.

Reaction Scheme and Data Analysis

The yields (Figure 1) of $Ru_3(CO)_9(P\text{-}n\text{-}Bu_3)_3$ from $Ru_3(CO)_{12}$ vary with [P-*n*-Bu$_3$] and temperature in a manner similar to those observed qualitatively for $Os_3(CO)_9(P\text{-}n\text{-}Bu_3)_3$ from $Os_3(CO)_{12}$.[7] Thus, at higher temperatures and low [P-*n*-Bu$_3$] the yields approach 100%. As [P-*n*-Bu$_3$] is increased, the yield decreases, and this decrease is more pronounced the lower the temperature. By analogy with the reactions of $Os_3(CO)_{12}$,[7] we propose that [P-*n*-Bu$_3$]-independent reactions lead only to $Ru_3(CO)_9(P\text{-}n\text{-}Bu_3)_3$ by a sequence of S_N1 processes as shown in Scheme I. On the other hand, associative reactions can lead to fragmentation by F_N2 processes[7,11] that are more pronounced at lower temperatures because of the relatively low activation enthalpies for such bimolecular reactions. Although the bimolecular reactions can lead to fragmentation, they do not necessarily do so, and we have included in Scheme I the possibility that they can also lead to S_N2 processes. The proportions of the latter are defined by the parameters x, x', and x'' for reactions of $Ru_3(CO)_{12}$, $Ru_3(CO)_{11}(P\text{-}n\text{-}Bu_3)$, and $Ru_3(CO)_{10}(P\text{-}n\text{-}Bu_3)_2$ respectively, while the corresponding second-order rate constants are defined by k_2, k_2', and k_2''. The yield, Y_0, of $Ru_3(CO)_9(P\text{-}n\text{-}Bu_3)_3$ from $Ru_3(CO)_{12}$ can therefore be expressed quantitatively by eq 2 (L = P-*n*-Bu$_3$)

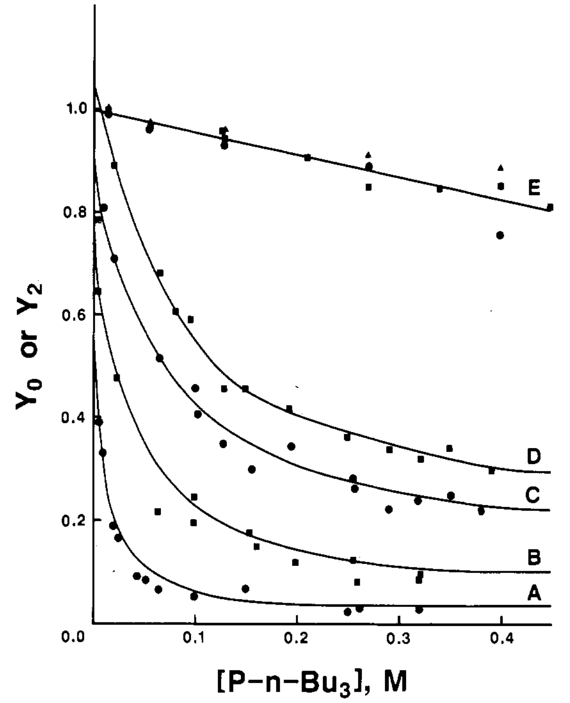


Figure 1. Fractional yields of $Ru_3(CO)_9(P\text{-}n\text{-}Bu_3)_3$: (A–D) Y_0 at 25.0, 40.0, 50.0, and 60.0 °C, respectively, with the continuous lines drawn as calculated according to the derived parameters given in Table II; (E) Y_2 at 15.8 (■), 25.0 (●), and 39.3 °C (▲), with the line drawn corresponding to $Y_2 = 1 - 0.33[\text{P-}n\text{-Bu}_3]$.

