Registry No. 3, 141344-43-6; **3a**, 141344-44-7; **4**, 141344-45-8; **4a**, 141344-46-9; **5**, 141344-47-0; **5a**, 141344-48-1; CPA, 11075-17-5; Cu, 7440-50-8; Ni, 7440-02-0; methyl 2-carboxy-6-nitrobenzoate, 6744-85-0; methyl 6-amino-2-carboxybenzoate, 113579-20-7; dimethyl 3-nitrophthalate, 13365-26-9; *N,N*-dimethyl-2-carboxymethoxy-6-nitrobenzamide, 129356-57-6; methyl 2-carboxy-3-nitrobenzoate, 21606-04-2; 4-imidazoleacetic acid, 645-65-8.

Supplementary Material Available: Values of Abs$_{MS}$ and k_{MS} for the deacylation of **3** and **4** at various values of log [CAK]/[CA] (1 page). Ordering information is given on any current masthead page.

Systematic Kinetics of High Nuclearity Metal Carbonyl Clusters. Associative Substitution Reactions of Ru$_6$C(CO)$_{17}$ with P-Donor Nucleophiles

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Abstract: The high nuclearity carbonyl cluster (HNCC) Ru$_6$C(CO)$_{17}$ has been shown to react with a wide variety of P-donor nucleophiles exclusively by associative processes. The rate constants, k_2, can be subdivided into electronic and steric contributions which depend on the σ-donicity (pK_a' values) and size (Tolman cone angles, θ) of the P-donor nucleophiles. The data fit well to the equation $\log k_2 = \alpha + \beta(\mathrm{p}K_a' + 4) + \gamma(\theta - \theta_{th})\lambda$. The standard reactivity for a weak and small hypothetical nucleophile of pK_a' = −4 is defined by $\log k_2° = \log k_2 - \beta(\mathrm{p}K_a' + 4)$ and shows an exceptionally high value of 1.51 ± 0.26. The electronic sensitivity (β = 0.41 ± 0.04) is also very high and indicates a high degree of bond making in the transition state. The steric threshold, θ_{th}, below which no steric effects are apparent (switching function (λ) = 0) is 119°, showing that the transition states are quite congested as expected from the high degree of bond making. These transition states are proposed to contain a well-defined Ru$_6$C(CO)$_{17}$ moiety that is isomeric with the ground-state cluster and which is opened up to an extent that it can accommodate all nucleophiles of various sizes up to the cone angle 119°, defined by θ_{th}, without any steric repulsions. Above the steric threshold, when λ = 1, the flexibility of the transition state is found to be exceptionally low as indicated by the value $\gamma = -0.20 \pm 0.01$ deg^{-1} which means that the rate of the reaction will decrease by 37% for each degree increase in the cone angle of the incoming nucleophile when electronic effects are absent or constant. This steric effect leads to values of $k_2°$ that vary by 10^{10} over the θ range 119–170°. Values of $\Delta H_2^{\ddagger}$ and $\Delta S_2^{\ddagger}$ are low (7 to 13 kcal mol^{-1}) and very negative (−10 to −36 cal K^{-1} mol^{-1}), respectively, again showing the exceptionally high degree of bond making in the transition state. These kinetic parameters are compared with those found for smaller clusters and a mononuclear carbonyl.

Introduction

The importance of electronic and steric properties of P-donor nucleophiles in determining rates of associative reactions of metal carbonyls has been known for many years,[1] and the quantitative separation of their contributions to the rates has more recently been shown to be possible for a growing number of reactions.[1d,e,2-5] Virtually all published or otherwise available data have been found[6] to fit extremely well to eq 1, which is essentially the same as that

$$\log k_2 = \alpha + \beta(\mathrm{p}K_a' + 4) + \gamma(\theta - \theta_{th})\lambda \qquad (1)$$

proposed by Giering et al.[5] The parameter λ is a switching factor that is zero when θ (the Tolman cone angle for the nucleophiles[7]) $\leq \theta_{th}$, so that steric effects are not important for nucleophiles smaller than the steric threshold, θ_{th}. When the nucleophile cone angles exceed the steric threshold, λ becomes unity, steric effects come into play, and their importance is quantified by the steric parameter γ. The parameter β defines quantitatively the sensitivity of the rates to the σ basicity, pK_a',[8] of the nucleophiles and can be related to the extent of bond making in the transition states.[1b,3] For a standard, weakly basic (pK_a' = −4), and small ($\theta \leq \theta_{th}$) hypothetical nucleophile the value of $\log k_2° = \log k_2 - \beta(\mathrm{p}K_a' + 4)$ provides a measure of the standard reactivity (SR) of the carbonyl, and this can be taken as an approximate estimate of its intrinsic reactivity.[4,9]

The excellent fit of all available data[6] to eq 1 is the more fortunate because eq 1 therefore provides an objective way of deriving values for the parameters SR, β, and γ, together with their uncertainties, through a multilinear regression analysis.[5,10] This requires the choice of an initial value for θ_{th} which can be obtained graphically, the best value being obtained subsequently by variation of θ_{th} until a minimum value of the root-mean-square deviation (RMSD) of the values of $(\log k_2)_{calc}$ and $(\log k_2)_{expt}$ is obtained.[6]

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(1) (a) Schuster-Woldan, H. G.; Basolo, F. *J. Am. Chem. Soc.* **1966**, *88*, 1657–1663. (b) Poë, A. J.; Twigg, M. V. *J. Organomet. Chem.* **1973**, *50*, C39–C42. Poë, A. J.; Twigg, M. V. *J. Chem. Soc., Dalton Trans.* **1974**, 1860–1866. (c) Jackson, R. A.; Kanluen, R.; Poë, A. J. *Inorg. Chem.* **1984**, *23*, 523–527. (d) Zizelman, P. M.; Amatore, C.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 3771–3784. (e) Moreno, C.; Delgado, S.; Macazaga, M. J. *Organometallics* **1991**, *10*, 1124–1130.

(2) Golovin, M. N.; Rahman, M. M.; Belmonte, J. E.; Giering, W. P. *Organometallics* **1985**, *4*, 1981–1991.

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

(4) Brodie, N. M. J.; Chen, L.; Poë, A. J. *Int. J. Chem. Kinet.* **1988**, *20*, 467–491. Poë, A. J. *Pure Appl. Chem.* **1988**, *60*, 1209–1217 and references therein.

(5) Liu, H. Y.; Eriks, K.; Prock, A.; Giering, W. P. *Organometallics* **1990**, *9*, 1758–1766 and references therein.

(6) Chen, L. Ph.D. Thesis, 1991, University of Toronto.

(7) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313–348. Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2956–2965.

(8) Although experimental pK_a values[2] can be used successfully, we have used pK_a' values derived from the χ_d values obtained by Giering et al.[5] essentially by multiplying them by a constant factor to allow for the change of units and choosing θ = 145° as a reference for steric correction.[6] This has the advantage of eliminating the steric effects, evident[5] on experimental pK_a values, due to various degrees of hydration of the protonated P-donor ligands, without losing the advantage[4] of obtaining dimensionless β values.

(9) Chen, L.; Poë, A. J. *Can. J. Chem.* **1989**, *67*, 1924–1930.

(10) We are very grateful to Professor W. P. Giering for providing us with his original multilinear regression program.

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The parameters obtained in this way provide a quantitative dynamic characterization of metal carbonyls to set alongside their structural, spectroscopic, and fluxional properties[11] and so complete their overall characterization.[12] However, no such approach has been reported for any high nuclearity carbonyl clusters (HNCCs), a large and diverse group of compounds about which a great deal of synthetic and structural information is available.[11] The absence[13] of any systematic kinetic and mechanistic studies of these important and interesting compounds shows that much remains to be done before their natures can be claimed to be fully understood. We describe here the first such study, namely the kinetics of reactions of the cluster $Ru_6C(CO)_{17}$ with a wide variety of P-donor nucleophiles.

