methylene chloride is used as the solvent, it can act as such a reagent in that it is known to react with trimethylamine[11,14] to form [(CH$_3$)$_3$N·CH$_2$Cl]Cl, which precipitates from the solution, thus effectively removing the amine from the carborane site. Substituting CHCl$_3$ for CH$_2$Cl$_2$ as the solvent in the Br/Cl exchange reaction between (CH$_3$)$_3$N·5BrC$_2$B$_5$H$_6$ and benzyltriethylammonium chloride reduces the yield of 5-ClC$_2$B$_5$H$_6$ from nearly 100% to about 50%. The ^{11}B NMR spectrum of the reaction carried out in CHCl$_3$ strongly suggests that the remaining carborane material is manifested as 2(CH$_3$)$_3$N·XC$_2$B$_5$H$_6$ (X = Br, Cl). Under the conditions of the reaction CHCl$_3$ does not remove the amine; instead it is suggested that this task is effectively carried out by another such molecule of the (CH$_3$)$_3$N·5-XC$_2$B$_5$H$_6$, forming the diamine adduct of the latter. In control experiments it is found that (CH$_3$)$_3$N·5-XC$_2$B$_5$H$_6$ (X = Br, Cl) compounds can react with additional (CH$_3$)$_3$N to form diamine adducts of the halocarboranes.[27]

The dihalocarborane 5,6-Br$_2$C$_2$B$_5$H$_5$ combines with trimethylamine and benzyltriethylammonium chloride in CD$_2$Cl$_2$ to give a nearly quantitative yield of 5,6-Cl$_2$C$_2$B$_5$H$_5$. Monitoring

the reaction during intermediate stages indicates the buildup of a modest amount of 5-Cl-6-BrC$_2$B$_5$H$_5$ and the eventual conversion of this species to the final 5,6-Cl$_2$C$_2$B$_5$H$_5$ product. Halogen ion exchanges of dihalogenated cage species generally occur much more rapidly than those involving monohalogenated cage species. It is not difficult to imagine that the presence of a second halogen on the polyhedral framework could significantly alter the cage boron electron density at the site of attack, resulting in a different (in this case, faster) rate of halogen exchange.

A couple of halogen ion exchange reactions, (CH$_3$)$_3$N·5-ClC$_2$B$_5$H$_6$/tetrabutylammonium fluoride/CH$_2$Cl$_2$ and (CH$_3$)$_3$N·5-BrC$_2$B$_5$H$_6$/tetrabutylammonium fluoride/CH$_2$Cl$_2$, produce a substantial amount of the parent C$_2$B$_5$H$_7$ along with the expected *B*-halocarborane product. A measurable quantity of (CH$_3$)$_3$N·BH$_3$ is also formed in these reactions, suggesting that this simple amine–borane, or some other similar cage breakdown product, may well have acted as a reducing agent on one of the halocarborane reactants (or intermediates) to give the observed C$_2$B$_5$H$_7$.

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Substitution and Fragmentation Kinetics of Os$_3$(CO)$_{12}$, Os$_3$(CO)$_{11}$(P-*n*-Bu$_3$), and Os$_3$(CO)$_{10}$(P-*n*-Bu$_3$)$_2$

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The kinetics of the stepwise reactions of Os$_3$(CO)$_{12}$ with P-*n*-Bu$_3$ in Decalin have been studied. Substitution to form Os$_3$(CO)$_9$(P-*n*-Bu$_3$)$_3$ occurs via a series of [P-*n*-Bu$_3$]-independent steps, but nucleophilic attack on Os$_3$(CO)$_{12}$ and Os$_3$(CO)$_{11}$(P-*n*-Bu$_3$) leads to fragmentation products by a bimolecular process that can be classified as F$_N$2. Os$_3$(CO)$_{10}$(P-*n*-Bu$_3$)$_2$ is not susceptible to nucleophilic attack and does not undergo fragmentation. The relative activation energies of the various reactions are such that Os$_3$(CO)$_9$(P-*n*-Bu$_3$)$_3$ is formed quantitatively at 170 °C and fairly low [P-*n*-Bu$_3$] whereas under much milder conditions (70 °C, and much higher [P-*n*-Bu$_3$]), only mononuclear fragmentation products are found. The introduction of P-*n*-Bu$_3$ substituents into the Os$_3$(CO)$_{12}$ cluster has a pronounced effect on the activation parameters for further reaction.

