Substituent Effects on Associative Reactions of the Clusters Ru$_5$C(CO)$_{14}$L (L = P(OPh)$_3$ and P(C$_6$H$_{11}$)$_3$) with Phosphorus-Donor Nucleophiles

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The substitution reactions of the high-nuclearity carbonyl clusters Ru$_5$C(CO)$_{14}$L (L = P(OPh)$_3$ and PCy$_3$) with a series of P-donor nucleophiles in heptane have been shown to proceed readily by associative pathways. The effects of the different electronic and steric properties of the nucleophiles at 25 °C can be separated quantitatively in a way that has been previously shown to be widely successful. Comparing the fastest and slowest reactions for L = P(OPh)$_3$ shows that increasing nucleophile basicity increases the rates by a factor of ca. 20, but this is offset by a 2800-fold retardation due to steric effects. These show up even for the smallest nucleophile etpb (P(OCH$_2$)$_3$CEt) so that no steric threshold is observed, but the decrease in rates with increasing nucleophile size is not exceptional. The substituents reduce the rates of reaction with etpb at 25 °C by 750 (L = P(OPh)$_3$) and 3 × 10^4 (L = PCy$_3$) compared with the unsubstituted cluster. These steric effects act to prevent a high degree of bond making in the transition states. The temperature dependence of many of the reactions have been studied, and an overall unfavorable increase of 16 kcal mol^{-1} in $\Delta H^{\ddagger}_2$ is overcome by a favorable increase of 19 kcal mol^{-1} in $T\Delta S^{\ddagger}_2$, so the relative rates with different nucleophiles are controlled largely by entropic factors. This causes the relative rates to converge as temperatures decrease, and the implications of this type of behavior in the study of linear free energy effects can be serious. Quite unexpected effects of temperature on the separate sensitivity of the rates to the electronic and steric properties of the nucleophiles are revealed. Thus, the small favorable electronic effect is almost temperature independent and, therefore, based mainly on entropic factors, and the much larger and unfavorable steric effects are due to *favorable* enthalpic contributions that are overcome by unfavorable entropic contributions. Some suggestions regarding the geometries of the reaction paths are offered.

Introduction

Associative reactions of P-donor and related nucleophiles with metal carbonyl clusters have been of steadily growing importance from the time Candlin and Shortland observed them for Ru$_3$(CO)$_{12}$,[1] and the field has been reviewed regularly since then.[2] They are generally believed to occur via formation of intermediates in which the nucleophile has been added to a metal atom with concurrent breaking of a metal−metal bond and possible changing of some CO ligands from terminal to bridging configurations in such a way that the metal atoms can maintain their normal electron count.[3] An alternative hypothesis[2f,4] is to suppose that all the bonds in the cluster are weakened to some extent rather than one being completely broken, but intermediate adducts,[5] or close analogues,[6] with one completely broken metal−metal bond have been isolated in some cases. For substitution reactions, adduct formation is followed by expulsion of CO and reformation of the metal−metal bond, but fragmentations[2d,f,3a,b,7b,c] is an alternative process that the adduct can undergo.

The quantitative study of the dependence of the rates of associative reactions of metal carbonyls on the electronic and steric properties of the nucleophiles has been developing since 1973,[2i,3a,4,5b,7a,8−10] following the observation of a systematic dependence of rates of

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associative reactions of mononuclear carbonyls on nucleophile basicity,[2g,11] and use has been made of a variety of electronic and steric parameters.[8,10,12,13]

Relatively few systematic studies have been carried out on the kinetics of reactions of high-nuclearity carbonyl clusters (HNCCs) with P-donor or other similar nucleophiles,[14] and equally few detailed studies of the effects of substituents in carbonyl clusters of any kind on their associative reactions have been fully reported.[2i] The HNCCs $M_5C(CO)_{15}$ (M = Ru or Fe) show particularly interesting features in that smaller P-donor nucleophiles, L, react via $M_5C(CO)_{15}L$ adducts which subsequently lose CO to form substituted products.[14a,b] With larger nucleophiles and M = Ru, substitution reactions proceed in only one observable step, which is quite distinct from the adduct formation path,[14b] but when M = Fe, the reactions lead to decomposition and/or cluster fragmentation.[14a] We have chosen to extend our knowledge of substituent effects[2d,i,15] on reactions of clusters and report here studies of the kinetics of reactions of the HNCCs $Ru_5C(CO)_{14}\{P(OPh)_3\}$ and $Ru_5C(CO)_{14}(PCy_3)$ (Cy = C_6H_{11}) with a substantial number of P-donor nucleophiles. The substituent in $Ru_5C(CO)_{14}(PCy_3)$ has been shown[16] to be attached, in an axial position, to one of the basal Ru atoms of the square pyramidal Ru_5C core.

Experimental Section

Chemicals. Solvents (heptane and CH_2Cl_2) were dried and stored over molecular sieves and degassed by at least three freeze−pump−thaw cycles immediately before use with air-sensitive reagents. The P-donor nucleophiles L = P(n-Bu)$_3$, P(OPh)$_3$, P(OMe)$_3$, P(OEt)$_3$, PPh(OMe)$_2$, PPh$_2$(OEt), PPhMe$_2$, PPh$_2$Me, and PPh$_2$Cy, obtained from commercial sources, were distilled under a reduced pressure of Ar before use or before storage under Ar in Schlenk tubes with air-tight stoppers. P(OCH$_2$)$_3$CEt (etpb, Strem) was sublimed at ca. 50 °C under reduced pressure before use, and PPh$_3$ (Aldrich) was recrystallized from hexane. P(p-MeOΦ)$_3$ and P(p-FΦ)$_3$ (Φ = C_6H_4, Strem) were used as received. PCy$_3$ was either used as received or obtained from the adduct PCy$_3$·CS$_2$ by distilling off CS$_2$ with ethanol under Ar.[14c] $Ru_5C(CO)_{15}$ was prepared exactly as described elsewhere,[5c] and the clusters $Ru_5C(CO)_{14}L$ (L = P(OPh)$_3$ and PCy$_3$) were prepared according to the following procedure. $Ru_5C(CO)_{15}$ (0.20 g, 0.21 mmol) was dissolved in ca. 20 mL of CH_2Cl_2 in a side-arm flask. An equivalent of L (0.060 g of PCy$_3$ or 0.065 g of P(OPh)$_3$) was added to the solution and stirred under Ar for ca. 1 h, giving a pink-red solution. The IR spectrum of the solution showed the disappearance of the bands due to $Ru_5C(CO)_{15}$. The solution was then evaporated under vacuum, and the product was isolated by column chromatography. The column was evenly filled with 40−140 mesh silica gel (Baker Chemical Co.) and wrapped with aluminum foil. The purple band of