Experimental Section

Materials. For air-sensitive compounds all manipulations were carried out by using standard Schlenk techniques under an atmosphere of oxygen-free N_2. $Ru_3(CO)_{12}$ was used as received (Strem). All nucleophiles were obtained from commercial sources. Liquid phosphorus ligands ($P(OC_6H_5)_3$, $P(OEt)_3$, $P(OMe)_3$, $P(n\text{-}Bu)_3$, and $P(O\text{-}i\text{-}Pr)_3$) were purified by distillation under reduced pressure of argon immediately before use. Etpb ($P(OCH_2)_3CEt$) was sublimed (50 °C, reduced pressure) immediately before use. The crystalline ligands $P(p\text{-}XC_6H_4)_3$ (X = MeO, Me, H, F, Cl, CF_3) were recrystallized from ethanol at least once before use. $PPh(OMe)_2$ was used as received (Strem). Pure $P(C_6H_{11})_3$ was obtained as follows. First, $P(C_6H_{11})_3{\cdot}CS_2$ (Strem) was dissolved in boiling ethanol under argon, and the ethanol was then distilled off until the red solutin became colorless, indicating that the CS_2 had been completely removed together with the ethanol. The residue was then cooled to yield snow white crystalline $P(C_6H_{11})_3$. The crystals were collected in an argon-filled glovebag and dried under vacuum. The purity of some of the air-sensitive ligands was confirmed by the measurement of their ^{31}P-NMR spectra. For example, for $P(OEt)_3$ in chlorobenzene and using $P(OMe)_3$ in $(CD)_3CO$ as the insert reference, a single resonance peak was observed at −2.68 ppm which is in good agreement with the reported value of −2.7.[14] All solvents for synthetic use were reagent grade. Heptane (Caledon) and chlorobenzene (Fisher Scientific) were distilled and stored over activated molecular sieves. Molecular sieves (4 Å, BDH) were activated by methanol washing followed by drying at ca. 600 °C for several hours and subsequent cooling in a vacuum desiccator. For air-sensitive ligands, the solvents were degassed by means of at least 3 freeze–pump–thaw cycles before use. All gases were obtained from Matheson or Canox Ltd. and were research grade.

The cluster $Ru_6C(CO)_{17}$ was obtained in nice crystalline form from the synthesis using the published method,[15] starting from $Ru_3(CO)_{12}$, and characterized by its spectroscopic data. IR (in heptane) 2066.4 (s), 2047.4 (s), 2003.2 (w), 1852.6 (vw), which is in good agreement with the reported (in cyclohexane)[16] data 2064 (s), 2049 (s), 2007 (w), 1993 (w), 1958 (w), 1845 (vw) cm^{-1}. FAB mass spectrum (M^+): maximum m/e found 1095, calcd 1094 based on Ru_6 = 606. On TLC plates (silica gel, Baker) the crystalline sample gives only one brown band ($R_f = 0.71$ with 1:2 (v/v) hexane–dichloromethane) and slowly decomposes. The cluster is stable in solid form and in solution for a period of a few days. On long-term exposure to air, it decomposes to black unidentified material. For kinetic studies, $Ru_6C(CO)_{17}$ was recrystallized at least once from toluene before use.

The monosubstituted products were prepared by mixing 1 equiv each of $Ru_6C(CO)_{17}$ and the nucleophiles and subsequently monitoring the FTIR spectral changes until the peaks due to the parent cluster all disappeared. The products were then identified by comparing their FTIR spectra with the known compounds or analogues. For example, $Ru_6C(CO)_{16}P(C_6H_5)_3$ in heptane, 2084.1 (m), 2056.1 (vs), 2046.2 (ms), 2031,.4 (vs), 2000.3 (m), 1987.4 (m), 1850.6 (vw), 1840.4 (vw), and in carbon tetrachloride,[16] 2084 (m), 2056 (vs), 2045 (ms), 2029 (vs), 2003 (m), 1984 (m), 1844 (w). Further reaction in the presence of an excess of nucleophile led much more slowly to disubstituted products which were also characterized by their IR spectra, e.g. $Ru_6C(CO)_{15}\{P(C_6H_5)_3\}_2$ in heptane, 2067.5 (m), 2046.5 (s), 2017.9 (s, br), 1992.3 (w), 1861.0 (vw), and in carbon tetrachloride,[17] 2069 (w, sh), 2064 (w), 2046 (s), 2018 (s, br), 1998 (w), 1987 (w), 1845 (w, br).

Instruments. FTIR spectra were obtained by using a Nicolet 10DX FTIR spectrophotometer. UV–vis monitoring of slower reactions was carried out with either a Cary 2200 UV–vis spectrophotometer or a Hewlett-Packard 8452A diode array spectrophotometer equipped with a cell holder thermostated by a water bath (±0.1 °C). Stopped-flow measurements were made with a Hi-Tech SF-51 apparatus equipped with an SU-40 spectrophotometer interfaced with a Hewlett Packard Series 300 computer and connected with a Hewlett Packard printer. ^{31}P-NMR spectra were recorded on a Varian XL-200 spectrometer. FAB mass spectra were obtained by using a VG 70-250S mass spectrometer, with a Xenon flux and a matrix of nitrobenzene alcohol.

Kinetic Studies. Kinetic runs monitored by FTIR spectroscopy were carried out as described elsewhere.[9] Initial concentrations of reacting complex were generally ca. 5–10 × 10^{-5} M.

For slow reactions ($t_{1/2} > 5$ min), monitored by UV–vis spectrophotometry, 10-mm quartz cells with a capacity of ca. 3.5 mL were used. Usually 3.00 mL of complex solution was added into the cell under an inert gas atmosphere and the cell was then sealed tightly with a Teflon stopper and allowed to stand for thermal equilibration. A small portion of the ligand solution was then added through a hypodermic syringe, and the cell was immediately resealed and shaken and then replaced in the cell holder for kinetic study. The temperatures of the reaction solutions were determined, before and after the runs were conducted, by inserting a thermometer with a reading accurate to 0.01 °C into a cell filled with water in the same cell holder, through a cover matched with the compartment.

A stoppered Helma tandem-mix quartz cell (238-QS, 2 × 4.38 mm) was used for faster reactions ($t_{1/2} < 5$ min). Aliquots (1.00 mL each) of the complex and ligand solutions were added into the separate cell compartments, under inert gas if necessary. The cell was then sealed with Teflon stoppers and time allowed for thermal equilibration. After that the cell was quickly removed from the cell holder, shaken vigorously to assure thorough mixing of the two solutions, and immediately replaced prior to commencement of the kinetic monitoring.

Even faster reactions ($t_{1/2} < 30$ s) required the use of stopped-flow techniques. The complete stopped-flow circuit for the instrument, including sample reservoirs, is immersed in a water bath. Temperatures of the bath were controlled by an Endacol RTE 110 thermostated water bath (±0.1 °C) and measured through a temperature sensor attached to the base of the cell housing through a bulkhead connector. The path length of the optical cell is 2.0 mm. The instrument was usually operated with a slit width of 1.0 mm and drive pressure of 70 psi (5 atm). The optical filter was always set to be less than the time base. With solvent in the flow system, prior to each set of runs, the photomultiplier voltage was adjusted so that full scale deflection (0–100% T) was 4 V. The syringes in the stopped-flow apparatus were loaded and flushed several times with the solution and then allowed to equilibrate at a given temperature. For air-sensitive ligands, all solutions were prepared and transferred to the flow system under inert gas atmosphere.

After equilibration and firing one or two "shots" without recording the spectrum, data were accumulated for the reaction. The rate constants were usually an average of five to eight repetitions which were reproducible to within 5–10%.

Results

The Course of the Reactions. The pattern of a given reaction was initially investigated by using repetitive FTIR monitoring at room temperature. This gave direct information about product

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(11) (a) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988; Chapter 28. (b) Johnson, B. F. G., Ed. *Transition Metal Clusters*; Wiley: New York, 1980. (c) Moskovits, M., Ed. *Metal Clusters*; Wiley: New York, 1986. (d) Vargas, M. D.; Nicholls, J. N. *Adv. Inorg. Radiochem.* **1986**, *30*, 123–222. (e) Shriver, D. J.; Kaesz, H. D.; Adams, R. D. *The Chemistry of Metal Cluster Complexes*; VCH Publishers, Inc.: New York, 1990, and references therein.