Introduction

The kinetics of thermal reactions of metal carbonyl clusters have received surprisingly little study compared with the vast efforts devoted to synthesis and structural determination. Thus, although Ru$_3$(CO)$_{12}$,[1] Co$_4$(CO)$_{12}$,[2] and Ir$_4$(CO)$_{12}$[3] and their derivatives[2c–e,3,4] have been the subject of fairly extensive kinetic

studies, virtually nothing is known about other archetypal carbonyl clusters. Apart from the ^{14}CO-exchange reaction,[1a] only two kinetic studies of a substitution reaction of Fe$_3$(CO)$_{12}$ have been reported,[5] and the only thermal reactions of Os$_3$(CO)$_{12}$ that have been studied kinetically are the exchange reaction with ^{14}CO,[1a] reactions with Cl$_2$ and Br$_2$,[6] and, quite recently, reactions with very low concentrations of some P donors.[5b] We report here a kinetic study of the reactions of Os$_3$(CO)$_{12}$ with P-*n*-Bu$_3$ and PPh$_3$ and of Os$_3$(CO)$_{11}$(P-*n*-Bu$_3$) and Os$_3$(CO)$_{10}$(P-*n*-Bu$_3$)$_2$ with P-*n*-Bu$_3$.

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Table I. Rate Constants[a] for Reactions of $Os_3(CO)_{12}$ and $Os_3(CO)_{11}(P\text{-}n\text{-}Bu_3)$ with $P\text{-}n\text{-}Bu_3$ in Decalin under Ar

T, °C	[L], M	no. of determins	$10^5 k_1$, s^{-1}	$10^5 k_2$, M^{-1} s^{-1}	$\sigma(k_{obsd})$, %
			$Os_3(CO)_{12}$		
75.0	0.05–1.0	6	0.0715 ± 0.0032	0.863 ± 0.021	⎫
96.1	0.05–0.8	4	1.37 ± 0.04	5.12 ± 0.23	⎬ 3.7
123.5	0.024–0.67	4	33.4 ± 0.8	36.4 ± 3.4	⎪
148.7	0.038–0.80	4	400 ± 8	197 ± 30	⎭
			$Os_3(CO)_{11}(P\text{-}n\text{-}Bu_3)$		
70.0	0.10–0.40	4	0.001 ± 0.070	5.07 ± 0.16	⎫
110.0	0.04–0.40	6	4.05 ± 0.03	51.0 ± 2.4	⎬ 7.6
124.5	0.02–0.20	4	23.8 ± 1.7	118 ± 24	⎪
140.1	0.10–0.40	4	178 ± 20	478 ± 96	⎭

[a] Values of k_1 and k_2 were determined from a linear least-squares analysis of the dependence of k_{obsd} on $[P\text{-}n\text{-}Bu_3]$. All values of k_{obsd} for each reaction were weighted according to the assumption of a common percent uncertainty. The quoted uncertainties are estimates of the probable error (standard deviation) adjusted for the number (10 in each case) of degrees of freedom so that 95% confidence limits can be obtained by doubling them. $\sigma(k_{obsd})$ is the corresponding probable error of a single measurement of k_{obsd}. Concentrations of complexes were ca. $(2–5) \times 10^{-4}$ M.

Experimental Section

Dodecacarbonyltriosmium (Strem Chemicals, Inc.) was used as received. $Os_3(CO)_{11}(NCMe)$ and $Os_3(CO)_{10}(NCMe)_2$ were prepared by published methods[7] and characterized by their IR spectra.[7,8] Decalin (Aldrich) was purified by successively washing several times with concentrated H_2SO_4 under N_2 until the acid layer was colorless, with chlorosulfonic acid under N_2, with aqueous NH_3, and finally with water. The wet Decalin was dried over $CaCl_2$, filtered, and distilled twice under reduced pressure (63 °C, 13 mmHg) before being stored over molecular sieves. The purified Decalin showed negligible absorbance at those wavelengths at which Tetralin absorbs.[9] $P\text{-}n\text{-}Bu_3$ (Aldrich) was distilled under reduced pressure and either used immediately or stored under N_2 before use, and PPh_3 (BDH) was recrystallized from ethanol.

Solutions for kinetic study were prepared in Schlenk tubes by dissolving the requisite complex and ligand in Decalin. They were degassed by standard freeze–pump–thaw techniques. Solutions of $Os_3(CO)_{11}(P\text{-}n\text{-}Bu_3)$ and $Os_3(CO)_{10}(P\text{-}n\text{-}Bu_3)_2$ were prepared in situ by dissolving the corresponding acetonitrile complexes in Decalin together with a known excess of free $P\text{-}n\text{-}Bu_3$. Similar methods have been shown to lead to $Os_3(CO)_{11}(PPh_3)$ and $Os_3(CO)_{10}(PPh_3)_2$.[7] The IR spectra showed bands at 2095 (m), 2042 (ms), 2020 (s), 2008 (s), 1985 (m), 1970 (m), 1960 (w), and 1950 (w) cm^{-1} and at 2070 (m), 2012 (s), 1995 (s) 1958 (m), 1950 (w), and 1935 (w) cm^{-1}, respectively, in good agreement with those quoted[10] for $Os_3(CO)_{11}(PEt_3)$ and $Os_3(CO)_{10}(PEt_3)_2$ in cyclohexane, thus confirming the nature of the complexes prepared in situ. IR spectra were measured with a Perkin–Elmer 298 spectrophotometer.

