

Reaction kinetics of some substituted tetrahodium carbonyl clusters

Nancy M.J. Brodie and Anthony J. Poë *

Lash Miller Chemical Laboratories, 80 St. George St., Toronto, Ontario M5S 1A1 (Canada)

(Received April 25th, 1989)

Abstract

Quantitative kinetic data have been obtained for reactions, in 1,2-dichloroethane at 25° C, of the known cluster $\text{Rh}_4(\text{CO})_9(\text{etpb})_3$ ($\text{etpb} = \text{P}(\text{OCH}_2)_3\text{CEt}$), and of the new cluster $\text{Rh}_4(\text{CO})_{10}(\text{PCy}_3)_2$ ($\text{Cy} = \text{C}_6\text{H}_{11}$), with some P-donor nucleophiles and, for the latter cluster, with AsPh_3 . Both clusters obey the two term rate equation: $k_{\text{obs}} = k_1 + k_2[\text{L}]$ although the value of k_1 for $\text{Rh}_4(\text{CO})_{10}(\text{PCy}_3)_2$ is only observed for reactions with AsPh_3 and is relatively very small and quite approximate. The values of k_2 can be used to obtain electronic and steric profiles from which it can be concluded that bond-making is very low for reactions of the intrinsically much more reactive $\text{Rh}_4(\text{CO})_{10}(\text{PCy}_3)_2$, but significant for reactions of the intrinsically less reactive $\text{Rh}_4(\text{CO})_9(\text{etpb})_3$. Steric effects due to different nucleophile cone angles are consequently much less pronounced for $\text{Rh}_4(\text{CO})_{10}(\text{PCy}_3)_2$ than for $\text{Rh}_4(\text{CO})_9(\text{etpb})_3$. Comparison with data reported elsewhere for $\text{Rh}_4(\text{CO})_9\{\text{HC}(\text{PPh}_2)_3\}$ shows that the intrinsic susceptibility of these clusters towards nucleophilic attack increases along the series $\text{Rh}_4(\text{CO})_9\{\text{HC}(\text{PPh}_2)_3\} < \text{Rh}_4(\text{CO})_9(\text{etpb})_3 < \text{Rh}_4(\text{CO})_{10}(\text{PCy}_3)_2$ whereas the degree of bond-making, and the consequent steric effects, decrease along this series. $^{31}\text{P}(\text{H})$ NMR studies of $\text{Rh}_4(\text{CO})_9(\text{etpb})_3$ suggest that it exists as two fluxional isomers but this does not affect the discussion of the kinetics. The associative reactions of $\text{Rh}_4(\text{CO})_{10}(\text{PCy}_3)_2$ lead mainly to fragmentation whereas those of $\text{Rh}_4(\text{CO})_9(\text{etpb})_3$ lead mainly to substitution.

Although the kinetic behavior of the $\text{M}_3(\text{CO})_{12}$ triad of clusters ($\text{M} = \text{Fe}, \text{Ru}, \text{Os}$) has received quite thorough study [1] the same cannot be said of the series $\text{M}_4(\text{CO})_{12}$ ($\text{M} = \text{Co}, \text{Rh}, \text{Ir}$) for which, until very recently, quantitative data were available only for CO exchange and fragmentation reactions of $\text{Co}_4(\text{CO})_{12}$ [2,3] and substitution reactions of $\text{Ir}_4(\text{CO})_{12}$ [4]. Substitution reactions of $\text{Co}_4(\text{CO})_{12}$ are too fast to measure by conventional techniques [2], and fragmentation to $\text{Co}_2(\text{CO})_8$, even in the presence of high concentrations of CO, is quite slow [3]. In contrast, the fragmentation reactions of $\text{Rh}_4(\text{CO})_{12}$ with CO are considerably faster than those of