(12) The obtained empirical relationship among log k_2, pK_a', and θ values (eq 1) can also serve as a model from which pK_a' or θ values for a given nucleophile can be estimated or justified.[6]

(13) To our knowledge the only kinetic studies reported of HNCCs, apart from some semiquantitative CO-exchange kinetics on $Rh_6(CO)_{16}$ (Nomiya, K.; Suzuki, H. *J. Organomet. Chem.* **1979**, *168*, 115–121), are of reactions of I^- with $Os_6(CO)_{18}$ (John, G. R.; Johnson, B. F. G.; Lewis, J.; Mann, A. L. *J. Organomet. Chem.* **1979**, *171*, C9–C13), an isomerization reaction of $Os_6Pt(CO)_{17}(\mu_3\text{-}NCMe)(C_8H_{12})$ (Couture, C.; Farrar, D. H. *J. Chem. Soc., Dalton Trans.* **1987**, 2245–2252), the very interesting isomerization reaction of *cis*-$[Fe_4Rh_2(CO)_{16}B]^-$ to *trans*-$[Fe_4Rh_2(CO)_{16}B]^-$ induced by nucleophiles (Khattar, R.; Puga, J.; Fehlner, T. P. *J. Am. Chem. Soc.* **1989**, *111*, 1877–1882), and the equally interesting study of rates of H^+ removal from $H_3Rh_{13}(CO)_{24}{}^{2-}$ (Weberg, R. T.; Norton, J. R. *J. Am. Chem. Soc.* **1990**, *112*, 1105–1108).

(14) Crutchfield, M. M.; Dungen, C. H.; Letcher, J. H.; Mack, V.; Van Wazer, J. R. In *^{31}P Nuclear Magnetic Resonance. Topics in Phosphorus Chemistry*; New York: Wiley-Interscience, 1967; Vol. 5, pp 231–457.

(15) Johnson, B. F. G.; Lewis, J.; Nicholls, J. N.; Puga, J.; Raithby, P. R.; Rosales, M. J.; McPartlin, M.; Clegg, W. *J. Chem. Soc., Dalton Trans.* **1983**, 277–290.

(16) Johnson, B. F. G.; Lewis, J.; Williams. I. G. *J. Chem. Soc. A* **1970**, 901–903.

(17) Brown, S. C.; Evans, J.; Webster, M. *J. Chem. Soc., Dalton Trans.* **1981**, 2263–2270.

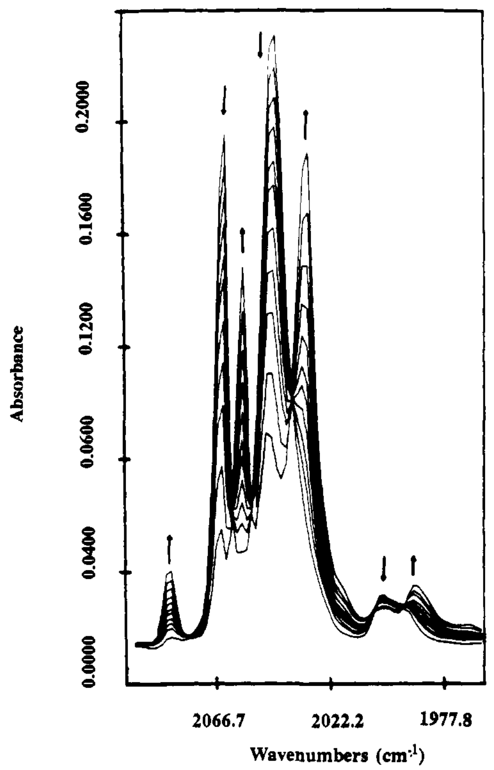

Figure 1. FTIR spectral changes during the reaction $Ru_6C(CO)_{17}$ + $P(p\text{-}ClC_6H_4)_3 \rightarrow Ru_6C(CO)_{16}P(p\text{-}ClC_6H_4)_3$ + CO in heptane at 25.0 °C.

distributions and rough rate constants. $Ru_6C(CO)_{17}$ reacts with pseudo-first-order excesses of the 14 nucleophiles (L) used to give simple monosubstituted products in the first step. The IR bands in the CO stretching region due to $Ru_6C(CO)_{17}$ and $Ru_6C(CO)_{16}L$ are well-separated and allow accurate kinetic monitoring of the disappearance of the reactant. Figure 1 shows a series of FTIR spectra recorded during a typical kinetic run. As the characteristic IR bands for $Ru_6C(CO)_{17}$ change to the ones assigned to the $Ru_6C(CO)_{16}L$ species, sharp isosbestic points are formed, indicating a clean reaction as shown in eq 2, without detectable intermediates or disubstituted products.

$$Ru_6C(CO)_{17} + L \rightarrow Ru_6C(CO)_{16}L + CO \qquad (2)$$

Sequential multisubstitutions were observed. The subsequent reactions of the monosubstituted products with nucleophiles such as etpb, $P(OEt)_3$, and $P(n\text{-}Bu)_3$ were followed and the results show that usually a given step is much slower than the previous one.

$Ru_6C(CO)_{17}$ has a broad absorption band in the visible region (λ_{max} = 418 nm) and the monosubstituted products $Ru_6C(CO)_{16}L$ have very similar absorption spectra to the parent compound but with a red shift of λ_{max} of ca. 10 nm and about a 50% increase in intensity. It is impossible to monitor the disappearance of the reactant and growth of product was monitored instead. Fast reactions studied by stopped-flow techniques were concluded to have the same patterns as the reactions studied by FTIR or UV-vis monitorings on the basis of the FTIR spectra of the products and the success of the kinetic data analysis when the growth of absorbance at a given wavelength was monitored.

The Kinetics. Pseudo-first-order rate constants (k_{obs}) for slower reactions were obtained by fitting the exponential dependence of the absorbance vs time data by using a nonlinear least-squares regression program, KORE,[18] which provides values of k_{obs} and A_∞, the absorbance after completion of the reactions. In all cases the rates of subsequent reactions were slow enough for the values of A_∞ to be well-defined. Values of A_∞ were also measured after at least 5 half-lives of the reaction and plots of ln (A_t–A_∞) vs time were usually linear for more than 3 half-lives. When KORE was used to obtain the k_{obs} values the correlation coefficient was generally 0.999–0.999999 for up to 99% reaction. Rate constants obtained by monitoring the same reactions by FTIR and UV–vis spectroscopy were always in good agreement as were rate constants obtained by monitoring a given reaction at different wavelengths.

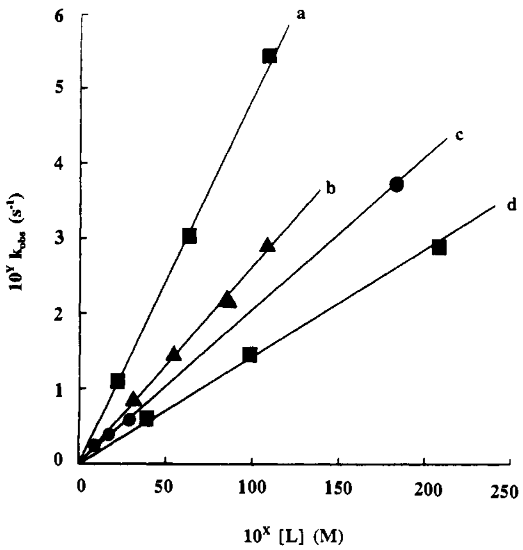

Figure 2. Plots of k_{obs} vs nucleophile concentration for the reactions of $Ru_6C(CO)_{17}$ with L in heptane at 25.0 °C: (a) L = $P(p\text{-}MeC_6H_4)_3$, X = 5, Y = 4; (b) L = $P(OMe)_3$, X = 5, Y = 0; (c) L = $P(O\text{-}i\text{-}Pr)_3$, X = 4, Y = 0; (d) L = $P(p\text{-}FC_6H_4)_3$, X = 4, Y = 4.