The Schlenk tubes were immersed in a thermostated oil bath for kinetic runs and were well shielded from light. Temperatures were measured with an iron–constantan thermocouple and maintained constant to within ±0.2 °C. Samples were removed periodically by means of a syringe and the course of each reaction was monitored by IR spectroscopy. The decreasing intensities of well-separated, prominent bands characteristic of the reacting complexes, and not of any products, were measured so that the absorbances at the end of the reaction were small. Plots of ln $(A_t - A_\infty)$ against time were linear for up to 3 half-lives.

Results and Discussion

Rate Equations. The complexes $Os_3(CO)_{12}$ and $Os_3CO)_{11}(P\text{-}n\text{-}Bu_3)$ both react with $P\text{-}n\text{-}Bu_3$ according to the rate equation (1).

$$k_{obsd} = k_1 + k_2[P\text{-}n\text{-}Bu_3] \quad (1)$$

Values of k_1 and k_2, shown in Table I, were obtained from a linear least-squares analysis of the data,[11] each value of k_{obsd} being weighted according to the assumption of a common percentage uncertainty or probable error, $\sigma(k_{obsd})$, for measurements on a

Table II. Rate Constants for Reactions in Decalin of $Os_3(CO)_{12}$ with PPh_3 (A) and $Os_3(CO)_{10}(P\text{-}n\text{-}Bu_3)_2$ with $P\text{-}n\text{-}Bu_3$ (B) under Ar

reacn	T, °C	[L], M	no. of determins	$10^5 k_1$,[a] s^{-1}
A	93.0	0.10–0.40	3	0.883 ± 0.036
A	123.5	0.02–0.50	4	33.7 ± 1.2
A	148.7	0.10–0.50	3	399 ± 16
B	110.9	0.10–0.30	3	1.98 ± 0.09
B	126.0	0.10–0.30	3	12.9 ± 0.6
B	142.7	0.10–0.30	3	73.3 ± 3.3
B	155.0	0.10–0.30	3	240 ± 11

[a] Uncertainties are based on a probable error for an individual determination of a rate constant of ±7.0% for reaction A and ±7.9% for reaction B, these values being obtained from the residuals in the least-squares derivation of $\Delta H_1^\ddagger$ and $\Delta S_1^\ddagger$. Concentrations of complexes were ca. $(2–5) \times 10^{-4}$ M.

particular complex irrespective of the temperature involved. Thus, values of $\sigma(k_{obsd})$ were first estimated from the expression $100\text{-}[\sum \Delta^2/(N - n)]^{1/2}$ where $\Delta = (k_{obsd} - k_{calcd})/k_{calcd}$, N = total number of measurements of k_{obsd}, and n = total number of parameters obtained from the data (two at each temperature). The values of k_{calcd} are those obtained from the least-squares analysis. This application of the method of pooled variances[11] allows for a greater number of degrees of freedom, $N - n$, to be involved in the estimates of $\sigma(k_{obsd})$ so that much smaller "Student's t" factors[11] had to be used to calculate any particular confidence level from those estimates. In practice the estimated values for $\sigma(k_{obsd})$ or the other standard deviations (probable errors) were multiplied by the "Student's t" values appropriate for giving 95% confidence levels and divided by 1.96. This gives "perfect" values of standard deviations (i.e. ones effectively based on an infinite number of degrees of freedom) in that they lead *exactly* to 95% confidence limits when multiplied by the "Student's t" value of 1.96 that is needed to transform a perfect estimate of a standard deviation into a 95% confidence level. The assumption of a constant percentage uncertainty irrespective of temperature has been shown elsewhere[12] to be valid. It is also implicit in any unweighted least-squares analysis of the temperature dependence of ln (k_{obsd}/T) on $1/T$ to obtain activation parameters. This is because a constant percentage uncertainty in k_{obsd} transforms to a constant *absolute* uncertainty in ln k_{obsd} or, to a good approximation, in ln (k_{obsd}/T). The activation parameters were obtained from a linear least-squares analysis of the dependence of ln (k_1/T) or ln (k_2/T) on $1/T$, each value of ln (k_1/T) or ln (k_2/T) being weighted according to the inverse of its variance.[11] These variances were derived from the standard deviations of k_1 and k_2 shown in Table I.