$$Y_0 = \frac{k_1 + xk_2[L]}{k_1 + k_2[L]}\left(\frac{k_1' + x'k_2'[L]}{k_1' + k_2'[L]}\right)\frac{k_1'' + x''k_2''[L]}{k_1'' + k_2''[L]} \qquad (2)$$

and the yields, Y_1 and Y_2, from $Ru_3(CO)_{11}(P\text{-}n\text{-}Bu_3)$ and $Ru_3(CO)_{10}(P\text{-}n\text{-}Bu_3)_2$, respectively, can be expressed by eq 3 and 4.

$$Y_1 = \frac{k_1' + x'k_2'[L]}{k_1' + k_2'[L]}\left(\frac{k_1'' + x''k_2''[L]}{k_1'' + k_2''[L]}\right) \qquad (3)$$

$$Y_2 = \frac{k_1'' + x''k_2''[L]}{k_1'' + k_2''[L]} \qquad (4)$$

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(10) Malik, S. K.; Poë, A. J. *Inorg. Chem.* **1979**, *18*, 1241–1245.

(11) Brodie, N. M. J.; Poë, A. J.; Sekhar, V. C. *J. Chem. Soc., Chem. Commun.* **1985**, 1090–1091.

Table II. Parameters Derived from Yields of $Ru_3(CO)_9(P\text{-}n\text{-}Bu_3)_3$ Obtained by Reaction of P-*n*-Bu_3 with $Ru_3(CO)_{12-n}(P\text{-}n\text{-}Bu_3)_n$ (n = 0–2)

n	T, °C	no. of points[a]	x	x'	x''[b]	k_2'/k_1', M^{-1}	$\sigma(A_{obsd})$, %
2	15.8	5/5			0.76 ± 0.05	(3.18 ± 0.50[c])	7.4
0	25.0	11/12	0.64 ± 0.06	0.002 ± 0.011		118 ± 19	12.6
1	25.0	5/5		0.016 ± 0.004		135 ± 13	7.7
2	25.0	10/10			0.69 ± 0.10	(2.09 ± 0.32[c])	2.3
0	40.0	12/14	0.81 ± 0.06	0.03 ± 0.03		30 ± 7	12.9
1	39.3	4/4		0.015 ± 0.010		39 ± 4	6.5
2	39.3	5/5			0.62 ± 0.15	(1.14 ± 0.27[c])	1.8
0	50.0	14/14	0.91 ± 0.04	0.16 ± 0.08		16.3 ± 3.6	7.7
1	47.1	5/5		0[d]		26 ± 4	8.3
0	60.0	12/12	1.09 ± 0.06	0.17 ± 0.08		13.0 ± 2.8	4.6
1	57.1	3/4		0.010 ± 0.005		14.5 ± 1.0	3.0

[a] Number of measurements used in computation/number of points available. [b] Values obtained from eq 4 by making use of values of k_2''/k_1'' from direct kinetic measurements.[15] [c] k_2''/k_1''. [d] $\sum(\Delta A)^2$ increases steadily as x' increases from zero.

It is shown by the data in Figure 1 that the dependence of Y_2 on [L] can be expressed empirically by eq 5 over the range 16–39 °C, and we assume that this small dependence on [L] will also

$$Y_2 = 1 - 0.33[L] \quad (5)$$

be shown at 50 and 60 °C. Under all the conditions used for reactions of $Ru_3(CO)_{12}$, we have $k_2[L] \gg k_1$,[5] and since x is also quite large,[12] $xk_2[L] \gg k_1$. Equations 2 and 3 can therefore be simplified to eq 6 and 7.

$$Y_0' = Y_0/Y_2 = Y_0/(1 - 0.33[L]) = \frac{x + xx'(k_2'/k_1')[L]}{1 + (k_2'/k_1')[L]} \quad (6)$$

$$Y_1' = Y_1/Y_2 = Y_1/(1 - 0.33[L]) = \frac{1 + x'(k_2'/k_1')[L]}{1 + (k_2'/k_1')[L]} \quad (7)$$