Stopped-flow data were processed by using a Hi-Tech HS-1 technical Datapro software suite which provides a complete data acquisition, presentation, and analysis package. A single exponential with a floating end point is successfully used to obtain the pseudo-first-order rate constant. The residual variance is normally smaller than 1%.

Linear least-squares analyses of the dependence of k_{obs} on [L] values showed that the data fit closely to eq 3, where k_2 is the second-order rate constant and a is a constant which in most cases

$$k_{obs} = a + k_2[L] \qquad (3)$$

is very close to zero as shown in the rate plots in Figure 2. Each value of k_{obs} was weighted according to the assumption of a constant probable error, expressed as a percentage, and these percentage errors are provided by the analyses. Values of a and k_2 are listed in Tables I and II for reactions, respectively, in heptane and chlorobenzene, together with their standard deviations and the probable errors of each value of k_{obs}.[19]

The temperature dependence of values of k_2 for some of the reactions was also studied. Activation parameters were obtained by an unweighted linear least-squares analysis of the dependence of ln (k_2/T) on $1/T$, where values of k_2 were obtained by directly dividing values of k_{obs} by the concentrations of the ligand, [L], a procedure allowed by the negligible values found for a in eq 3. The activation parameters are listed in Table III together with their standard deviations and the probable errors of each k_2 value as obtained from the data analyses.

Discussion

The existence of clear isosbestic points seen in FTIR monitoring, the excellent fit of the rate data to the KORE program, and the generally low probable errors found for individual measurement of the rate constants as found from the least-squares analyses of the dependence of k_{obs} on [L] or of ln (k_2/T) on $1/T$ all attest

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(18) Swain, C. G.; Swain, M. S.; Berg, L. F. *J. Chem. Inf. Comp. Sci.* **1980**, *20*, 47–51.

(19) Although the values of a are small they occasionally appear to be significant with respect to the standard deviations provided by the weighted least-squares analysis. However, they vary widely and are frequently slightly negative, even "significantly" so. We do not, therefore, regard them as having any mechanistic significance and have to conclude that there are occasional systematic errors or statistical accidents that lead to the apparently significant values. They have no practical effect in the sense that values of k_2 obtained from $k_{obs}/[L]_{max}$ still fit well with the data analysis presented in the Discussion Section.

Table I. Rate Constants for the Reactions of $Ru_6C(CO)_{17}$ with Nucleophiles, L, in Heptane ([Complex] = 5–10 × 10^{-5} and 5–10 × 10^{-6} M for IR and UV–vis Monitoring, Respectively)

no.[a]	L	pK_a′[b]	θ, deg	T, °C	N[c]	10^4[L], M	a, s^{-1}	k_2, M^{-1} s^{-1}	$\sigma(k_{obs})$,[d] %
1	etpb	−0.30	101	25.0	81[e]	0.457–11.1	1.93 ± 0.12	(7.31 ± 0.59) × 10^3	3.7
2	$P(OMe)_3$	0.83	107	25.0	40[e]	3.27–10.9	(−0.70 ± 7.28) × 10^{-2}	(2.58 ± 0.15) × 10^3	3.1
3	$P(OEt)_3$	1.64	109	25.0	38[e]	3.97–33.1	2.39 ± 0.11	(1.51 ± 0.08) × 10^3	3.1
4	$PC_6H_5(OMe)_2$	1.48	120	25.0	24[e]	2.94–11.8	−0.16 ± 0.03	(1.26 ± 0.09) × 10^3	4.3
5	$P(OC_6H_5)_3$	−2.79	128	6.5	5[f]	2.54–31.7	(9.98 ± 5.06) × 10^{-5}	2.20 ± 0.09	4.8
				25.0	3[g]	6.69–12.6	(1.51 ± 0.51) × 10^{-3}	7.84 ± 1.15	
				34.9	1[g]	1.75	0	18.7 ± 0.91[h]	
6	$P(O\text{-}i\text{-}Pr)_3$	3.38	130	25.0	18[e]	5.97–183.2	(9.15 ± 0.95) × 10^{-3}	(1.97 ± 0.05) × 10^2	0.8
7	$P(n\text{-}Bu)_3$	8.67	132	25.0	12[e]	0.251–3.00	−0.69 ± 0.02	(3.04 ± 0.06) × 10^4	0.2
8	$P(p\text{-}MeOC_6H_4)_3$	5.13	145	6.5	5[g]	2.27–21.6	(−3.08 ± 0.98) × 10^{-5}	(5.52 ± 0.17) × 10^{-1}	4.6
				18.0	4[g]	7.57–21.3	(−1.53 ± 3.42) × 10^{-5}	(8.04 ± 0.61) × 10^{-1}	
				27.3	2[g]	5.30–6.62	0	1.17 ± 0.05[h]	
				35.4	2[g]	2.65–5.30	0	1.68 ± 0.08[h]	
9	$P(p\text{-}MeC_6H_4)_3$	4.46	145	6.5	4[g]	2.02–20.2	(3.93 ± 46) × 10^{-7}	(2.00 ± 0.10) × 10^{-1}	6.8
				25.0	3[f]	2.18–10.9	(3.08 ± 10.6) × 10^{-6}	(4.76 ± 0.68) × 10^{-1}	
10	$P(C_6H_5)_3$	3.28	145	5.0	4[f]	69.5–382.0	(8.56 ± 27.5) × 10^{-6}	(4.03 ± 0.33) × 10^{-2}	7.4
				6.5	7[g]	45.6–640.0	(−1.04 ± 0.18) × 10^{-4}	(5.04 ± 0.20) × 10^{-2}	
				25.0	3[g]	21.6–143.0	(6.51 ± 5.17) × 10^{-5}	(8.94 ± 1.04) × 10^{-2}	
				44.4	2[g]	20.3–72.0	(1.51 ± 37) × 10^{-5}	(2.16 ± 0.27) × 10^{-1}	
				60.4	4[g]	20.3–196.7	(1.62 ± 0.86) × 10^{-4}	(4.07 ± 0.12) × 10^{-1}	
11	$P(p\text{-}FC_6H_4)_3$	1.63	145	25.0	4[f]	9.80–208.0	(7.18 ± 0.69) × 10^{-6}	(1.36 ± 0.03) × 10^{-2}	2.9
12	$P(p\text{-}ClC_6H_4)_3$	0.87	145	48.2	5[f]	11.5–36.4	(−2.36 ± 1.01) × 10^{-6}	(3.12 ± 0.11) × 10^{-2}	3.4
				55.0	6[f]	7.39–43.5	(−7.47 ± 1.59) × 10^{-6}	(4.50 ± 0.12) × 10^{-2}	
				65.0	5[f]	35.6–115.0	(5.12 ± 1.89) × 10^{-5}	(6.49 ± 0.29) × 10^{-2}	
13	$P(p\text{-}CF_3C_6H_4)_3$	−1.39	145	50.0	3[f]	86.4–368.0	(−9.52 ± 4.46) × 10^{-6}	(8.40 ± 0.24) × 10^{-3}	2.1
				60.0	3[f]	78.2–237.0	(−2.26 ± 0.43) × 10^{-5}	(1.71 ± 0.06) × 10^{-2}	
				70.0	3[f]	49.8–264.0	(8.24 ± 2.92) × 10^{-6}	(2.58 ± 0.09) × 10^{-2}	
14	$P(C_6H_{11})_3$	11.26	170	25.0	2[f]	22.7–24.1	0	(4.51 ± 0.65) × 10^{-3} [h]	14

[a] Nucleophile number. This numbering will be used throughout the paper. [b] These pK_a′ values are corrected for steric effects[8] and are taken from ref 6. [c] Number of individual determinations of k_{obs}; $k_{obs} = a + k_2$[L]. [d] Probable 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 the number of degrees of freedom (ref 9). [e] Studied by using stopped-flow techniques. [f] Studied by using FTIR monitoring. [g] Studied by using UV–vis monitoring. [h] Calculated from $k_2 = k_{obs}$/[L] by assuming a = 0.