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Table III. Activation Parameters[a] for Reactions of $Os_3(CO)_{12-n}(P-n-Bu_3)_n$ with L in Decalin

n	L	$\Delta H_1^{\ddagger}$, kcal mol^{-1}	$\Delta S_1^{\ddagger}$, cal K^{-1} mol^{-1}	$\Delta H_2^{\ddagger}$, kcal mol^{-1}	$\Delta S_2^{\ddagger}$, cal K^{-1} mol^{-1}	$\sigma(k_{obsd})$, %
0	CO[b]	35.03 ± 1.12[b]	+14.3 ± 3.0[b]			6.7
0	L[c]	33.68 ± 1.50[c]	+10.7 ± 4.1[c]			10.1
0	PPh$_3$	32.77 ± 0.34[d]	+7.5 ± 0.9[d]			7.0
0	P-n-Bu$_3$	33.05 ± 0.47[d]	+8.2 ± 3.2[d]	20.64 ± 0.16	−22.7 ± 0.6	3.7
1	P-n-Bu$_3$	39.3 ± 1.2	+23.1 ± 3.1	15.0 ± 1.4	−35.0 ± 4.3	7.6
2	P-n-Bu$_3$	34.7 ± 0.4	+10.0 ± 1.1			7.9
0	PPh$_3$[e]	31.81 ± 0.19	+20.2 ± 0.6			2.3
0	P-n-Bu$_3$[f]			12.05 ± 0.19[f]	−27.5 ± 0.6[f]	3–6

[a] Uncertainties are probable errors. [b] For the exchange reaction of $Os_3(CO)_{12}$ with ^{14}CO in benzene (ref 1a); the activation parameters have been recalculated from the original rate constants. [c] Reaction in decane with L = PPh$_3$, P(OMe)$_3$, P-n-Bu$_3$; [L] < 0.0015 M; the activation parameters have been recalculated, according to our procedure, from the data in ref 5b. The values quoted in that reference are substantially different; viz., $\Delta H_1^{\ddagger}$ = 38.6 ± 0.5 kcal mol^{-1} and $\Delta S_1^{\ddagger}$ = 24.4 ± 1.5 cal K^{-1} mol^{-1}, where the uncertainties purport to be 95% confidence limits. No indication was given as to how these limits were arrived at, and we are at a loss to understand how this discrepancy has arisen. Recalculation of the data in ref 5b for PPh$_3$ alone leads to $\Delta H_1^{\ddagger}$ = 33.6 ± 6.4 kcal mol^{-1} and $\Delta S_1^{\ddagger}$ = 10.7 ± 17.6 cal K^{-1} mol^{-1} where the uncertainties are 95% confidence levels and are very large because of the small number of degrees of freedom, 2, involved. [d] The weighted averages of our values for reactions with PPh$_3$ and P-n-Bu$_3$ are $\Delta H_1^{\ddagger}$ = 32.87 ± 0.28 kcal mol^{-1} and $\Delta S_1^{\ddagger}$ = 7.6 ± 0.9 cal K^{-1} mol^{-1}. [e] For reaction with $Ru_3(CO)_{12}$ (ref 1c). [f] For reaction with $Ru_3(CO)_{12}$; k_2 = 0.2 M^{-1} s^{-1} at 75 °C (ref 1d); cf. a value of 8 × 10^{-6} M^{-1} s^{-1} for reaction with $Os_3(CO)_{12}$ (Table I).

Reactions of $Os_3(CO)_{12}$ with PPh$_3$, and of $Os_3(CO)_{10}(P-n-Bu_3)_2$ with P-n-Bu$_3$, showed no dependence on the concentration of entering ligand up to 0.5 and 0.3 M phosphine, respectively, and the activation parameters were obtained by an unweighted linear least-squares analysis of the dependence of ln (k_{obsd}/T) on $1/T$ (see above). Rate constants for these reactions are summarized in Table II, and activation parameters for all the reactions are shown in Table III.

Significance of the k_1 Terms. The values of the parameters $\Delta H_1^{\ddagger}$ and $\Delta S_1^{\ddagger}$ for the [ligand]-independent paths for reaction of $Os_3(CO)_{12}$ with ^{14}CO, P-n-Bu$_3$, and PPh$_3$ are essentially indistinguishable in view of their uncertainties and the different solvent used for reaction with ^{14}CO.[1a] This is consistent with the conclusion that the reactions all proceed by the classical CO dissociative mechanism usually assigned to such first-order reactions.[13] The same can be concluded for the [ligand]-independent paths for reactions of $Os_3(CO)_{11}(P-n-Bu_3)$ and $Os_3(CO)_{10}(P-n-Bu_3)_2$. However, it has been pointed out[14] that [ligand]-independent paths for substitution reactions of metal carbonyls are also consistent with initial slow and reversible isomerization of the complex where the isomerization produces a vacant coordination site on the metal. Addition of the substituting ligand then precedes loss of CO and a final isomerization to give the product.[14] It can be shown[15] that, if the loss of CO is reversible, the rate equation can be identical in form with that for a simple reversible CO dissociative mechanism, viz. $k_{obsd} = a[L]/(b[CO] + c[L])$, where a, b, and c are constants; i.e. the CO dissociative mechanism cannot be proved even by studies of the rates as a function of [CO].[16] While the CO dissociative mechanism is clearly the simplest explanation for such a rate equation the potential that clusters have for isomerization[4a,17,18] suggests that it may be premature to conclude too confidently that CO dissociation is indeed the mechanism.