Equations 6 and 7 can be rearranged to eq 8, and plots of $Y_1'/(1 - Y_1')$ against 1/[L] are shown in Figure 2 to be linear as predicted. Plots of $Y_0'/(1 - Y_0')$ against 1/[L] are also reasonably

$$\frac{Y_0'}{x - Y_0'} = \frac{Y_1'}{1 - Y_1'} = \frac{x'}{1 - x'} + \frac{k_1'}{(1 - x')k_2'}\left(\frac{1}{[L]}\right) \quad (8)$$

linear, at least at high values of [L], and this suggests that x is not very different from unity.[12] Plots such as these provide initial values of x, x', and k_2'/k_1' that can then be used in a nonlinear least-squares search program[13] to find the best values for the parameters in eq 9 by minimizing $\sum(\Delta Y_0')^2$ ($\Delta Y_0' = (Y_0')_{obsd} - (Y_0')_{calcd}$).

$$Y_0' = (a + b[L])/(1 + c[L]) \quad (9)$$

The parameters a, b, and c are identical with x, $xx'(k_2'/k_1')$, and k_2'/k_1', respectively, and the values of x, x_1', and k_2'/k_1' derived from them are given in Table II together with estimates of their standard deviations. The values of a, b, and c were used to calculate values of Y_0'.

Values of expected absorbances, A_{calcd}, were also calculated, and deviations from those actually observed estimated as $\Delta A = 100[A_{obsd} - A_{calcd}]/A_{calcd}$. This leads to values of the standard deviations of an individual absorbance measurement, $\sigma[A_{obsd}] = (\sum(\Delta A)^2/(N - 3))^{1/2}$, that are also listed in Table II.[14]

The parameters x' and k_2'/k_1' can also be obtained from the product yields from reactions of $Ru_3(CO)_{11}(P\text{-}n\text{-}Bu_3)$. They were obtained from linear least squares analysis of plots shown in Figure 2, and the results are also given in Table II.

The data for reactions of $Ru_3(CO)_{10}(P\text{-}n\text{-}Bu_3)_2$ cannot be analyzed to give independent values of x'' and k_2''/k_1'' by application of eq 4 because the decrease of absorbance is not great enough. However, if values of k_2''/k_1'' = 3.18 ± 0.50, 2.09 ± 0.32, and 1.14 ± 0.27 M^{-1} obtained,[15] respectively, from direct kinetic studies at 15.8, 25.0, and 39.3 °C, are taken, then values of x'' can be obtained. The uncertainties are quite large owing to the small decrease in absorbance and the relatively large uncertainties in k_2'', which are caused by the small contribution of the term $k_2''[L]$ to the value of k_{obsd}.

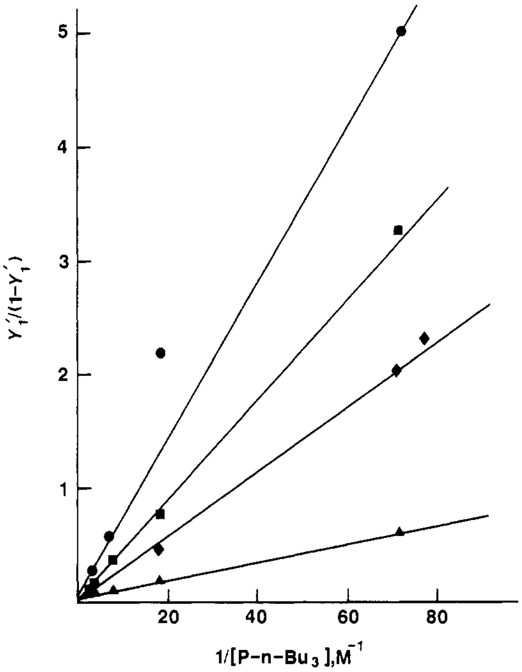

Figure 2. Dependence of Y_1' on [P-*n*-Bu_3] at 25.0 (▲), 39.3 (◆), 47.1 (■), and 57.1 °C (●).