Table II. Rate Constants for the Reactions of $Ru_6C(CO)_{17}$ with Nucleophiles, L, in Chlorobenzene at 25.0 °C ([Complex] = 5–10 × 10^{-6} M)

L	N[a]	10^4[L], M	a, s^{-1}	k_2, M^{-1} s^{-1}	$\sigma(k_{obs})$,[b] %
$P(OC_6H_5)_3$	20[c]	101–446	(−1.59 ± 2.08) × 10^{-3}	1.60 ± 0.09	9.8
$P(O\text{-}i\text{-}Pr)_3$	20[c]	2.96–73.9	(−1.38 ± 0.47) × 10^{-2}	(1.63 ± 0.09) × 10^2	4.1
$P(n\text{-}Bu)_3$	7[c]	25.4	0	(9.21 ± 0.51) × 10^2 [d]	5.6
$P(p\text{-}MeOC_6H_4)_3$	1[e]	2.10	0	(9.86 ± 0.71) × 10^{-1} [d]	7.2
$P(p\text{-}MeC_6H_4)_3$	3[e]	7.56–37.8	0	0.31 ± 0.06[d]	[f]
$P(C_6H_5)_3$	3[e]	12.4–377	(5.77 ± 0.41) × 10^{-5}	(6.66 ± 0.13) × 10^{-2}	2.5
$P(p\text{-}FC_6H_4)_3$	4[e]	317–1590	(−8.91 ± 0.29) × 10^{-4}	(4.42 ± 0.07) × 10^{-2}	2.5
$P(p\text{-}CF_3C_6H_4)_3$	3[e]	843–2110	(−3.24 ± 0.11) × 10^{-4}	(5.73 ± 0.11) × 10^{-3}	2.0

[a] Number of individual determinations of k_{obs}; $k_{obs} = a + k_2$[L]. [b] Probable error of k_{obs}. [c] Studied by using stopped-flow techniques. [d] Calculated from $k_2 = k_{obs}$/[L] by assuming a = 0. [e] Studied by using UV–vis monitoring. [f] Data for this nucleophile were rather scattered with a mean deviation for k_2 of 24%.

to the very satisfactory precision of the rate constants.

Derivation of Electronic and Steric Profiles. The plot of log k_2 (25.0 °C) vs pK_a′ for reactions of $Ru_6C(CO)_{17}$ with 14 P-donor nucleophiles in heptane is presented in Figure 3. Two sets of ligands can be used to obtain electronic profiles. One is the exactly isosteric group of nucleophiles $P(p\text{-}XC_6H_4)_3$ (X = H, MeO, Me, F, Cl, and CF_3, θ = 145°), and the electronic profile is given by the least-squares line drawn through the data. The value of the electronic sensitivity, β, is found from the gradient to be 0.42 ± 0.04. Another set is the three small and nearly isosteric nucleophiles $P(OC_6H_5)_3$ (θ = 128°), $P(O\text{-}i\text{-}Pr)_3$ (θ = 130°), and $P(n\text{-}Bu)_3$ (θ = 132°). Small adjustments were made to the values of log k_2 to allow for the difference in the cone angles. These adjustments were made by using values of γ, the gradient of the steric profile found, as described below, by plotting log $k_2 - \beta(pK_a' + 4)$ against the cone angles. The value of β obtained from the least-squares plot was 0.38 ± 0.06, showing that the electronic sensitivity of the cluster is essentially independent of which set of isosteric or near-isosteric nucleophiles is used to define it. Data due to other nucleophiles deviate more or less from the two lines. It is obvious that steric effects are significant because reactions are much slower for bulky ligands (e.g. $P(C_6H_{11})_3$) and faster for smaller ligands (e.g. etpb) even though the former has a much greater pK_a′ value. The absence of any detectable dependence of β on the size of the nucleophiles used to obtain it means that the data for all 14 nucleophiles should give a good fit to eq 1 by using the multilinear regression program.

Table III. Activation Parameters for the Associative Reactions of $Ru_6C(CO)_{17}$ with the Isosteric P-Donor Nucleophiles, L (θ = 145°), and with $P(OC_6H_5)_3$ (θ = 128°)

L	pK_a′	N[a]	$\Delta H_2^{\ddagger}$, kcal mol^{-1}	$\Delta S_2^{\ddagger}$, cal K^{-1} mol^{-1}	$\sigma(k_{obs})$,[b] %
$P(p\text{-}CF_3C_6H_4)_3$	−1.39	9	12.8 ± 0.5	−28.7 ± 1.5	5.4
$P(p\text{-}ClC_6H_4)_3$	0.87	16	10.5 ± 0.3	−33.0 ± 1.0	3.9
$P(C_6H_5)_3$	3.28	20	7.52 ± 0.10	−38.5 ± 0.3	2.0
$P(p\text{-}MeC_6H_4)_3$	4.46	7	7.24 ± 0.41	−35.7 ± 1.4	6.1
$P(p\text{-}MeOC_6H_4)_3$	5.13	13	7.00 ± 0.24	−34.9 ± 0.8	4.8
$P(OC_6H_5)_3$	−2.79	9	13.0 ± 0.4	−10.4 ± 1.2	6.5

[a] N represents the number of individual determinations of k_{obs} values. [b] Probable error in k_{obs} estimated from the scatter of ln (k_2/T) values around the Eyring plot.

The value of θ_{th} that leads to a minimum RMSD is 119°, the RMSD depending on changing θ_{th} as follows, θ_{th} (RMSD): ≤101° (0.727), 116° (0.448), 118° (0.416), 119° (0.413), 120° (0.420), 122° (0.424). When θ_{th} = 119° is used the analysis provides values of α = 3.17 ± 0.26, β = 0.41 ± 0.04, and γ = −0.20 ± 0.01 deg^{-1}

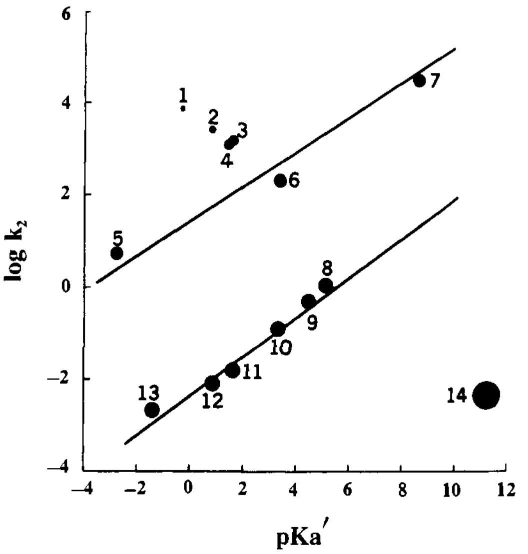

Figure 3. Electronic profiles for the reactions of $Ru_6C(CO)_{17}$ with L in heptane at 25.0 °C. The numbers correspond to those in Table I, and the sizes of the points are an indication of the relative sizes of the nucleophiles.