$\text{Co}_4(\text{CO})_{12}$ and occur by a process first order in $[\text{CO}]$ at convenient rates between -30 and $+30^\circ\text{C}$ [5]. Qualitative results suggested that substitution reactions of $\text{Rh}_4(\text{CO})_{12}$ would also be too rapid for conventional study but that some substituted clusters would react at convenient rates [6–8] and that a study of their kinetics would be rewarding. We report below some quantitative studies on one tri- and one di-substituted Rh_4 cluster. During the course of these investigations a study of the kinetics of reactions of PPh_3 with $\text{Rh}_4(\text{CO})_{12}$ and $\text{Rh}_4(\text{CO})_{11}(\text{PPh}_3)$ at 28°C was reported [9], and results of a detailed kinetics study of the clusters $\text{M}_4(\text{CO})_9\{\text{HC}(\text{PPh}_2)_3\}$ ($\text{M} = \text{Co}, \text{Rh}, \text{Ir}$) were communicated to us [10].

Experimental

Materials

The cluster $\text{Rh}_4(\text{CO})_{12}$ (Strem Chemicals, Inc.) was used as received, and was stored under nitrogen in a glove box. Tri-*n*-butylphosphine (Aldrich) was distilled over sodium and stored under argon in stoppered Schlenk tubes. Triphenylphosphine, tri(*p*-tolyl)phosphine, and triphenylarsine (Aldrich) were recrystallized from hexane and etpb ($\text{P}(\text{OCH}_2)_3\text{CEt}$) was purified by sublimation. All other P-donor ligands were provided in pure form by Professor R.J. Morris. Solvents were dried over activated molecular sieves, deoxygenated by several freeze-pump-thaw cycles, and stored under argon.

Instruments

UV-vis spectra were recorded with Varian Cary 20 or 210 spectrophotometers, and IR spectra with Nicolet 5DX or 10DX Fourier Transform spectrophotometers. ^{31}P NMR spectra were recorded with a Varian XL-400 spectrometer, the chemical shifts being referred to $\text{P}(\text{OMe})_3$ (external insert) and decoupled from ^1H .

Carbonyl clusters

All manipulations with $\text{Rh}_4(\text{CO})_{12}$ were carried out in an inert atmosphere glove box. The cluster was weighed into a round-bottomed flask which was then stoppered with an air-tight twist top, removed from the glove box, and attached to a vacuum line.

The known complex $\text{Rh}_4(\text{CO})_9(\text{etpb})_3$ was synthesized using Haszeldine's method [7]. The initial product, dissolved in dichloroethane, was purified by elution down a 40–140 mesh silica gel column with dichloromethane. An unidentified orange compound eluted first followed by $\text{Rh}_4(\text{CO})_9(\text{etpb})_3$ and, subsequently on some occasions, some $\text{Rh}_4(\text{CO})_8(\text{etpb})_4$. $\text{Rh}_4(\text{CO})_9(\text{etpb})_3$ was obtained as an orange solid in 75% yield, by vacuum evaporation of the solvent, and characterized by its IR spectrum (Table 1) and its FAB mass spectrum (parent ion m/e 1150). Apart from a band missing at 2085 cm^{-1} , our IR spectrum (Table 1) is in good agreement with that reported by Haszeldine et al. [7].

The known complex $\text{Rh}_4(\text{CO})_8(\text{etpb})_4$ [7] was prepared in the same way as $\text{Rh}_4(\text{CO})_9(\text{etpb})_3$ but with a 4/1 mol ratio of etpb/ $\text{Rh}_4(\text{CO})_{12}$. Elution down a 60–100 mesh florisisil column with dichloromethane, and evaporation of the solvent, led to an orange solid that was characterized as $\text{Rh}_4(\text{CO})_8(\text{etpb})_4$ by its IR spectrum (Table 1). The spectrum was in excellent agreement with that reported for dichloromethane solution [7].

Table 1

Spectroscopic data for some substituted Rh₄ carbonyl clusters in 1,2-dichloroethane

Cluster	$\nu(\text{CO})$ (cm ⁻¹) ^a	λ_{max} (nm)
Rh ₄ (CO) ₉ (etpb) ₃	2059(42), 2033(88), 2015(100), 1842(68)	310 ^b 344 ^b 470sh
Rh ₄ (CO) ₈ (etpb) ₄	2046sh, 2016sh, 2002(100), 1827(78)	316 358 480sh
Rh ₄ (CO) ₁₀ (PCy ₃) ₂	2067(47), 2048sh(90), 2041(100), 2013(42), 1815br(12), 1761br(23)	364 440sh 540
Rh ₄ (CO) ₁₀ (PPh ₃) ₂	2068(80), 2042(100), 2014(89), 1845(47) 1826(38)	366

^a Numbers in parentheses represent absorbances relative to that (100) of the most intense band. ^b ϵ , 1.8×10^4 l mol⁻¹ cm⁻¹.