[Ligand]-Independent Rate Parameters. $Os_3(CO)_{12}$ undergoes substitution by the [ligand]-independent path very much more

Table IV. Rate Parameters[a] for the [Ligand]-Independent Reactions of $Os_3(CO)_{12-n}(P-n-Bu_3)_n$ and $Ir_4(CO)_{12-n}(P-n-Bu_3)_n$

	$10^5 k_1$(110 °C), s^{-1}		$\Delta H_1^{\ddagger}$, kcal mol^{-1}		$\Delta S_1^{\ddagger}$, cal K^{-1} mol^{-1}	
n	Os	Ir	Os	Ir	Os	Ir
0	7.0	7[a]	32.9	32.1[a]	8	6[a]
1	3.6	1.2 × 10^{3}[b]	39.3	33.0[b]	23	18[b]
2	1.9	1.0 × 10^{4}[c]	34.7	29.4[c]	10	11[c]

[a] Data from ref 3b. [b] Data from ref 4f. [c] Data from ref 4g.

slowly than $Ru_3(CO)_{12}$.[1] However, the data in Table III show that this has somewhat more to do with $Os_3(CO)_{12}$ having a less positive value of $T\Delta S_1^{\ddagger}$ than $Ru_3(CO)_{12}$ rather than simply a higher value of $\Delta H_1^{\ddagger}$. The clearly dissociative reaction of $W(CO)_6$ is also much slower than that of $Mo(CO)_6$, but this is because $\Delta H_1^{\ddagger}$ is 9 kcal mol^{-1} higher, the value of $\Delta S_1^{\ddagger}$ being considerably more favorable.[13] This difference in behavior is not inconsistent with the simple CO dissociative mechanism for the clusters. Clusters can adjust to the loss of a ligand in a variety of ways not available to mononuclear carbonyls.[18] These can involve a strengthening of the bonding within the cluster, thus leading to lower values of $\Delta H^{\ddagger}$ and a less positive value of $\Delta S^{\ddagger}$.[4c] If this happens to a greater extent in $Os_3(CO)_{11}$ than in $Ru_3(CO)_{11}$, then the activation parameters can be understood in terms of the CO dissociative mechanism.

The trend of the rate parameters for the [ligand]-independent reactions of $Os_3(CO)_{12-n}(P-n-Bu_3)_n$ ($n = 0–2$) can be compared (Table IV) with that for $Ir_4(CO)_{12-n}(P-n-Bu_3)_n$ ($n = 0–2$). The rate parameters for $Os_3(CO)_{12}$ and $Ir_4(CO)_{12}$ are virtually identical. Introduction of one P-n-Bu$_3$ into $Ir_4(CO)_{12}$ produces a substantial increase in rate, but a second produces a much smaller acceleration. The labilizing effect of the P-n-Bu$_3$ substituents seems therefore to be approaching saturation. The trend for $Os_3(CO)_{12}$ is for introduction of successive P-n-Bu$_3$ substituents to produce a monotonic but quite small *decrease* in rates. Although the trends in the values of k_1 are different, the trends in $\Delta H_1^{\ddagger}$ and $\Delta S_1^{\ddagger}$ for the two sets of clusters do show similarities. Successive introduction of two P-n-Bu$_3$ ligands produces an increase and then a decrease in $\Delta H_1^{\ddagger}$ and $\Delta S_1^{\ddagger}$ in both cases. The difference in the rate constant trends arises from the different extents of the changes in the activation parameters.[19]

In terms of the values of $\Delta H_1^{\ddagger}$ the introduction of the first P-n-Bu$_3$ ligands stabilizes both clusters toward further substitution while the second destabilizes them. This contrasts with successive labilization of the Ir_4 cluster, and successive stabilization of the Os_3 cluster, when only rate constants are considered. It has been

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(19) These difference are unlikely to be due simply to the presence of bridging carbonyls in the substituted Ir_4 clusters (a feature not shared by the Os_3 clusters). Very much smaller substituent effects are observed with $Ir_4(CO)_{12-n}(P(OPh)_3)_n$, although the structural effects are the same[4f,g] and cannot, therefore, be important.

argued that a combination of differential electronic effects on ground and transition states[4g] together with steric and stereochemical effects[2c,4h] are needed to explain substituent effects of this sort. If the reactions are CO dissociative, then the effect of the first substituent can be understood largely in terms of ground-state stabilization of M–CO bonds in the usual way,[4g] and the labilizing effect of the second can be understood in terms of steric repulsions.[4h] The application of these effects are likely to be modified according to the exact positions of the ligands in the complex.[4h] It is known that the disubstituted clusters $Os_3(CO)_{10}L_2$ (L = P donors) exist in solution as isomers in labile equilibrium.[20] This is not likely to be a serious complication because the values of $\Delta H^{\ddagger}$ and ΔH° for isomerization seem to be small although it will have to be considered when further results become available. It is clear that many more kinetic and other data will have to be obtained before a full understanding of substituent effects in such clusters is reached.