$Ru_5C(CO)_{14}L$ was eluted by a mixture (1:1 by volume) of hexanes and CH_2Cl_2 and identified by comparing its CO stretching frequencies with those of similar $Ru_5C(CO)_{14}L$ (L = PPh$_3$, P(p-MeOΦ)$_3$, etc.[5c,14b]) clusters. Single crystals of the cluster $Ru_5C(CO)_{14}(PCy_3)$ were prepared in suitable form for X-ray crystallographic study[16] by slow evaporation of a 1:1 hexane−CH_2Cl_2 solution. The IR spectra in the C−O stretching region are L = P(OPh)$_3$ 2091.1 (w), 2060.0 (vs), 2050.7 (m), 2031.6 (m), 2020.7 (m), 2006.1 (w) cm^{-1} in CH_2Cl_2, and L = PCy$_3$ 2086.4 (w), 2053.3 (s), 2044.4 (sh), 2017.8 (s), 1990.0 (w) cm^{-1} in CH_2Cl_2 and 2085.9 (w), 2053.3 (vs), 2044.4 (m), 2019.9 (s), 1987.1 (w) cm^{-1} in heptane.

Instruments. IR spectra were measured with a Nicolet 10DX FTIR spectrophotometer using 1 mm path length cells with NaCl windows. UV−vis spectra were measured with a Hewlett-Packard 8452A spectrophotometer which, for kinetic studies, was equipped with a thermostated cell holder (±0.1 °C).

Kinetics. Solutions of complexes and nucleophiles were prepared by conventional anaerobic procedures.[14] Standard concentrations were determined by weighing and others by dilution. Reaction mixtures to be monitored by IR techniques were made up in Schlenk tubes under Ar as described elsewhere,[14] and the Schlenk tubes were immersed in a thermostated bath. Samples were withdrawn periodically by syringe, and the reaction was quenched by rapid cooling prior to subsequent measurement of their IR spectra. Reaction mixtures to be monitored by UV−vis spectroscopy were made up in 10 mm path length quartz cells with stock solutions, and the total volume was adjusted to 3 mL by addition of solvent. Pseudo-first-order excesses of nucleophile were maintained at all times, except when characterization of the reaction products was being investigated, in which case equivalent amounts of complex and nucleophile were reacted. The IR spectra of the products were closely similar to that of $Ru_5C(CO)_{13}(PPh_3)_2$,[5c] which, together with $Ru_5C(CO)_{13}(etpb)_2$[16] and $Ru_5C(CO)_{13}(dppb)$ (dppb = $Ph_2P(CH_2)_4PPh_2$),[17] has been fully characterized by crystallography.[5c] Thus, $Ru_5C(CO)_{13}\{P(OPh)_3\}_2$ (2077.5 (w), 2052.6 (s), 2025.3 (vs), 1994.3 (m) cm^{-1}) and $Ru_5C(CO)_{13}(PCy_3)_2$ (2066 (m), 2043 (s), 2014 (s), 2000 (s) cm^{-1}) can be compared with $Ru_5C(CO)_{13}(PPh_3)_2$ (2066 (w), 2041 (s), 2010 (s,br) (all in CH_2Cl_2) cm^{-1}) and $Ru_5C(CO)_{13}(dppb)$ (2072 (m), 2046 (vs), 2020 (s), 2012 (s), 1994 (m) cm^{-1} in cyclohexane (and some weak bands at lower energies)). IR spectroscopy showed that the same products were formed in the presence of pseudo-first-order excesses of nucleophile. Subsequent reactions to form more highly substituted clusters are, therefore, very slow and do not complicate the kinetic analysis of the initial substitution reactions. Concentrations of complex were chosen so as to give initial UV−vis absorbances in the range 0.5−1 and IR absorbances of ca. 0.1. Absorbances measured at at least two wavenumbers or wavelengths were monitored as a function of time and changed monotonically from those of reactant clusters to those of the products. Pseudo-first-order rate constants were, therefore, readily obtainable by use of the nonlinear least-squares KORE program,[18] modified in this laboratory.[19] Results obtained at different wavelengths and by different monitoring techniques were in good agreement with each other, but those found from the largest absorbance changes and/or with the smallest final absorbances were chosen for data analysis. Values of k_{obs} are reported as Supporting Information.

Results

The reactions all occur in one step without any spectroscopic evidence for intermediates, and the oc-

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Table 1. Rate Constants for the Reactions of $Ru_5C(CO)_{14}\{P(OPh)_3\}$ with L' in Heptane ([Complex] = $2-10 \times 10^{-5}$ M)[a]