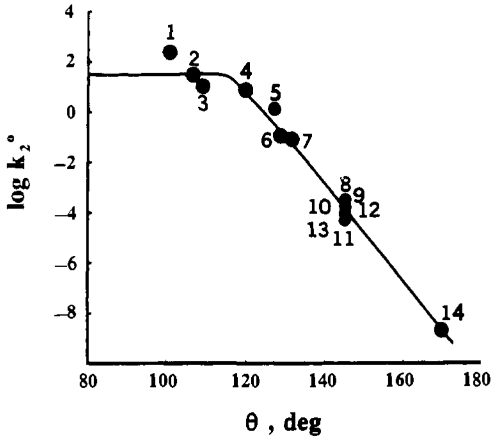

Figure 4. Steric profile for the reactions of $Ru_6C(CO)_{17}$ with L in heptane at 25.0 °C. The numbers correspond to those in Table I.

with RMSD = 0.41 and $R = 0.99$. These values can be used to draw the steric profile, i.e. the dependence of $\log k_2^\circ = \log k_2 - \beta(\mathrm{p}K_a' + 4)$ on θ, as shown in Figure 4. The RMSD deviation of 0.41 must be considered perfectly good in the light of the almost 7 orders of magnitude dependence of k_2 on $\mathrm{p}K_a'$ over the range $\mathrm{p}K_a' = -2.79$ to 11.26 (Figure 3) and the over 10 orders of magnitude dependence of k_2° on θ over the cone angle range 119–170° (Figure 4).[20,21]

The above analyses were also conducted by using $\delta(^{13}CO)$ (ppm)[22] and χ (cm^{-1})[23] values as measures of the donicity of the P-donor nucleophiles instead of $\mathrm{p}K_a'$ values. The fit to eq 1, in terms of RMSD values, changed in the order $\mathrm{p}K_a'$ (0.413) < $\delta(^{13}CO)$ (0.665) < χ (0.819), indicating that $\mathrm{p}K_a'$ values are indeed a better measure of the donicity of P-donor nucleophiles in the transition states for these reactions, i.e. it is the σ donicity that is important and inclusion of π acidity in the electronic parameters is not required.

The validity of the existence of the steric threshold is shown by the very high RMSD of 0.727 found when $\theta_{th} \leq 101°$, and it can also be demonstrated as follows. Equation 1 ($\lambda = 1$) was used to analyze all the data for nucleophiles with $\theta \geq 130°$ (viz. 6–14). The β and γ parameters obtained were within the uncertainty limits of those derived by using all the data, and the rate constants that would have been expected for the nucleophiles etpb, $P(OMe)_3$, $P(OEt)_3$, $PC_6H_5(OMe)_2$, and $P(OC_6H_5)_3$ were calculated. The values of $(\log k_2)_{calc} - (\log k_2)_{expt}$ were respectively 2.80, 2.50, 2.67, 0.42, and −0.87. It is clear that the rate constants for the nucleophiles $PC_6H_5(OMe)_2$ and $P(OC_6H_5)_3$ are correctly predicted, within the error limits, by the parameters based on nucleophiles with θ greater than any reasonable steric threshold. On the other hand, the calculated rate constants for the three smaller nucleophiles are well over 2 orders of magnitude higher than the experimental values so that the latter do genuinely lie below a steric threshold that is ≤120°.[24]

The Intimate Mechanism. The small positive values of $\Delta H_2^\ddagger$ and the large negative values of $\Delta S_2^\ddagger$ are in line with a straightforward associative reaction mechanism involving attack by the nucleophile at a metal atom in the cluster.[27] The changes in $\Delta H_2^\ddagger$ as the basicity of the nucleophile changes (Table III) are of interest. Thus, as the $\mathrm{p}K_a'$ value for the five isosteric nucleophiles increases from −1.39 ($P(p\text{-}CF_3C_6H_4)_3$) to 5.13 ($P(p\text{-}MeOC_6H_4)_3$), the activation enthalpy decreases from 12.8 to 7.00 kcal mol^{-1}, suggesting that the strength of the Ru···P bond in the transition state increases significantly with increasing basicity of the nucleophile. This is indicative of a transition state with a high degree of bond making, as indicated also by the high β value of 0.41. Because of the systematic changes in $\Delta H_2^\ddagger$, this value of β will decrease as the temperature increases. Thus at 50 °C the β value is only 0.39 ± 0.04. A similar small decrease in β with increasing temperature was found for reactions of $Ir_4(CO)_{12}$.[3]

The value of $\Delta S_2^\ddagger$ for the reaction with $P(OC_6H_5)_3$ is considerably less negative than the almost constant values for the $P(p\text{-}XC_6H_4)_3$ nucleophiles, but in the absence of activation parameters for a wider range of nucleophiles the significance of this is not yet clear. An interesting example of a full study of the

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(20) The goodness of fit is perhaps better indicated by RMSD/{$(\log k_2)_{max} - (\log k_2)_{min}$} which allows for the very large sensitivity of the log k_2 values to $\mathrm{p}K_a'$ and θ, uncertainties in which will have particularly large effects in such a case. This assessment of goodness of fit will be particularly important when comparing results for different systems (Table IV).

(21) The above analysis shows that reliable β values can be independently obtained by the construction of electronic profiles when kinetic data are not rich enough for a multilinear regression analysis. This is important in cases where kinetic data for reactions of a given complex with nucleophiles covering a wide range in size are not accessible but where it is less difficult to obtain kinetic data for several isosteric nucleophiles or a few small nucleophiles. The so obtained β values will still be useful in providing some insight into the significance of bond making in the transition state.

(22) Bodner, G. M.; May, M. P.; McKinney, L. E. *Inorg. Chem.* **1980**, *19*, 1951–1958.

(23) Bartik, T.; Himmler, T.; Schulte, H.-G.; Seevogel, K. *J. Organomet. Chem.* **1984**, *272*, 29–41.

(24) Another measure of the steric requirements of P-donor nucleophiles other than cone angles, namely Brown's F_R values,[25] was also used to correlate the kinetic data according to eq 1. However, the fits were generally very poor with RMSD > 1.22 and $R < 0.831$. The fits also became worse as $\mathrm{p}K_a'$ was replaced by $\delta(^{13}CO)$ (ppm) and χ (cm^{-1}) values. There are still steric thresholds but they are much less well defined than they are when Tolman's cone angle values are used. The question of the validity of the Tolman cone angles for the nucleophiles $P(OMe)_3$, $P(OEt)_3$, and, to a lesser extent, $P(n\text{-}Bu)_3$ has to be considered in the light of the larger values proposed[26] for these P-donors when acting as *ligands*. A reconsideration of the data analysis in ref 26, together with analysis of extensive kinetic data involving these ligands, and some molecular mechanics calculations, has led[6] to an upward adjustment of only 10° for $P(OMe)_3$ and $P(OEt)_3$ and a negligible adjustment for $P(n\text{-}Bu)_3$. Even if this adjustment is made, the existence of the steric threshold will still be quite strongly indicated by the data for L = etpb for which the cone angle is quite unambiguous. The upward adjustment, even of 10°, may not be necessary when these P donors are acting as *nucleophiles*. This is suggested by successful use[6] of the Tolman cone angle in analyzing data for associative reactions with eq 1 even when $\theta_{th} < 107°$, the cone angle for $P(OMe)_3$, and we continue to believe that they are empirically useful and meaningful in analyses such as these. It is important to note that none of these difficulties will affect the outcome of our discussion of the parameters for $Ru_6C(CO)_{17}$ in comparison with other related data. It should also be noted, parenthetically, that Giering et al.[5] have accepted an upward adjustment of 4° to $\theta(P(n\text{-}Bu)_3)$ but have continued to use the Tolman values for $P(OMe)_3$, $P(OEt)_3$, and PEt_3. We prefer to continue to use the Tolman cone angle for $P(n\text{-}Bu)_3$ as well, although the whole question of appropriateness of particular values of cone angles, especially with respect to any chemical inferences that they lead to, has to be considered carefully in each individual system.

(25) Personal communication from Professor T. L. Brown. See also: Caffery, M. L.; Brown, T. L. *Inorg. Chem.* **1991**, *30*, 3907–3914.

(26) Stahl, L.; Ernst, R. D. *J. Am. Chem. Soc.* **1987**, *109*, 5673–5680. Shriver, D. F.; Atkins, P. W.; Langford, C. H. *Inorganic Chemistry*; Freeman: New York, 1990; p 512.

(27) Howell, J. A. S.; Burkinshaw, P. M. *Chem. Rev.* **1983**, *83*, 557–599.