[Ligand]-Dependent Rate Parameters. The rate parameters for the second-order reaction of P-n-Bu$_3$ with $Os_3(CO)_{12}$ are substantially different from those for $Ru_3(CO)_{12}$.[1c,d] $Os_3(CO)_{12}$ is less susceptible to nucleophilic attack in terms of all the parameters k_2, k_2/k_1, $\Delta H_2^{\ddagger}$, and $\Delta H_2^{\ddagger} - \Delta H_1^{\ddagger}$. The differences in $\Delta H_2^{\ddagger}$ and $\Delta S_2^{\ddagger}$ for these second- and third-row-metal carbonyls are similar to those for reactions of P-n-Bu$_3$ with $Mo(CO)_6$ and $W(CO)_6$[13] although the clusters have lower values of $\Delta H_2^{\ddagger}$ and more negative values of $\Delta S_2^{\ddagger}$. Bimolecular reactions of metal carbonyls with P-donor ligands have been ascribed to direct nucleophilic attack at the metal atom.[1c,3b,13] The susceptibility of metal carbonyl clusters, in particular, to nucleophilic attack has been claimed to be due largely to steric effects.[3b] However, $Ru_3(CO)_{12}$ is very much more susceptible to nucleophilic attack than $Ru(CO)_5$,[21] in spite of the more favorable geometry of the latter, and $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ have virtually identical molecular geometries[22] but very different susceptibilities to nucleophilic attack. Steric effects are clearly not dominant in these cases. However, enlarging the coordination sphere around the metal cluster on forming the transition state most probably requires a general expansion of the cluster. The contribution of this factor to the ease of nucleophilic attack can perhaps be related to the overall heat of disruption of the cluster, and this is greater for $Os_3(CO)_{12}$ than for $Ru_3(CO)_{12}$.[23] The degree of bond making must also be important, and the dependence of rates on the nature of the nucleophile is usually quite pronounced.[1c,3b,24] This is also true for $Os_3(CO)_{12}$ since reaction with PPh$_3$ does not show a $k_2[L]$ term in the rate equation while reactions with P-n-Bu$_3$ (and with P(OEt)$_3$ and PPhEt$_2$)[26] do.

The presence of one P-n-Bu$_3$ substituent increases the susceptibility of the cluster to nucleophilic attack in terms of all the parameters mentioned above. A second P-n-Bu$_3$, however, reduces it greatly. This type of behavior has also been observed qualitatively with $Ir_4(CO)_{12-n}(P-n-Bu_3)_n$ (n = 0–2)[3b,4f,4g] but contrasts with that shown by reaction of P-n-Bu$_3$ with $Co_2(\mu-C_2Ph_2)(CO)_6$ where introduction of one P-n-Bu$_3$ ligand greatly reduces the susceptibility of the complex to nucleophilic attack.[27] Some structural data on substituted M$_3$ clusters are probably relevant to these observations. $Os_3(CO)_{11}[P(OMe)_3]$ has greater Os–Os bond lengths than $Os_3(CO)_{12}$, the one cis to the substituent being ca. 0.03 Å longer.[28] $Ru_3(CO)_{11}L$ (L = PPh$_3$[29] or P(C$_6$H$_{11}$)$_3$[30])

also shows expansion of the metal cluster compared with the unsubstituted complex, the Ru–Ru bonds cis to the substituent being ca. 0.05 Å longer. By contrast $Ru_3(CO)_{10}(P(OMe)_3)_2$ has an average Ru–Ru bond length that is almost identical with that in $Ru_3(CO)_{12}$. The kinetic behavior can, therefore, be quite easily understood in view of the probable role played by expansion of the M$_3$ cluster during nucleophilic attack (see above), the greater steric repulsions expected during reaction of a disubstituted cluster, and the lower electrophilicity of an M$_3$ cluster with two quite strongly electron-donating ligands attached. The role played by expansion of the Os$_3$ cluster during nucleophilic attack is related closely to the nature of the products of the reactions, as will be seen in the next section.

Reaction Products. The main feature observed with the reactions of $Os_3(CO)_{12}$ is that when they are carried out at high temperatures and low values of [P-n-Bu$_3$], i.e. when reaction proceeds via the k_1 path alone, the product is $Os_3(CO)_9(P-n-Bu_3)_3$ in virtually 100% yield, the growth and decay of IR bands due to $Os_3(CO)_{11}(P-n-Bu_3)$ and $Os_3(CO)_{10}(P-n-Bu_3)_2$ being clearly observed. $Os_3(CO)_{11}(P-n-Bu_3)$ reacts exclusively to form $Os_3(CO)_9(P-n-Bu_3)_3$ via $Os_3(CO)_{10}(P-n-Bu_3)_2$ under the same conditions. On the other hand, when $Os_3(CO)_{12}$ and $Os_3(CO)_{11}(P-n-Bu_3)$ are reacted with high concentrations of P-n-Bu$_3$ at low temperatures (i.e. when reaction occurs via the $k_2[L]$ path) the products are solely mixtures of $Os(CO)_4(P-n-Bu_3)$ and $Os(CO)_3(P-n-Bu_3)_2$,[31] no $Os_3(CO)_9(P-n-Bu_3)_3$ being observed. Reaction of $Os_3(CO)_{10}(P-n-Bu_3)_2$ leads only to $Os_3(CO)_9(P-n-Bu_3)_3$ irrespective of the conditions.