| L'	N[b]	T, °C	10^3[L'], M	10^4a, s^{-1}	k_2, M^{-1} s^{-1}	$\sigma(k_{obs})$,[c] %
etpb[d]	4	25.0	0.9–1.9	1.53 ± 3.69	3.942 ± 0.341	
	4	17.5	0.9–4.7	1.21 ± 0.17	1.740 ± 0.087	4.0
	4	10.0	0.9–4.7	1.74 ± 0.12	0.669 ± 0.049	
P(OMe)$_3$	4	25.0	0.3–2.8	35.6 ± 6.0	11.22 ± 0.73	
	4	17.5	0.5–2.8	31.8 ± 6.1	4.890 ± 0.498	7.5
	5	10.0	0.3–2.8	16.3 ± 1.6	1.856 ± 0.164	
P(OEt)$_3$	3	40.0	0.8–2.0	−39.4 ± 3.8	19.04 ± 0.35	
	4	25.0	1.0–2.5	1.18 ± 1.30	4.262 ± 0.088	1.2
	3	15.0	0.8–3.3	4.49 ± 0.34	1.457 ± 0.024	
PPh(OMe)$_2$	3	40.0	1.4–2.5	50.2 ± 35.6	7.466 ± 1.944	
	4	35.0	1.0–10.5	21.92 ± 6.09	3.472 ± 0.243	
	4	25.0	1.0–10.5	26.22 ± 6.22	1.838 ± 0.318	7.9
	11	15.0	1.0–10.5	10.29 ± 1.15	0.774 ± 0.035	
P(OPh)$_3$	4	45.0	1.0–7.1	1.885 ± 0.597	0.6580 ± 0.0383	
	4	35.0	1.0–10.2	0.960 ± 0.367	0.3677 ± 0.0167	6.2
	3	25.0	1.0–10.2	0.887 ± 0.206	0.1739 ± 0.0093	
PPh$_2$(OEt)	7	32.5	1.1–10.9	10.54 ± 2.42	1.583 ± 0.093	
	9	25.0	1.1–10.9	3.85 ± 1.42	1.127 ± 0.054	9.2
	5	15.0	1.1–8.4	1.50 ± 1.30	0.728 ± 0.054	
PPh$_3$	3	65.0	1.0–10.2	2.896 ± 0.438	0.1216 ± 0.0123	
	4	45.0	2.0–10.2	−0.497 ± 1.411	0.0601 ± 0.0047	9.2
	3	25.0	1.2–10.2	−0.347 ± 0.044	0.0428 ± 0.0030	
P(p-MeOΦ)$_3$[e]	4	25.0	0.1–0.5	−0.0231 ± 0.0105	0.2268 ± 0.0057	1.6
P(p-FΦ)$_3$[e]	3	25.0	0.2–0.9	0.596 ± 0.013	0.1489 ± 0.0030	0.9
PPh$_2$Cy	4	25.0	0.4–0.8	−0.0069 ± 0.0048	0.08098 ± 0.00089	0.5
PCy$_3$	4	25.0	0.6–0.8	0.0299 ± 0.0456	0.06398 ± 0.00630	0.6

[a] Reactions monitored by UV–vis techniques unless indicated otherwise. [b] Number of individual determinations of k_{obs}. [c] Standard error of an individual determination of k_{obs} obtained, where possible, by pooling all data for a given nucleophile at all temperatures and then adjusting according to the number of degrees of freedom.[20] [d] Reactions monitored by FTIR techniques. [e] Φ = C_6H_4 here and elsewhere.

Table 2. Rate Constants for the Reactions of $Ru_5C(CO)_{14}(PCy_3)$ + L' in Heptane ([Complex] = $2-10 \times 10^{-5}$ M)[a]

L'	N[b]	T, °C	10^3[L'], M	10^5a, s^{-1}	10^3k_2, M^{-1} s^{-1}	$\sigma(k_{obs})$,[c] %
etpb	5	25.0	6.6–55.6	−25.4 ± 6.0	107.9 ± 5.6	7.5
P(OMe)$_3$	6	25.0	60–302	6.03 ± 4.06	6.933 ± 0.428	7.1
P(OEt)$_3$	5	25.0	23–303	−1.31 ± 0.78	6.323 ± 0.166	4.5
PPh(OMe)$_2$	4	25.0	56–283	7.29 ± 3.02	2.525 ± 0.209	8.3
PPhMe$_2$[d]	4	45.0	18–179	0.24 ± 7.23	74.82 ± 2.11	
	4	35.0	18–179	1.46 ± 4.07	40.74 ± 1.17	4.1
	9	25.0	21–213	−1.73 ± 2.26	20.40 ± 0.42	
P(OPh)$_3$	5	75.0	46–248	2.38 ± 2.59	3.062 ± 0.285	
	4	65.0	18–179	−3.13 ± 4.47	2.124 ± 0.285	10
	7	45.0	12–80	0.964 ± 0.210	0.956 ± 0.077	
P(n-Bu)$_3$	6	25.0	20–200	−2.35 ± 0.91	2.490 ± 0.116	5.2
PPh$_2$Me[d]	4	45.0	18–182	6.99 ± 1.35	8.728 ± 0.317	
	4	35.0	18–182	−0.063 ± 0.684	5.949 ± 0.196	4.8
	11	25.0	20–204	−0.283 ± 0.304	2.797 ± 0.053	

[a] Reactions monitored by FTIR techniques unless indicated otherwise. [b] Number of individual determinations of k_{obs}. [c] Standard error of an individual determination of k_{obs} obtained, where possible, by pooling all data for a given nucleophile at all temperatures and then adjusting according to the number of degrees of freedom.[20] [d] Reactions monitored by UV–vis techniques.

currence of sharp isosbestic points in the IR spectra over the whole course of the reactions and the spectroscopic characterization of the products leaves little doubt that the latter are disubstituted clusters and that the reactions occur cleanly as indicated in eq 1. The values of k_{obs} depend on [L'] according to eq 2. The results of

$$Ru_5C(CO)_{14}L + L' \rightarrow Ru_5C(CO)_{13}LL' + CO \quad (1)$$
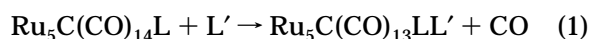
$$k_{obs} = a + k_2[L'] \quad (2)$$

least-squares analyses, in which each value of k_{obs} was weighted according to the assumption[20] of a constant percentage standard error of measurement, $\sigma(k_{obs})$, are given in Tables 1 and 2. The values of a are not considered to be kinetically significant[10b,14] and will not

be considered further. The temperature dependence of the values of k_2 were examined for several of the reactions, and the results are given in Table 3. The values of $\sigma(k_{obs})$ in Tables 1–3 show that the rate constants were obtained with good-to-excellent precision.

Dependence of k_2 on the Electronic and Steric Properties of the Nucleophiles. Values of log k_2 for reactions at 25 °C are given in Table 4 together with values of parameters that characterize the ligand basicity (pK_a' [10b,14]) and size (cone angles, θ[8] or cone angle equivalents, θ' [10b]) of the P-donor nucleophiles. Protocols for analyzing the dependence of log k_2 on the electronic and steric properties of the nucleophiles are now well-established,[2i,10] and accordingly the data have been analyzed in terms of eq 3.[14c,21] The parameter λ

$$\log k_2 = \alpha + \beta(pK_a' + 4) + \gamma(\theta - \theta_{th})\lambda \quad (3)$$

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Table 3. Activation Parameters[a] for the Associative Reactions of $Ru_5C(CO)_{14}L$ (L = $P(OPh)_3$ and PCy_3) with L′ in Heptane