The new complex Rh₄(CO)₁₀(PCy₃)₂ (PCy₃ = P(C₆H₁₁)₃) was prepared by dissolving Rh₄(CO)₁₂ (115 mg, 0.152 mmol) in a mixture of deoxygenated hexane (10 ml) and THF (10 ml). The PCy₃ (130 mg, 0.464 mmol), in a mixture of deoxygenated hexane (12 ml) and THF (8 ml), was added under argon to the Rh₄(CO)₁₂ solution slowly and with stirring. The cluster solution immediately turned a dark brick-red and became darker as more PCy₃ was added until finally the color was purple-black. After 15 h of stirring a purple solid had separated from a brown supernatant solution. The solid was separated by filtration and dried and stored under argon in the dark because of its high sensitivity towards air and light. This sensitivity made it impossible to purify further, and difficult to characterize. FAB mass spectrometry proved not to be successful as the cluster decomposed and no Rh₄ fragments were observed. The cluster was ultimately characterized by neutron activation analysis for Rh and its purity shown by ³¹P NMR. Neutron irradiation under identical conditions of a number of weighed samples in the University of Toronto's Slowpoke Reactor produced ¹⁰⁴Rh which is characterizable and quantifiable by its γ -ray emission at 552 keV and half life of 44 s. The intensities of these emissions were compared with those from similarly sized samples of Rh₄(CO)₉(etpb)₃, which had been characterized by FAB mass spectroscopy, and Rh₄(CO)₈(etpb)₄ (see above). The average % Rh obtained using these two references was $34.0 \pm 0.4\%$ as compared to values of 41.0, 32.8, and 27.3% expected for the clusters Rh₄(CO)₁₁(PCy₃), Rh₄(CO)₁₀(PCy₃)₂, and Rh₄(CO)₉(PCy₃)₃, respectively. The experimental result is very much closer, therefore, to that for Rh₄(CO)₁₀(PCy₃)₂ * than to what would be expected from the other two clusters. Although the slightly high value could be interpreted as indicating the presence of ca. 15% Rh₄(CO)₁₁(PCy₃) as an impurity, the ³¹P spectrum in CD₂Cl₂ at room temperature showed a sharp doublet (due to ¹⁰³Rh-³¹P coupling) at -95.7 and -94.4 ppm ($J(\text{Rh-P})$ 100 Hz). No other resonances were observed although those for Rh₄(CO)₁₁(PCy₃) would have been expected to be close to but quite distinct from those for Rh₄(CO)₁₀(PCy₃)₂ [6]. The kinetic data (see below) showed no signs of the presence of any impurities and we can therefore conclude that the cluster was indeed pure Rh₄(CO)₁₀(PCy₃)₂.

* This cluster was tentatively assigned as Rh₄(CO)₉(PCy₃)₃ on the basis only of its IR spectrum [11].

The known complex $\text{Rh}_4(\text{CO})_{10}(\text{PPh}_3)_2$ was prepared by Whyman's method [8] and characterized by its IR spectrum (Table 1). This was in excellent agreement with that measured by Whyman [8].

Results

The course of the reactions

Reactions of $\text{Rh}_4(\text{CO})_9(\text{etpb})_3$ in dichloroethane with all the P-donor ligands used led initially to the clusters $\text{Rh}_4(\text{CO})_8(\text{etpb})_3\text{L}$ as shown by their IR spectra which were very similar to those of other tetrasubstituted Rh_4 clusters [7,8]. Thus, strong bands at ca. 2000 and 1820 cm^{-1} were observed, usually together with one or more higher energy shoulders. These reactions were slow enough to be monitored continuously at room temperature in an IR cell and, except for reactions with PCy_3 and PCy_2Ph , good isosbestic points were evident over the whole course of the reactions (e.g. at 2005 and 1818 cm^{-1} for reaction with $\text{P}(p\text{-tolyl})_3$). Reactions with PCy_3 and PCy_2Ph showed similar behavior at low concentrations (0.001 M) but at higher concentrations the isosbestic points disappeared after 75–80% of the reaction, subsequent slower formation of dinuclear products being indicated [7,8].