It is therefore quite clear that reaction of any of the complexes $Os_3(CO)_{12-n}(P-n-Bu_3)_n$ via the high-energy path governed by k_1 leads only to substitution. Reactions of $Os_3(CO)_{11}(P-n-Bu_3)$ via the associative path lead only to fragmentation because no $Os_3(CO)_{10}(P-n-Bu_3)_2$ or $Os_3(CO)_9(P-n-Bu_3)_3$ is formed at high [P-n-Bu$_3$]. $Os(CO)_4(P-n-Bu_3)$ and $Os(CO)_3(P-n-Bu_3)_2$ are the only products, and the ratio of their yields is of interest. Although they were not isolated, the former reacts with P-n-Bu$_3$ to form the latter at 170 °C. Partial decomposition of the product occurred before the reaction was complete. However, comparison over the early stages of the reaction of the decrease of the absorption at 1935 cm^{-1} due to $Os(CO)_4(P-n-Bu_3)$[31] with the increase of absorption at 1880 cm^{-1} due to $Os(CO)_3(P-n-Bu_3)_2$[31] showed that $\epsilon_{1880}/\epsilon_{1935}$ = ca. 0.6. Measurements of the relative intensities of these two bands during the course of the reaction of $Os_3(CO)_{11}(P-n-Bu_3)$ showed that the value of R = $[Os(CO)_3(P-n-Bu_3)_2]/[Os(CO)_4(P-n-Bu_3)]$ for [P-n-Bu$_3$] = 0.1 M remained constant at 0.53 ± 0.08 from ca. 10% reaction to completion and from 70 to 140 °C. Increasing [P-n-Bu$_3$] to 0.4M increased R by ca. 30% and the value of R extrapolated to [P-n-Bu$_3$] = 0 was 0.5 ± 0.1. One possible way in which this product ratio at low [P-n-Bu$_3$] can be obtained is by a series of reactions such as those shown in eq 2–5.

$$Os_3(CO)_{11}(P\text{-}n\text{-}Bu_3) + P\text{-}n\text{-}Bu_3 \rightarrow Os_3(CO)_{11}(P\text{-}n\text{-}Bu_3)_2 \quad (2)$$

$$Os_3(CO)_{11}(P\text{-}n\text{-}Bu_3)_2 + P\text{-}n\text{-}Bu_3 \rightarrow$$
$$Os(CO)_4(P\text{-}n\text{-}Bu_3) + Os_2(CO)_7(P\text{-}n\text{-}Bu_3)_2 \quad (3)$$

$$Os_2(CO)_7(P\text{-}n\text{-}Bu_3)_2 \rightarrow$$
$$Os(CO)_4(P\text{-}n\text{-}Bu_3) + Os(CO)_3(P\text{-}n\text{-}Bu_3) \quad (4)$$

$$Os(CO)_3(P\text{-}n\text{-}Bu_3) + P\text{-}n\text{-}Bu_3 \rightarrow Os(CO)_3(P\text{-}n\text{-}Bu_3)_2 \quad (5)$$
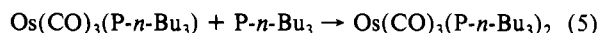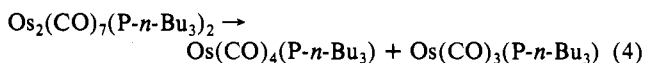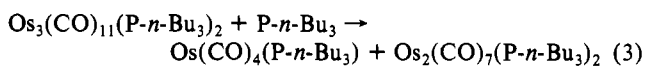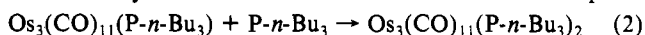
The intermediate $Os_3(CO)_{11}(P-n-Bu_3)_2$ could have the ring-opened structure shown diagrammatically in I in which all the

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(24) This argues against a two-stage process in which the initial step is the slow formation of a reactive isomer that very readily reverts to the stable complex in competition with relatively slow attack by the nucleophile. Such a process would show a relatively small dependence on the nature of the nucleophile.[25]
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(31) Bands were observed at 2060 (m), 1980 (m), and 1935 (s) cm^{-1}, corresponding to $Os(CO)_4(P-n-Bu_3)$, and at 1880 cm^{-1}, corresponding to $Os(CO)_3(P-n-Bu_3)_2$. These spectra are virtually identical with those reported for $Os(CO)_4(PPh_3)$ and $Os(CO)_3(PPh_3)_2$ in CCl$_4$, allowing for the change in the phosphine ligand.[32]
(32) L'Eplattenier, F.; Calderazzo, F. *Inorg. Chem.* **1968**, *7*, 1290–1293.
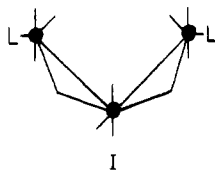
I