L′	N[b]	$\Delta H^{\ddagger}_2$, kcal mol^{-1}	$\Delta S^{\ddagger}_2$, cal K^{-1} mol^{-1}
		L = $P(OPh)_3$	
etpb	12	19.36 ± 1.26	9.19 ± 4.35
$P(OMe)_3$	13	19.50 ± 1.22	11.70 ± 4.17
$P(OEt)_3$	10	17.84 ± 0.18	4.18 ± 0.60
$PPh(OMe)_2$	22	12.94 ± 0.71	−14.05 ± 2.42
$P(OPh)_3$	11	11.98 ± 0.77	−21.78 ± 2.50
$PPh_2(OEt)$	21	7.20 ± 0.94	−34.14 ± 3.16
PPh_3	10	4.26 ± 1.26	−50.59 ± 4.04
		L = PCy_3	
$PPhMe_2$	17	11.66 ± 0.32	−27.13 ± 1.04
$P(OPh)_3$	16	7.87 ± 0.88	−47.73 ± 2.67
PPh_2Me	18	10.62 ± 1.56	−34.57 ± 5.13

[a] These values were obtained by a least-squares analysis of the data in Tables 1 and 2, where each value of $\{\ln(k_2/T)\}_{expt}$ was weighted according to the uncertainties in k_2 as described in ref 20. For L = $P(OPh)_3$, a value of $\sigma(k_2)_{expt}$ of 8.2% can be obtained by the method of pooled variances from the differences of all the values of $\{\ln(k_2/T)\}_{expt}$ from $\{\ln(k_2/T)\}_{calc}$, provided one imprecise and low-weighted value of $\{\ln(k_2/T)\}_{expt}$ is ignored. For L = PCy_3, a value of $\sigma(k_2)_{expt}$ of 8.6% is obtained. [b] Total number of individual determinations of k_{obs}.

Table 4. Dependence of the Rates of Reaction of $Ru_5C(CO)_{14}L$ (L = $P(OPh)_3$ and PCy_3) on the Basicity and Size of the Nucleophiles, L′, in Heptane at 25 °C

no.	L′	θ,[a] deg	θ',[b] deg	pK_a'[c]	log k_2[d]	(log k_2)$_{calc}$[e]	Δ[f]
				L = $P(OPh)_3$			
1	etpb	101	118	−0.30	0.596	0.919	−0.323
2	$P(OMe)_3$	107	133	0.83	1.050	0.747	+0.303
3	$P(OEt)_3$	109	136	1.64	0.630	0.739	−0.109
4	$PPh(OMe)_2$	120	142	1.48	0.264	0.174	+0.090
6	$P(OPh)_3$	128	140	−2.79	−0.760	−0.701	−0.059
8	$PPh_2(OEt)$	133	138	2.35	0.0577	−0.374	+0.316
10	PPh_3	145	145	3.28	−1.368	−0.866	−0.502
11	$P(p\text{-}MeO\Phi)_3$	145	146	5.13	−0.644	−0.659	+0.015
12	$P(p\text{-}F\Phi)_3$	145	145	1.63	−0.827	−1.050	+0.223
13	PPh_2Cy	153	146	5.60	−1.092	−1.003	−0.089
14	PCy_3	170	168	11.26	−1.194	−1.214	+0.020
				L = PCy_3			
1	etpb	101	118	−0.30	−0.967	−1.000	+0.033
2	$P(OMe)_3$	107	133	0.83	−2.159	−2.254	+0.095
3	$P(OEt)_3$	109	136	1.64	−2.199	−2.482	+0.283
4	$PPh(OMe)_2$	120	142	1.48	−2.598	−3.007	+0.409
5	$PPhMe_2$	122	128	5.07	−1.690	−1.656	−0.034
6	$P(OPh)_3$	128	140	−2.79	−3.417	−3.000	−0.417
7	$P(n\text{-}Bu)_3$	132	139	8.67	−2.604	−2.467	−0.134
9	PPh_2Me	136	135	4.06	−2.533	−2.301	−0.232

[a] Tolman cone angles.[8] [b] Cone angle equivalents.[2i,10b] [c] Ligand basicity.[2i,10b] [d] Values of k_2 from Tables 1 and 2. [e] Values calculated according to the parameters given in Table 5 by making use of θ and pK_a' when L = $P(OPh)_3$ and θ' and pK_a' when L = PCy_3. [f] Δ = log k_2 − (log k_2)$_{calc}$. When the data for L = PCy_3 are listed in the order of increasing θ' instead of θ, the values of Δ are randomly positive and negative, in contrast to the case here when they are listed in order of increasing θ values and there appears to be a systematic skewing of the results.

is a switching function[10a] that is zero when $\theta \leq \theta_{th}$, the steric threshold, and unity when $\theta > \theta_{th}$ and the steric effect is finite and quantified by γ. The electronic effect is quantified by β, which is a measure of the dependence of log k_2 on the σ-basicity of the nucleophiles as expressed by pK_a'. If there are nucleophiles that show no steric effect, then α is a measure of the standard

(21) The protocol used by Brown[10c] has not been adopted because it uses an electronic parameter $\{\delta(^{13}CO)\}$ that we believe unneccessarily[2i] includes[12c] π-acidity properties and it does not allow for the existence of steric thresholds.
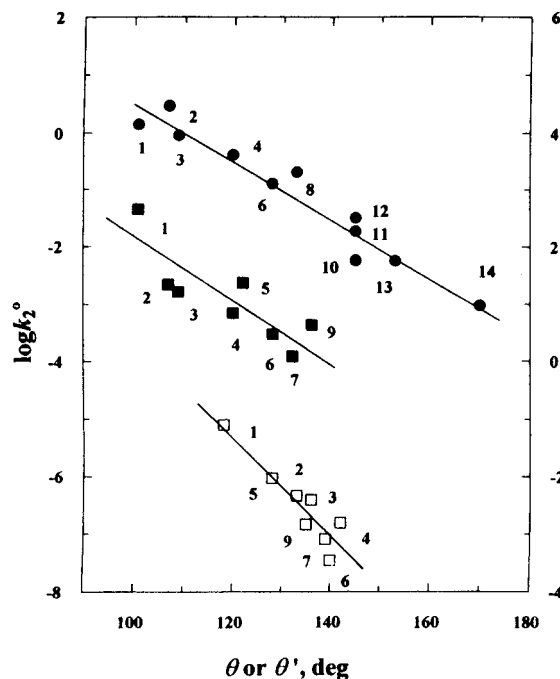

Figure 1. Steric profiles for reactions of $Ru_5C(CO)_{14}\{P(OPh)_3\}$ (●) and $Ru_5C(CO)_{14}(PCy_3)$ (■ and □). Nucleophile numbering is taken from Table 4; ● and ■ represent data for plots of log k_2° (left hand y axis) against θ, while □ represents data for the plot of log k_2° (right hand y axis) against θ'.