Discussion

The analysis of the data in terms of Scheme I leads to parameters that are quite precise and fully self-consistent. Thus, the values that are obtained for k_2'/k_1' (Table II) are independent of whether they are obtained from reactions of $Ru_3(CO)_{12}$ in toluene or from $Ru_3(CO)_{11}(P\text{-}n\text{-}Bu_3)$ in dodecane, and this supports the validity of the analysis and shows that the solvent effect is insignificant. Additional support for the analysis is the fact that the values of k_2'/k_1' are also in good agreement with those obtained[11,15] by direct kinetic measurements, and the decrease in k_2'/k_1' with increasing temperature is fully compatible with a lower value of the activation enthalpy expected for a second-order reaction compared with a first order reaction. The values of $\Delta H_2'^{\ddagger} - \Delta H_1'^{\ddagger}$ and $\Delta S_2'^{\ddagger} - \Delta S_1'^{\ddagger}$ are −13.2 ± 1.0 kcal mol^{-1} and −34.9 ± 3.2 cal K^{-1} mol^{-1}, respectively, in excellent agreement with those obtained[11,15] kinetically of −14.1 ± 0.7 kcal mol^{-1} and −39.8 ± 2.0 cal K^{-1} mol^{-1}.

The values of x in Table II show that the reaction of $Ru_3(CO)_{12}$ does proceed mainly by an S_N2 process at higher temperatures

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(12) This can be concluded since the yield of $Ru_3(CO)_9(P\text{-}n\text{-}Bu_3)_3$ is high at low [P-*n*-Bu_3] even though the reaction of $Ru_3(CO)_{12}$ is still proceeding mainly by the second-order path.[5]

(13) Written by T. Haslett of this department and based on the equations given by: Wentworth, W. E. *J. Chem. Educ.* **1965**, *42*, 96–103.

(14) These standard deviations are not, of course, simply related to the uncertainty of measuring an absorbance but are also related to any uncertainties in [P-*n*-Bu_3] and [$Ru_3(CO)_{12}$].

(15) Brodie, N. M. J. M.Sc. Thesis, University of Toronto, 1985, and unpublished work.

but that the competing F_N2 process becomes quite significant at lower temperatures.[16] This trend shows that the F_N2 process has a lower activation enthalpy than the S_N2 process. The difference would be given by the temperature dependence of $(1 - x)/x$ but this cannot be obtained because of the very large uncertainty in $(1 - x)$.

The values of x' are all very small and hardly distinguishable from zero. This implies that $k(F_N2) \gg k(S_N2)$ for $Ru_3(CO)_{11}(P\text{-}n\text{-}Bu_3)$. The values of x'', however, show that $k(F_N2) = \sim 0.5k(S_N2)$.

These results are the first quantitative demonstration that associative reactions of metal carbonyl clusters can lead to substitution and fragmentation in proportions that depend on the extent of substitution of the cluster and on the temperature. Similar, but only qualitative, studies of reactions of P-*n*-Bu$_3$ with $Os_3(CO)_{12-n}(P\text{-}n\text{-}Bu_3)_n$ (n = 0–2) showed that the associative reaction of the monosubstituted cluster leads only to fragmentation and that of the unsubstituted cluster leads to a significant but unquantified amount of fragmentation.[7] The bis-substituted Os_3 cluster does not undergo associative reaction, and only the S_N1 process occurs. The [ligand]-independent reactions of all the other Ru_3 and Os_3 clusters also lead only to substitution.

Some qualitative evidence for the ready fragmentation of some Fe_3 carbonyl clusters has also been obtained from synthetic studies but no indication was obtained as to whether low yields of trisubstituted clusters were due to fragmentation of less substituted intermediate clusters and whether fragmentation was caused by associative reactions.[2] However, Shojaie and Atwood[17] have carried out kinetic and product formation studies of reactions of $Fe_3(CO)_{12}$ and $Fe_3(CO)_{11}(PPh_3)$ with some P-donor ligands, L. The results show that $Fe_3(CO)_{12}$ undergoes only S_N1 reactions to form $Fe_3(CO)_{11}L$. No clear evidence for any associative paths was obtained at the rather low ligand concentrations used. When L = $P(OMe)_3$ or $P(OPh)_3$ further substitutions occur to form $Fe_3(CO)_9L_3$. Some fragmentation was also observed but which cluster or clusters underwent fragmentation was not evident. When L = PPh_3 or P-*n*-Bu$_3$ further reaction leads entirely to fragmentation. Reactions of $Fe_3(CO)_{11}(PPh_3)$ with PPh_3 or $P(OMe)_3$ occur only by [ligand]-independent paths.