Table IV. Characteristic Kinetic Parameters of Some Carbonyl Complexes at 25.0 °C[a]

complex (solvent)	θ_{th}, deg	SR	β	γ, deg^{-1}	RMSD	RMSD[20]/Δ(log k_2)
$Mo(CO)_6$[b] (decalin)	124	ca. −8	0.11 ± 0.01	−0.035 ± 0.002	0.02	0.018
$Ru_3(CO)_{12}$[c] (decalin)	122	−3.4 ± 0.2	0.16 ± 0.03	−0.059 ± 0.011	0.21	0.11
$Ir_4(CO)_{12}$[d] (chlorobenzene)	≤101	≥−3.4 ± 0.3	0.31 ± 0.05	−0.091 ± 0.010	0.30	0.085
$Rh_4(CO)_{10}\{P(C_6H_{11})_3\}_2$[e] ($CH_2Cl_2$)	≥145	1.6 ± 0.01	0.05 ± 0.001	≤−0.041 ± 0.001	0.001	0.0004
$Ru_6C(CO)_{17}$ (heptane)	119	1.51 ± 0.26	0.41 ± 0.04	−0.20 ± 0.01	0.41	0.041
$Ru_6C(CO)_{17}$ (chlorobenzene)	≤130	≥−0.10 ± 0.19	0.29 ± 0.03	−0.19 ± 0.01	0.19	0.036

[a] Data analyses for complexes other than $Ru_6C(CO)_{17}$ are taken from ref 6. [b] Original data are taken from: Graham, J. R.; Angelici, R. J. *Inorg. Chem.* **1967**, *6*, 2082–2085. [c] Original data are taken from ref 1b. [d] Original data are taken from ref 3. [e] Original data are taken from: Brodie, N. M. J.; Poë, A. J. *J. Organomet. Chem.* **1990**, *383*, 531–542.

temperature dependence of associative rate constants is given by the reactions of (η^5-C_5H_4COOMe)Co(CO)$_2$, and in this case the steric profile is shown to originate in systematic changes in the values of $\Delta S_2^\ddagger$.[1e] This is not, however, the case for reactions of $Ir_4(CO)_{12}$.[3] More such studies are required.

As suggested almost concurrently by Giering[2] and Poë,[3] the steric profile for a given complex conveys important information about the flexibility of the complex in the transition states of associative reactions. The good fit of the data to eq 1 for this system and a large number of others[1e,5,6] shows that the onset of steric effects is quite sudden and characterizable by a fairly precise value of θ_{th}. This conclusion contrasts with that reached earlier by Poë et al.,[3] who believed that the onset of steric effects could be quite gradual, the more gradual onset being characteristic of a more flexible cluster. The sharp onset of steric effects implies that θ_{th} is a good measure of the steric congestion in the transition state. The fact that the steric threshold for $Ru_6C(CO)_{17}$ is quite high has important implications. It is, at first sight, difficult to believe that even those small nucleophiles with $\theta < \theta_{th}$ will experience no steric effect at all when approaching a cluster such as $Ru_6C(CO)_{17}$ with its closely packed array of ligands,[17] or alternatively, that the steric effect would be the same as θ changes from 101 to 119° and then become larger and variable when $\theta > 119°$. We believe that when $\theta < 119°$ the absence of any apparent steric effect might arise from a sudden and constant change in structure of the complex that may be triggered or induced by the approach of the nucleophile. This is equivalent to the formation of an isomeric form of the cluster in which a space has been created that is effectively measured by the value of θ_{th}. Nucleophiles with $\theta < \theta_{th}$ will therefore have no energetic difficulty in fitting into this space, but when $\theta > \theta_{th}$ repulsion effects will come into play and these will be defined by γ which will be larger or smaller according to the flexibility of the *isomeric form* of the cluster.

The value of log $k_2°$ below the steric threshold is a measure of the standard reactivity of the cluster toward a nucleophile small enough to experience no steric repulsions in the transition state, and weakly basic enough to contribute rather little to stabilizing the transition state through metal–nucleophile bond making. It will therefore approximate to the intrinsic reactivity of the cluster (i.e. the ease of spontaneous isomerization of the cluster, unassisted by a nucleophile) to a greater or lesser extent depending, respectively, on how low or high β is, i.e. on the extent of bond making.

Comparison with Other Carbonyl Complexes. Compared with the known values of $\Delta H_2^\ddagger$ and $\Delta S_2^\ddagger$ for lower nuclearity carbonyl clusters (LNCCs) in analogous reactions, those for $Ru_6C(CO)_{17}$ are generally lower and more negative, respectively. For instance, values of $\Delta H_2^\ddagger$ and $\Delta S_2^\ddagger$ for reactions of $P(C_6H_5)_3$ with $Ru_3(CO)_{12}$ in decalin have been reported[1b] to be 15.5 ± 0.1 kcal mol^{-1} and −24.4 ± 0.5 cal K^{-1} mol^{-1}, and for reactions of $P(C_6H_5)_3$ with $Ir_4(CO)_{12}$ in chlorobenzene[3] they are 20.5 ± 0.4 kcal mol^{-1} and −16 ± 1 cal K^{-1} mol^{-1}, respectively, in comparison with the values for reaction of $P(C_6H_5)_3$ in this study which are 7.52 ± 0.10 kcal mol^{-1} and −38.5 ± 0.3 cal K^{-1} mol^{-1}, respectively (Table III).

Trimetal carbonyl clusters have been observed to have lower values of $\Delta H_2^\ddagger$ and more negative values of $\Delta S_2^\ddagger$ than mononuclear binary carbonyls[27,28] although no values are available for binary dinuclear carbonyls.[29] This decrease in values of $\Delta H_2^\ddagger$ and increasingly negative values of $\Delta S_2^\ddagger$ corresponds to a general increase in the susceptibility to nucleophilic attack as the nuclearity of metal carbonyls becomes higher.[31]

The values of the other kinetic parameters derived by fitting data to eq 1 provide further confirmation of this conclusion. Thus, Table IV lists parameters so derived[6] for reactions of several binary metal carbonyls, as well as a substituted cluster where data for the binary cluster are not available. The mononuclear binary carbonyl $Mo(CO)_6$ has a very low standard reactivity, only a small amount of bond making (low β value), and a rather high flexibility of the transition state (small negative value of γ) when the steric threshold is exceeded. The binary cluster $Ru_3(CO)_{12}$ has a very much higher standard reactivity with slightly more bond making, a similar steric threshold, and a slightly lower flexibility. Data for $Rh_4(CO)_{12}$ are not available but the substituted cluster $Rh_4(CO)_{10}\{P(C_6H_{11})_3\}_2$ shows an exceedingly high standard reactivity (1.6 ± 0.01) coupled with a very low degree of bond making and a high lower limit for θ_{th} (>145°). This shows that the Rh_4 cluster is able to open up very easily, that the space thus created by the isomerization is exceptionally large, and that little assistance from bond making is required. Data for $Ir_4(CO)_{12}$ show a much higher need for bond making in order to open up the cluster, as expected from the stronger metal–metal bonds in a cluster of third-row transition metals.[32] This is accompanied by a much lower steric threshold, again as expected, and when the steric threshold is exceeded the cluster is very inflexible.

The data for $Ru_6C(CO)_{17}$ in heptane show that the standard reactivity of this cluster is greater by ca. 5 orders of magnitude than that of $Ru_3(CO)_{12}$. There is, however, still the need for an exceptionally high degree of bond making although it is still likely that the intrinsic reactivity of $Ru_6C(CO)_{17}$ is considerably greater than that of $Ru_3(CO)_{12}$. The steric threshold is about the same as for $Ru_3(CO)_{12}$, in spite of the much greater degree of bond making, and this suggests that the isomeric form of the Ru_6C cluster in the transition state is considerably more open than the Ru_3 cluster when nucleophiles are relatively small. However, further opening up, needed when larger nucleophiles above the steric threshold are involved, is exceptionally difficult as shown by the very negative value of γ.