reactivity of the complex, i.e., the value of log k_2 for a hypothetical small ligand of weak basicity (pK_a' = −4). If steric effects are always operative, i.e., θ is always greater than θ_{th}, then α is simply the intercept of the plot of log k_2° (=log k_2 − β(pK_a' + 4)) against θ and the lower limit of the standard reactivity is given by the value of log k_2° for the smallest nucleophile used. The results of fitting the data to eq 3 are given in Table 5, where they are compared with those obtained when the size of the nucleophile is represented by the "cone angle equivalent", θ',[10b] which is defined relative to Brown's values of E_R, the repulsion energies calculated for the ligands L in $Cr(CO)_5L$.[10c] Data for some other Ru clusters are included for comparison. Plots of log k_2° vs θ or θ' are shown in Figure 1.

The success of the model in representing the data for $Ru_5C(CO)_{14}\{P(OPh)_3\}$ when Tolman cone angles are used is quite good in terms of the values of the RMSD (root mean square deviation) and R^2. The RMSD is reasonably small by comparison with the values for $Ru_6C(CO)_{17}$ and for $Ru_3(CO)_{12}$ with 12 smaller nucleophiles and also with those for a number of other carbonyls.[2i] The value of R^2 corresponds to the fact that only ca. 5% of the variation of log k_2 is unaccounted for by the model.[22] It is evident that when cone angle equivalents are used, the data are not represented as effectively by the model. However, it can be seen (Figure 1) that cone angle equivalents lead to a better fit than Tolman cone angles for the $Ru_5C(CO)_{14}(PCy_3)$ cluster, although the value of the RMSD when using Tolman cone angles is no worse than that found for $Ru_6C(CO)_{17}$. The question of whether Tolman cone

(22) Achen, C. H. *Interpreting and Using Regression;* Sage University Paper Series on Quantitative applications in the social sciences, Series No. 29; Sage Publications: Beverly Hills and London, 1982; p 58.

Table 5. Electronic and Steric Parameters for Associative Reactions of Some HNCCs with P-Donor Nucleophiles in Heptane at 25.0 °C

clusters	N^a	$\theta_{th},^b$ deg	SR	β	γ, deg^{-1}	RMSD^c	R^2
$Ru_6C(CO)_{17}$[d]	14	119	1.51 ± 0.26	0.41 ± 0.04	-0.20 ± 0.01	0.41	0.99
$Ru_5C(CO)_{15}$[e] ($\theta \leq 133°$)	7	117	2.86 ± 0.18	0.21 ± 0.04	-0.068 ± 0.013	0.13	0.97
$Ru_5C(CO)_{15}$[e] ($\theta \geq 145°$)	9	148	-2.30 ± 0.13	0.592 ± 0.024	-0.233 ± 0.012	0.12	0.995
$Ru_5C(CO)_{14}\{P(OPh)_3\}$	11	≤ 101	$\geq 0.50 \pm 0.24$	0.112 ± 0.041	-0.050 ± 0.007	0.25	0.95
	11[f]	≤ 118	$\geq 0.84 \pm 0.64$	0.047 ± 0.092	-0.062 ± 0.028	0.55	0.73
$Ru_5C(CO)_{14}\{PCy_3\}$	8	≤ 101	$\geq -1.92 \pm 0.40$	0.105 ± 0.060	$-0.052 \pm .017$	0.39	0.81
	8[f]	≤ 118	$\geq -1.14 \pm 0.31$	0.039 ± 0.034	-0.086 ± 0.015	0.25	0.93
$Ru_3(CO)_{12}$	12[g]	120	-3.43 ± 0.16	0.15 ± 0.02	-0.03 ± 0.01	0.25	
	6[h]			0.347 ± 0.013		0.06	

[a] Number of nucleophiles (L′) used. [b] θ and pK_a' are used unless indicated otherwise. [c] Root mean square deviation. [d] Data from ref 14c. [e] Data from ref 14b. [f] θ' and pK_a' are used. [g] In chlorobenzene with $\theta \leq 140°$. Data from ref 2i and refs therein. [h] In chlorobenzene with $\theta = 145°$. Data from ref 2i and refs therein.

angles or cone angle equivalents (Brown's E_R values) provide a better representation of nucleophile size is still moot. So far, Tolman cone angles seem to be somewhat more successful for data with associative reactions of metal carbonyl clusters, but the comparative success will depend on which particular set of nucleophiles is involved.

Values of $|\Delta\theta|_{av}$ and $|\Delta\theta'|_{av}$ are 3.3° and 4.8°, respectively, for L = P(OPh)$_3$ and 7.3° and 2.7° for L = PCy$_3$. These values represent the average adjustments of the cone angles or cone angle equivalents required to bring about an almost perfect fit of the model to the data and provide another way of estimating the goodness of fit, all the "blame" for any poorness of fit being assigned to problems with the cone angle values. Again, the fit for L = P(OPh)$_3$ is better using Tolman cone angles, smaller adjustments being needed, but for L = PCy$_3$ it is clearly better with cone angle equivalents. In neither case is the data fit improved if a term describing the aryl effect[10a] is included.

Although the precisions of the various derived parameters in Table 5 are clearly affected by which measure of nucleophile size is chosen, the actual values of the parameters are not appreciably affected, particularly when the uncertainties are taken into account.