Os atoms have an 18-electron configuration. Formation of an intermediate such as I would be encouraged by the specific lengthening of the metal–metal bond cis to L in $M_3(CO)_{11}L$ described above. $Os_2(CO)_7(P-n-Bu_3)_2$ would be isostructural with $Os_2(CO)_9$[33] and would have to undergo spontaneous fragmentation as shown in eq 4, rather than undergoing a concerted fragmentation as when eq 4 and 5 are amalgamated. This conclusion derives from the fact that nucleophilic *substitution* of an intermediate such as $Os_2(CO)_7(P-n-Bu_3)_2$ is needed to account for the increasing value of R found as $[P-n-Bu_3]$ is increased. Fragmentation of the $Os_2(CO)_6(P-n-Bu_3)_3$ formed would then lead to higher values of R. If fragmentation of $Os_2(CO)_7(P-n-Bu_3)_2$ were also second order, then no increase in R with $[P-n-Bu_3]$ would occur. R would simply be greater than 0.5 but independent of $[P-n-Bu_3]$ because both fragmentation and substitution would increase equally with increasing $[P-n-Bu_3]$. Although slightly different series of reactions can be postulated, they must, for this reason, always include a competition at some stage between associative substitution of an intermediate and spontaneous fragmentation. Only ca 10–15% of associative substitution is required at $[P-n-Bu_3] = 0.4$ M to account for the observed increase in R.

The yields of mononuclear products from nucleophilic attack on $Os_3(CO)_{12}$ are also informative. The initial product is mainly $Os(CO)_4(P-n-Bu_3)$ ($R \lesssim 0.1$), showing that bimolecular fragmentation of the $Os_3(CO)_{12}$ must be occurring. If only substitution to form $Os_3(CO)_{11}(P-n-Bu_3)$ were occurring, then R would be constant at $\gtrsim 0.5$ throughout the whole reaction since the mononuclear products would originate solely from $Os_3(CO)_{11}(P-n-Bu_3)$.

The occurrence of nucleophile-induced fragmentation reactions is relatively rare. Bimolecular reactions of phosphines with $Co_2(CO)_8$ are believed to lead initially to mononuclear fragmentation products,[34] and nucleophilic attack by $P-n-Bu_3$ on

$Ru_3(CO)_{11}(P-n-Bu_3)$ leads to $Ru(CO)_4(P-n-Bu_3)$ and $Ru(CO)_3(P-n-Bu_3)_2$ in the mole ratio 2:1.[1d,35] On the other hand, nucleophilic attack by $P-n-Bu_3$ on $Ru_3(CO)_{12}$ appears to lead mainly to substitution.[1d,35] $Ru_3(CO)_{10}(dppm)$ (dppm = $Ph_2PCH_2PPh_2$) undergoes fragmentation virtually every time it is attacked by $P-n-Bu_3$, but attack by $P(OEt)_3$ can lead either to fragmentation or substitution with approximately equal probability.[36] Thus it seems that nucleophilic attack at clusters can lead to fragmentation, substitution, or both, depending on the nature of the nucleophile and the cluster. Details of this dependence require elucidation but the occurrence of nucleophile-induced fragmentation reactions of metal carbonyl clusters seems to occur sufficiently often for them to be given the mechanistic classification F_N2.

Summary

(1) Substitution reactions of $Os_3(CO)_{12}$ with $P-n-Bu_3$ occur via a sequence of $[P-n-Bu_3]$-independent paths to form $Os_3(CO)_{11}(P-n-Bu_3)$, $Os_3(CO)_{10}(P-n-Bu_3)_2$, and, finally, $Os_3(CO)_9(P-n-Bu_3)_3$.

(2) The values of $\Delta H^{\ddagger}$ for this sequence of reactions shows that introduction of the first $P-n-Pu_3$ substituent stabilizes the cluster toward further substitution but a second one labilizes it compared with $Os_3(CO)_{11}(P-n-Bu_3)$, although not when compared with $Os_3(CO)_{12}$. This is probably due to stabilization through electron donation offset by steric effects.

(3) $Os_3(CO)_{12}$ is, in addition, susceptible to nucleophilic attack by $P-n-Bu_3$ (and $Os_3(CO)_{11}(P-n-Bu_3)$ even more so) and the products are then virtually exclusively mononuclear. This has important synthetic implications in that preparation of $Os_3(CO)_9(P-n-Bu_3)_3$ should be carried out at higher temperatures and with as low concentrations of $P-n-Bu_3$ as possible. Under these conditions the contribution of associative paths leading to unwanted mononuclear products is minimized.

(4) The bimolecular fragmentation reactions can be given the mechanistic assignment F_N2 and seem to be strongly dependent on the strength of the Os–Os bonds.

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