These parameters clearly establish the fact that, while LNCCs undergo associative reactions very much more readily than binary mononuclear carbonyls, HNCCs undergo such reactions even more

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

(29) Values of $\Delta H_2^\ddagger$ and $\Delta S_2^\ddagger$ are 15.5 ± 0.2 kcal mol^{-1} and −16.6 ± 0.6 cal K^{-1} mol^{-1} for reaction of the Fe → Co bonded (CO)$_4$Fe(μ-AsMe$_2$)Co(CO)$_3$ compound,[30] but it is difficult to estimate the effect of the presence of the As atom in the cluster.

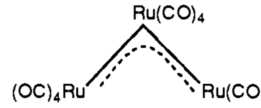
(30) Jackson, R. A.; Kanluen, R.; Poë, A. J. *Inorg. Chem.* **1981**, *20*, 1130–1133.

(31) A. J. Poë in ref 11c, Chapter 4.

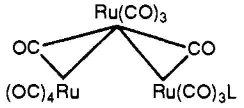
(32) Connor, J. A. *Top. Curr. Chem.* **1977**, *71*, 71–110.

readily. The associative reactivity of tri- and tetranuclear clusters has been ascribed[1b,3,28] to a readiness of the cluster to create a vacant coordination site on one metal atom by breaking one metal–metal bond. The energy required for this was thought to be provided by bond making by the nucleophile at the vacant coordination site. More generally the associative reactivity could have been ascribed to a gradual readjustment and expansion of the polytopal arrangement of the ligands as the nucleophile approaches, a readjustment that would have been accompanied by a general expansion of the metal cluster so as to maintain metal–ligand contact. Again the energy required for this would have been provided, in part, by metal–nucleophile bond making, and reactions would be more rapid the weaker the metal–metal bonding in the cluster. It might also have accounted for the greater reactivity of HNCCs where the extent of expansion and rearrangement of the ligand polytope would be relatively less pronounced. However, this approach would imply a rather gradual onset of steric effects and the concept of an intrinsic reactivity would not be clearly definable, and it therefore does not fit with the sharp onset of steric effects which is now well-established and the precise definition of intrinsic reactivity when $\beta = 0$ (see below).

An alternative model takes account of the fact that the bonding in clusters is best described by a delocalized bonding scheme, PSEPT (polyhedral skeletal electron pair theory).[33] Cluster opening by breaking one metal–metal bond is usually accompanied, in this scheme, by a need for an additional pair of electrons for cluster bonding. However, this need is not absolute since an electron-deficient cluster can be stabilized by formation of multiple metal–metal bonds. A classical example of this is given by the electron-deficient, 46-electron cluster $(\mu\text{-H})_2Os_3(CO)_{10}$ in which two Os atoms maintain their 18-electron count by formation of an Os=Os double bond between the Os atoms bridged by the hydride ligands.[11a] In this case the double bonding is localized by the presence of the bridging hydrides, but in a binary cluster such as $Ru_3(CO)_{12}$ this type of additional bonding could be delocalized over the three metal atoms. This can be illustrated as in I in which the delocalized bonding is a 3-center, 4-electron π system. Conversion of this, upon nucleophilic attack, to II would then remove the need for any Ru–Ru π bonding by forming an intermediate in which all the metals have 18 electrons. This would correspond to a system where β is essentially zero and the cluster opening process occurs spontaneously. The lifetime of the isomeric opened cluster is so short that the presence of L in the outer sphere of the cluster is still required for L to be able to compete with reversal of cluster opening. The reaction is therefore still first order in [L] in the same way as I_d anation reactions of classical Werner complexes are,[34] even though only bond breaking and no bond making occurs in the transition state. In cases where bond making in the transition state is appreciable, the transition state would have to be regarded as having a structure intermediate between I and II. This model also accounts for the even greater intrinsic reactivity of $Ru_6C(CO)_{17}$ because the double bonding can be delocalized over a larger number of metal atoms and will therefore be even more effective than in an LNCC.



I



II

Finally the question of the role of the C atom in the cluster has to be addressed. Although it is believed that it helps to maintain the integrity of the cluster,[35] $Ru_6C(CO)_{17}$ does react with CO to form $Ru_5C(CO)_{15}$ (80 atm, 80 °C).[15] Reactions with highly nucleophilic ligands like $P(n\text{-Bu})_3$ fail, however, to induce F_N2 reactions as they do in $Os_3(CO)_{12}$[28] which contains probably stronger metal–metal bonds.[32] The stereochemical versatility of the C atom in clusters[11d] suggests that it would have little effect on the cluster-opening process occurring during nucleophilic attack, or on the flexibility of the transition state when θ_{th} is exceeded. One is left with the impression, therefore, that the role of the C atom is little more than providing the electrons necessary to fill all the cluster-bonding orbitals in the $Ru_6(CO)_{17}$ moiety and in doing so it maintains the overall integrity of the cluster. It would obviously be of interest to extend these studies to HNCCs without C atoms such as $Rh_6(CO)_{16}$ and $Os_6(CO)_{18}$.

Solvent Effect. Reactions of $Ru_6C(CO)_{17}$ were also studied in chlorobenzene, largely with a view to investigating whether the greater solubility of the nucleophiles $P(p\text{-}XC_6H_4)_3$ in chlorobenzene had any effect on the rates and on the β values obtained when using these nucleophiles as compared with the very soluble smaller nucleophiles $P(OC_6H_5)_3$, $P(O\text{-}i\text{-}Pr)_3$, and $P(n\text{-Bu})_3$, with cone angles of ca. 130°.

After allowance for the steric effects of the slightly different cone angles for the smaller, nearly isosteric nucleophiles a β value of 0.24 ± 0.05 was obtained, a value essentially indistinguishable from that found from the exactly isosteric $P(p\text{-}XC_6H_4)_3$ nucleophiles ($\beta = 0.31 \pm 0.05$). Combining all these data and fitting them to eq 1 gave the parameters shown in Table IV. Because no small nucleophiles were used, only limiting values were obtained for θ_{th} and the standard reactivity, but the value of β is clearly less than that found in heptane, the value of γ being essentially unchanged. The lower value for β obtained for the 145° nucleophiles results from slightly slower reactions in chlorobenzene for $P(p\text{-}MeOC_6H_4)_3$ and $P(p\text{-}MeC_6H_4)_3$ whereas reactions of the less basic nucleophiles $P(p\text{-}XC_6H_4)_3$ ($X = CF_3$, Cl, and F) are slightly faster. Although this might be due to some differential solubility effects, the value of β from the much more soluble 130° ligands is still essentially the same, even though these nucleophiles too react slightly more slowly in chlorobenzene. The reasons for these somewhat different reactivities are not clear because the reactivities apply to a wide range of types of nucleophile, but the results do emphasize that the question of relatively significant solvent effects on β does have to be addressed when making comparisons between different systems.

Conclusions

(i) The kinetics of the substitution reactions of the HNCC-$Ru_6C(CO)_{17}$ show that it undergoes reactions solely by an associative path.

(ii) The data give an excellent fit to eq 1 which is generally applicable to all associative reactions of metal carbonyls. The kinetic parameters obtained from this analysis emphasize the exceptional intrinsic susceptibility of this HNCC toward nucleophilic attack coupled with an exceptionally high degree of metal–nucleophile bond making in the transition states.

(iii) The high intrinsic reactivity suggests that cluster opening to quite a high degree is a facile process. The reasons for this are probably rooted in the pronounced ability of an opened cluster with one less metal–metal σ bond to form metal–metal multiple bonds delocalized over all the metal atoms.

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Supplementary Material Available: Tables of values of k_{obs} and FTIR data (7 pages). Ordering information is given on any current masthead page.

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(33) Owen, S. M. *Polyhedron* **1988**, *7*, 253–283 and references therein.

(34) Langford, C. H.; Gray, H. B. *Ligand Substitution Process*; Benjamin: New York, 1966; Chapter 3.

(35) Johnson, B. F. G.; Lewis, J.; Nelson, W. J. H.; Nicholls, J. N.; Vargas, M. D. *J. Organomet. Chem.* **1983**, *249*, 255–272.