It is therefore evident that all the complexes $M_3(CO)_{11}L$ (M = Fe, L = PPh_3 or P-*n*-Bu$_3$; M = Ru or Os, L = P-*n*-Bu$_3$) are particularly susceptible to fragmentation. The Fe_3 clusters must be intrinsically weak enough for them to undergo fragmentation without the assistance of an attacking nucleophile.[18] However, when M = Fe and L = $P(OMe)_3$ or $P(OPh)_3$, the cluster $M_3(CO)_{11}L$ is much less susceptible to unassisted fragmentation. The Ru_3 and Os_3 clusters require nucleophilic assistance for fragmentation to occur. This is in spite of the substantial lengthening and presumed weakening of one M–M bond in $M_3(CO)_{11}L$ clusters (M = Ru, L = PPh_3,[20] $P(C_6H_{11})_3$,[21] or $P(C_2H_5)_3$;[22] M = Os, L = $P(OMe)_3$[23]).

The unsubstituted $M_3(CO)_{12}$ cluster (M = Ru or Os) can undergo F_N2 reactions with P-*n*-Bu$_3$, but they are less rapid than those of their $M_3(CO)_{11}(P\text{-}n\text{-}Bu_3)$ analogues and there is a greater tendency for some S_N2 processes to occur as well, or even instead. Of the bis-substituted clusters only $Ru_3(CO)_{10}(P\text{-}n\text{-}Bu_3)_2$ has been shown to undergo fragmentation and then only by an associative process that is comparable in rate to a parallel S_N2 process and much slower than the F_N2 reaction of the monosubstituted analogue.[11]

Fragmentation reactions of $Ru_3(CO)_{12-n}L_n$ (L = PPh_3, n = 1–3; L = $P(OPh)_3$ or P-*n*-Bu$_3$, n = 3) have been shown to proceed by dissociative or spontaneous processes,[10] the latter involving neither loss nor gain of a ligand in the rate-determining step. All these reactions are very much slower than those of the Fe_3 clusters.

The greater readiness of the $Fe_3(CO)_{11}L$ clusters to undergo unassisted fragmentation is clearly related to the much weaker metal–metal bonding found between first-row transition metals,[24] but it is still a borderline situation. Thus, when L = CO, $P(OMe)_3$, or $P(OPh)_3$, substitution appears to be much preferred over fragmentation, whereas when L = PPh_3 or P-*n*-Bu$_3$ fragmentation is favored.[17] The similar sizes[25] of P-*n*-Bu$_3$ and $P(OPh)_3$ suggest that the distinction is electronic and not steric, fragmentation evidently being favored by higher σ-basicity and/or weaker π-acidity.

Because of their stronger metal–metal bonding[24] the Ru_3 and Os_3 clusters are all intrinsically very much less susceptible to fragmentation, which is greatly assisted by nucleophilic attack, the intimate mechanism of which is still uncertain. Various possibilities have been proposed,[7,26–29] but they all have one feature in common; viz., reaction can occur via an initially formed[30] reactive intermediate that still retains 18-electron configurations around each metal atom. This is made possible by a reduction of two in the number of electrons involved in cluster bonding, but this is offset by the formation of a bond between a metal atom and the incoming nucleophile. In this respect the mechanism closely resembles those proposed by Basolo et al.[31] for the classical associative reactions of nitrosyl– and cyclopentadienyl–metal carbonyls, etc.

The weakening of the cluster bonding that accompanies nucleophilic attack at least provides the possibility for fragmentation to be the outcome of associative reaction although whether it is or not depends on the nature of the metal and any substituents present, the number of metal atoms in the cluster, and the nature of the attacking nucleophile.[7,11,26–28] A wider exploration of these variables is clearly needed before a clear understanding of the various factors involved can be obtained.