Discussion

Geometric Course of the Reactions. The reactions described here involve the associative displacement of a CO ligand from the Ru$_5$C(CO)$_{14}$L complexes, the solid state structures of which have the P-donor substituent attached to a basal Ru atom in an axial position (Figure 2). This position is the least sterically congested one,[5c] and it seems likely that this structure would be maintained in solution. There is one closely related cluster in which P-donor atoms exist in a labile axial–equatorial equilibrium, and that is the cluster Ru$_5$C(CO)$_{13}$(dppm) in which the two P atoms of the dppm ligand are attached to the same basal Ru atom.[17] In the more prevalent isomer, both P atoms are in equatorial positions, and in the other, one of the P atoms is attached axially. The bis(equatorial) isomer might be favored because the bite angle of the dppm ligand would be better matched to those two bonding sites on the Ru atom compared with the axial–equatorial bonding sites. However, if equatorial isomers of the mono-substituted Ru$_5$C(CO)$_{14}$L clusters are formed, either completely or in equilibrium with the axial form, the discussion below would not be affected.
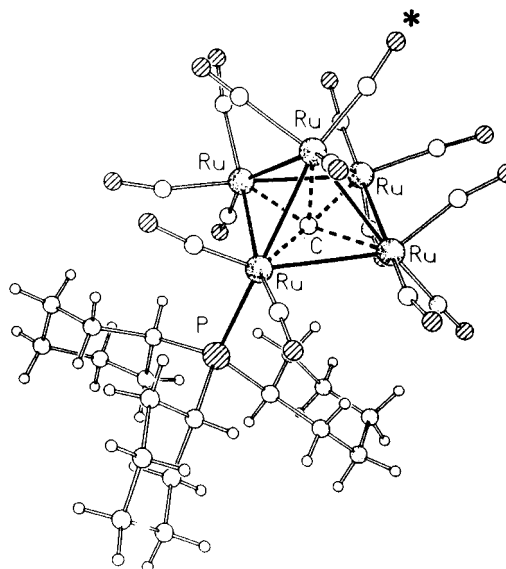

Figure 2. Diagram of a molecule of Ru$_5$C(CO)$_{14}$(PCy$_3$).

The observed products almost certainly contain the new ligand in a position across the basal Ru$_4$C plane from the original substituent, with both P-donors in axial positions. This is inferred from the close relationship between the IR spectra of the products and those of the crystallographically characterized clusters Ru$_5$C-(CO)$_{13}$(PPh$_3$)$_2$[5c] and Ru$_5$C(CO)$_{13}$(dppb), the latter with its two P-donor atoms attached in axial positions across the basal plane of the cluster[17] and almost certainly unable to exist with equatorial P-donor atoms.

Unlike the reactions of the unsubstituted parent cluster,[14b] no observable intermediate adducts are formed with any of the nucleophiles. It is, therefore, impossible to tell whether or not the reactions proceed via rate-determining formation of analogous adducts but with, in these cases, subsequent more rapid loss of CO to form the product clusters. However, we do suggest that there are good arguments that the reactions proceed simply as shown in Scheme 1. Slight modification to allow for the presence of the substituent in an equatorial position can easily be introduced.

Firstly, a strong case has been made[5c,14b] that, in reactions of the unsubstituted cluster, the smaller nucleophiles approach from *above* the Ru$_4$C basal plane to form the detectable adducts by breaking an apical–basal Ru–Ru bond. This allows, for example, for smooth formation of the NCMe adduct in exactly the configuration determined by crystallography.[5c] Sec-

Scheme 1[a]
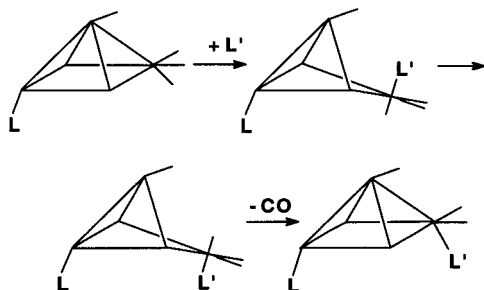
[a] The carbido atoms and the CO ligands that are not directly involved in the reactions (see text) are omitted for clarity.

ondly, attack at the unsubstituted cluster from below the Ru_4C plane is strongly disfavored for steric reasons[5c,14b] and will be much more difficult for the substituted clusters if they have the substituents in axial positions where groups on the P-donor atoms further block the region below the basal plane.[5c] The same reason as before will still operate, even if the clusters have substituents in equatorial positions in solution.

Thirdly, it does seem highly unlikely that the substituted clusters would proceed via the path followed by the unsubstituted cluster with *larger* nucleophiles.[14b] This path is sterically much more difficult and involves a large degree of bond making together with the need for the cluster to open up a great deal in order to be able to accept the nucleophile.[14b,23] If that path is difficult for the unsubstituted cluster, it would be even more difficult for the substituted ones, yet the standard reactivity (Table 5) for $Ru_5C(CO)_{14}(PCy_3)$ is greater than that for $Ru_5C(CO)_{15}$ with larger nucleophiles so a different path must be followed.

Finally, approach from above the basal plane toward the apical–basal Ru–Ru bond across the cluster from the substituted Ru atom will lead to an adduct which must isomerize before CO loss and reformation of the apical–basal Ru–Ru bond. Without this isomerization, Ru–Ru bond formation would simply lead to loss of the nucleophile but with it the product would have the new substituent in an axial position, as indicated for the ultimate product of these reactions. The sequence of reactions shown in Scheme 1 contrasts with the atomic movements suggested[14b] for the parent cluster. In that case, the Ru atom to which the incoming ligand is bound in the adduct moves on and makes a new Ru–Ru bond with what was formerly a basal Ru atom but which becomes the apical Ru. In the reactions of the substituted clusters, this process would result in one ligand ending up on an apical Ru atom, contrary to what is observed for the ultimate product.

Of course, other modes of reaction involving, for example, attack at different parts of the cluster, and followed by migration of the newly entered ligand from one Ru atom to another, can be proposed. However, in the cases where such rearrangements have been observed, bidentate ligands are involved and the rearrangements are quite slow compared with the reactions studied here.[17] For all of these reasons, we believe that

the simple sequence of reactions in Scheme 1 comprise a reasonable proposal. The presence of the substituents in the polytope of ligands surrounding the Ru_5C core will make the initial opening of the cluster sterically more difficult in general, and if the cluster has the same structure in solution as in the crystalline state, there is a CO ligand (marked with an asterisk in Figure 1) that bends down along the pertinent Ru–Ru bond,[16] and this would add to the steric problems.

Parameters in Equation 3 and Table 3. There is a growing number of sets of data for associative reactions of metal carbonyl clusters that have been analyzed in terms of eq 3, and it is becoming possible to discern some emerging patterns.[2i,10b,14,24] The major feature of the parameters derived for these $Ru_5C(CO)_{14}L$ clusters and given in Table 5 is that there is no steric threshold, steric effects being operative even when the smallest nucleophile (etpb, $\theta = 101°$) is used. By contrast, the clusters $Ru_6C(CO)_{17}$, $Ru_5C(CO)_{15}$, and $Ru_3(CO)_{12}$ all have steric thresholds of ca. 120° or more, showing that they can open up to a relatively large extent in order to accept the incoming nucleophiles.

Although only lower limits of the standard reactivities are available for the $Ru_5C(CO)_{14}L$ clusters, they are almost certainly considerably lower than that for the unsubstituted parent cluster with smaller nucleophiles by ca. two (L = $P(OPh)_3$) or five (L = PCy_3) orders of magnitude, the unfavorable steric effect clearly increasing with substituent size. This is also indicated by the relative rates with the small nucleophile etpb which reacts 750 (L = $P(OPh)_3$) and 3×10^4 (L = PCy_3) times more slowly at 25 °C than the unsubstituted cluster. The standard reactivities of the clusters listed in Table 5 decrease substantially in the order $Ru_5C(CO)_{15}$ (with smaller nucleophiles) > $Ru_6C(CO)_{17}$ > $Ru_5C(CO)_{14}$-$\{P(OPh)_3\}$ > $Ru_5C(CO)_{14}(PCy_3)$ > $Ru_5C(CO)_{15}$ (with larger nucleophiles) > $Ru_3(CO)_{12}$, the range covered being in excess of six orders of magnitude. The easier opening up to small nucleophiles of the unsubstituted square pyramidal Ru_5C cluster compared with the octahedral Ru_6C cluster is easily understood in steric terms, and the low reactivity of the Ru_3 cluster is characteristic of the intrinsically lower reactivity of clusters of smaller nuclearity.[2i,10b,14] The low values of the steric thresholds for the $Ru_5C(CO)_{14}L$ clusters imply that they cannot easily open up as much to accept the approaching nucleophiles, and this has a limiting effect on the degree of bond making that occurs, the values of β being appreciably smaller than those for the unsubstituted Ru_5C cluster. However, the ability of the cluster in the transition state to adjust to the growing size of the nucleophiles present (i.e., the flexibility of the transition state) is not very different for the substituted and unsubstituted Ru_5C clusters and suggests that the transition states are fairly flexible.[2i,10b]

The maximum difference in rates between the two nucleophiles is shown by etpb and PCy_3. According to the values of $(\log k_2)_{calc}$ in Table 4, etpb reacts 140 times faster than PCy_3 with $Ru_5C(CO)_{14}\{P(OPh)_3\}$, but the values of β and γ in Table 5 show that this is the result of a 2800-fold smaller steric retardation and an approximately 20-fold smaller electronic acceleration.

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(23) It may be that this path involves attack from below the basal plane which might be possible, albeit much slower, for these large nucleophiles because of a greater opening up of that region of the cluster.

(24) Neubrand, A.; Poë, A. J.; van Eldik, R. *Organometallics* **1995**, *14*, 3249.
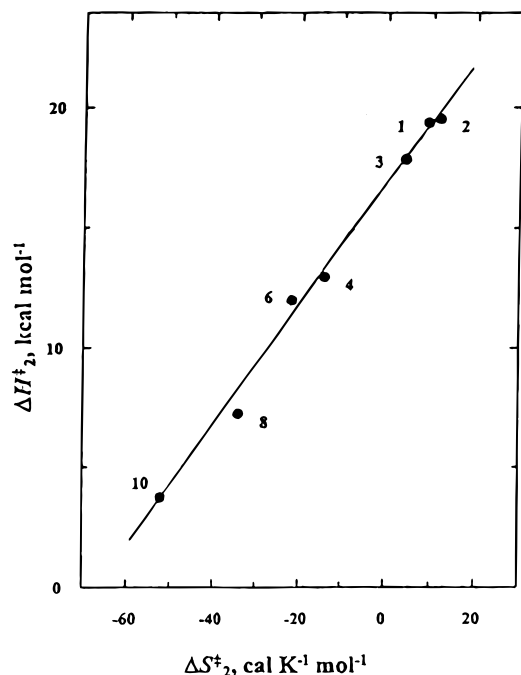
Figure 3. Isokinetic plot of $\Delta H^{\ddagger}_2$ vs $\Delta S^{\ddagger}_2$ for reactions of $Ru_5C(CO)_{14}\{P(OPh)_3\}$ with nucleophiles numbered as in Table 4. The gradient corresponds to an isokinetic temperature of ca. -20 °C.

This shows the major importance of steric effects in determining the relative rates of nucleophilic attack.

Temperature Dependence of the Kinetic Parameters. The activation parameters in Table 3 have some interesting features. When the substituent is $P(OPh)_3$, there is a very wide range of $\Delta H^{\ddagger}_2$ and $\Delta S^{\ddagger}_2$ (ca. 16 kcal mol^{-1} and 64 cal K^{-1} mol^{-1}, respectively) and the existence of some positive values of $\Delta S^{\ddagger}_2$ is unexpected for second-order reactions. This might be ascribable, in a very qualitative way, to a pronounced weakening of the bonding in the transition states, a weakening that might be expected of adducts formed by opening up of the cluster. This is the inverse of the explanation offered for negative entropies of activation found for CO dissociative reactions[20] but does not seem to be relevant to reactions of the unsubstituted Ru$_5$C cluster.[14b]

The ranges of $\Delta H^{\ddagger}_2$ and $T\Delta S^{\ddagger}_2$ at $T = 300$ K (16 and 19 kcal mol^{-1}, respectively, for L = P(OPh)$_3$ and 3.8 and 6.2 kcal mol^{-1} for L = PCy$_3$) show that the relative rates for both clusters are more dependent on entropy than enthalpy differences. This is confirmed by the plot of $\Delta H^{\ddagger}_2$ vs $\Delta S^{\ddagger}_2$ which is shown in Figure 3 to be a very good straight line ($R^2 = 0.993$). Although this does not in itself confirm that there is an isokinetic temperature,[25] the gradient corresponds to a temperature of ca. -20 °C at which all the rates would be expected to be similar. An analogous plot of the three sets of activation parameters for L = PCy$_3$ indicates an isokinetic temperature of -90 °C. These low isokinetic temperatures indicate, again, that relative rates are determined more by entropic factors than enthalpic ones, and this point can be examined in more detail as follows. These temperatures are sufficiently different from the temperatures at which the kinetics were measured that the trends in the data can easily be resolved into separate electronic and steric effects, as shown above, and the

(25) Linert, W. *Chem. Soc. Rev.* **1994,** 429.