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Registry No. $Ru_3(CO)_{11}(P\text{-}n\text{-}Bu_3)$, 99639-75-5; $Ru_3(CO)_{10}(P\text{-}n\text{-}Bu_3)_2$, 99639-78-8; $Ru_3(CO)_{12}$, 15243-33-1; $Ru_3(CO)_9(P\text{-}n\text{-}Bu_3)_3$, 12258-07-0; $Ru(CO)_4(P\text{-}n\text{-}Bu_3)$, 52699-23-7; $Ru(CO)_3(P\text{-}n\text{-}Bu_3)_2$, 16369-47-4; $Ru(CO)_5$, 16406-48-7; P-*n*-Bu$_3$, 998-40-3.

Supplementary Material Available: Tables of values of A_{obsd} and A_{calcd} (4 pages). Ordering information is given on any current masthead page.

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(16) The absolute values of x are strongly dependent (eq 1 and 6) on the value of $A_{100} - A_0$ and are affected by any uncertainty in that difference. However, they are not very dependent on A_0 (which is generally small compared with A_{obsd}, especially for those data that contribute mainly to the value of x) so that the trend in x with changing temperature is quite well-defined.

(17) Shojaie, A.; Atwood, J. D. *Organometallics* **1985**, *4*, 187–190.

(18) It is not clear, however, whether these reactions are spontaneous or whether they proceed by dissociative activation[10,19] since no attempt was made[17] to study the effect of CO on the rates.

(19) Huq, R.; Poë, A. J. *J. Organomet. Chem.* **1982**, *226*, 277–288.

(20) Forbes, E. J.; Goodhand, N.; Jones, D. L.; Harmor, T. A. *J. Organomet. Chem.* **1979**, *182*, 143–154.

(21) Bruce, M. I.; Matisons, J. G.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1983**, 2375–2384.

(22) Brodie, N. M. J.; Sawyer, J., unpublished observations.

(23) Benfield, R. E.; Johnson, B. F. G.; Raithby, P. R.; Sheldrick, G. M. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1978**, *B34*, 666–667.

(24) Connor, J. A. *Top. Curr. Chem.* **1977**, *71*, 71–110.

(25) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313–348.

(26) Poë, A. J.; Twigg, M. V. *J. Chem. Soc., Dalton Trans.* **1974**, 1860–1866.

(27) Dahlinger, K.; Falcone, F.; Poë, A. J. *Inorg. Chem.* **1986**, *25*, 2654–2658.

(28) Bor, G.; Dietler, U. K.; Pino, P.; Poë, A. J. *J. Organomet. Chem.* **1978**, *154*, 301–315.

(29) Brodie, N. M. J.; Chen, L.; Poë, A. J. *Int. J. Chem. Kinet.* **1988**, *20*, 467–491.

(30) The events, leading to fragmentation, that occur subsequently may be more complex than the simple formation of $M(CO)_4L$ from $M_3(CO)_{12}$, $M(CO)_4L$ and $M(CO)_3L_2$ (in the mole ratio 2:1) from $M_3(CO)_{11}L$, and $M(CO)_4L$ and $M(CO)_3L_2$ (in the mole ratio 1:2) from $M_3(CO)_{10}L_2$. Thus, the increase in the ratio $[Os(CO)_3L_2]$:$[Os(CO)_4L]$ with increasing [L] after reaction of $Os_3(CO)_{11}L$ with L (L = P-*n*-Bu$_3$) has been ascribed[7] to associative substitution of an Os_2 intermediate before it undergoes further fragmentation to mononuclear products. A similar phenomenon may be operating in the reaction of $Ru_3(CO)_{12}$ with P-*n*-Bu$_3$ because the mole ratio $[Ru(CO)_4L]$:$[Ru(CO)_3L_2]$ is still ca. 2:1 at 25 °C. This is so even though the value of $1 - x$ indicates that appreciable direct fragmentation of $Ru_3(CO)_{12}$ is occurring so that a higher relative yield of $Ru(CO)_4$ L might be expected. This subtle aspect of these reactions requires further study.

(31) Basolo, F. *Inorg. Chim. Acta* **1985**, *100*, 33–39.