Table 6. Temperature Dependence of the Sensitivity of $Ru_5C(CO)_{14}\{P(OPh)_3\}$ to Nucleophile Basicity and Size[a]

T, °C	β	γ, deg^{-1}	RMSD	R^2
50	0.073 ± 0.082	-0.077 ± 0.010	0.258	0.95
25	0.086 ± 0.071	-0.057 ± 0.009	0.225	0.93
0	0.101 ± 0.061	-0.034 ± 0.008	0.191	0.87

[a] Estimated by the application of eq 3 ($\theta_{th} \leq 101°$) to values of log k_2 calculated from the activation parameters in Table 3.

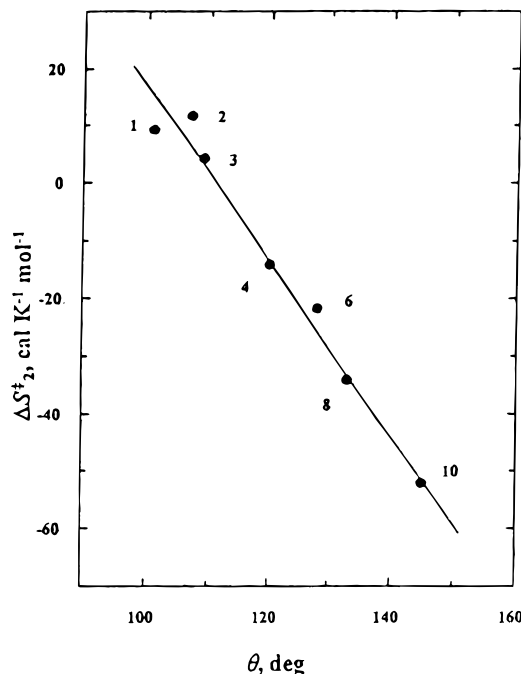**Figure 4.** Correlation ($R^2 = 0.97$) between $\Delta S^{\ddagger}_2$ and nucleophile cone angles for reactions of $Ru_5C(CO)_{14}\{P(OPh)_3\}$ with nucleophiles numbered as in Table 4.

dependence of the trends on temperature can be determined. Values of β and γ for L = P(OPh)$_3$ are given in Table 6 for 0, 25, and 50 °C and show that the correlation coefficients decrease slightly as the temperature decreases, presumably because of the closer approach to the isokinetic temperature at -20 °C. Although they are less precise, the values of β and γ at 25 °C agree with the more precise ones found (Table 3) from the larger selection of nucleophiles used at that temperature. The values of β in Table 6 lead to the surprising conclusion that the increasing rates with increasing nucleophile basicity (i.e., the positive value of β) seems to be almost temperature independent, so that this small electronic effect could be mainly due to more favorable entropic factors. Moreover, the increasingly unfavorable steric effects (i.e., more negative γ values) as the temperature increases shows, very surprisingly, that the enthalpy contribution actually reduces the steric barrier, but the fact that the overall steric barrier is unfavorable means that an unfavorable entropic contribution to the steric effect must overcome the favorable enthalpic contribution. The strong link between the steric effects and entropy factors is illustrated further by the excellent inverse correlation ($R^2 = 0.97$) between the values of $\Delta S^{\ddagger}_2$ and nucleophile cone angle shown in Figure 4.

This link may also be evident in the substituent effect. The much slower reaction with P(OPh)$_3$ when L = PCy$_3$ is caused by an 8 kcal mol^{-1} less favorable value of

$T\Delta S^{\ddagger}_2$ at 300 K which overcomes a 4 kcal mol^{-1} more favorable value of $\Delta H^{\ddagger}_2$. As with the nucleophile dependence, it may be that there is a negligible electronic effect due to the greater basicity of the PCy$_3$ substituent but that its greater size inhibits the reaction by producing a very unfavorable entropy of activation which overcomes a favorable enthalpic contribution.

Summary

The study of these substituted clusters has shown that they undergo rapid substitution reactions with P-donor nucleophiles exclusively via associative paths, as for other HNCCs,[14] and that they form products in which the two substituents are in positions across the basal Ru$_4$C plane from each other. The rate constants conform to the well-established equation (eq 3) relating rates to the electronic and steric properties of the nucleophiles, and there is no evidence in these reactions for any need of a term due to the aryl effect.[10a] Tolman cone angles provide a successful quantitative measure of nucleophile size for the P(OPh)$_3$ cluster. Cone angle equivalents (related directly to Brown's E_R values) are better for the PCy$_3$ cluster, although Tolman cone angles still give an acceptable fit. Even the smallest nucleophile is subject to steric retardation, and the standard reactivities of the Ru$_5$C clusters decrease steadily and significantly from the parent cluster (with smaller nucleophiles) through the P(OPh)$_3$- to the PCy$_3$-substituted cluster because of the increasing size of the substituents. The early onset of steric effects and relatively low standard reactivities indicate that opening up the clusters to accommodate the incoming nucleophiles is quite difficult, and this is reflected in the low extent of bond making in the transition states. However, the transition state flexibility is quite large, i.e., although the steric effect comes into play at a low cone angle, the magnitude of the steric retardation is quite small.

The activation parameters show a strong enthalpy–entropy compensation, the rates converging as the temperatures decrease. This emphasises the impor-tance of temperature-dependence measurements in conjunction with linear free energy relationship studies when equations such as eq 3 are used and comparison of values of β and γ, etc., are made for various complexes. If data for a particular complex were inadvertently obtained close to an isokinetic temperature, then its β and γ values could be small for that reason alone and comparison with values for other complexes would be vitiated. In any case, effects of temperature on the parameters should generally be allowed for when making comparisons.

Moreover, the derived electronic and steric parameters show a very unexpected temperature dependence. Thus, as well as the relative rates of reaction with different nucleophiles being determined overall more by entropy than enthalpy factors, there is evidence that the small but favorable specifically electronic effect is almost temperature independent and due mainly to entropic factors while the large and unfavorable specifically steric effects are temperature dependent and show up in entropic terms that are sufficiently unfavorable that they overcome favorable enthalpic contributions. The effect of the substituents could also operate in the same way, i.e., with a negligible contribution due to the electronic differences between P(OPh)$_3$ and PCy$_3$ and a favorable enthalpic contribution to steric effects (i.e., rates would *increase* with increasing substituent size) that is overcome by unfavorable entropic contributions. The effects of substituents on these reactions are, therefore, pronounced, but when their temperature dependence is studied, they are found to operate in subtle and unexpected ways that deserve further exploration.

Supporting Information Available: A table giving values of k_{obs} as a function of [L′] (5 pages). Ordering information is given on any current masthead page.

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