The reactions were also accompanied by clear changes in the UV-vis spectra. These involved rather small blue or red shifts in the absorbance bands, depending on the nucleophile. In one case ($\text{L} = \text{P}(\text{CH}_2\text{Ph})_3$) an isosbestic point was observed at 365 nm but reactions with other nucleophiles were accompanied either by a decrease or increase of absorbance over the range of wavelengths monitored.

Reactions of $\text{Rh}_4(\text{CO})_{10}(\text{PCy}_3)_2$ with 0.01 M PCy , PPh_3 , $\text{P}(\text{OEt})_3$, and $\text{P}(\text{OPh})_3$ in dichloroethane all led immediately to solutions with IR spectra similar to those of $\text{Rh}_2(\text{CO})_2(\mu\text{-CO})_2(\text{PPh}_3)_4$ [7,8]. The initial products of reactions with PCy_3 and PPh_3 reacted further to give final products with single IR bands at 1941 and 1968 cm^{-1} , respectively. All these reactions were accompanied by complete disappearance of the band characteristic of $\text{Rh}_4(\text{CO})_{10}(\text{PCy}_3)_2$ at 540 nm. The kinetics of reactions of this cluster could therefore be followed easily by UV-vis monitoring, using stopped-flow techniques if necessary. Reaction with AsPh_3 was slow enough for IR monitoring of solutions reacting in situ in an IR cell at ambient temperatures. Slight shifts in the bands to lower frequencies occurred that were consistent with simple substitution and the appearance of isosbestic points showed the reaction to be quite clean.

Reactions of $\text{Rh}_4(\text{CO})_{10}(\text{PPh}_3)_2$ in dichloroethane with PPh_3 led to different products depending on $[\text{PPh}_3]$. When $[\text{PPh}_3] = 1 \text{ mM}$ the IR spectra [8] showed almost immediate formation of $\text{Rh}_4(\text{CO})_9(\text{PPh}_3)_3$, followed by further slow reaction to $\text{Rh}_4(\text{CO})_8(\text{PPh}_3)_4$. Reaction with 10 mM PPh_3 led immediately to solutions with IR spectra characteristic of $\text{Rh}_2(\text{CO})_2(\mu\text{-CO})_2(\text{PPh}_3)_4$ [7,8] followed by a slower reaction to form the yellow product ($\nu(\text{CO})$ 1968 cm^{-1}) reported by Haszeldine et al. [7]. Reaction with 10 mM etpb led immediately to product spectra characteristic of a tetrasubstituted Rh_4 cluster, whereas reaction with 10 mM PCy_3 led directly to an uncharacterized product showing a single IR band at 1943 cm^{-1} . All these reactions of $\text{Rh}_4(\text{CO})_{10}(\text{PPh}_3)_2$ were too fast to monitor kinetically by IR spectroscopy. Monitoring by UV-vis spectroscopy was unlikely to be successful because of the occurrence of successive reactions and the consequent difficulty of

Table 2

³¹P{¹H} NMR data ^a for some Rh₄(CO)₉L₃ clusters

L	δ(P _{ax})	δ(P _{rad})	¹ J(Rh–P _{ax})	¹ J(Rh _{ap} –P _{rad})	² J(Rh _{bas} –P _{rad})	² J(Rh _{ap} –P _{rad})	³ J(P _{rad} –P _{rad})
etpb ^b	100.9	116	–208.4	–250.5	+13.6	0	132.3
etpb ^{b,c}				–260.9	+14.6	0	136.5
P(OPh) ₃ ^d	102.8	118	–215	–263	+18	7	167
etpb ^e	100.6		–216.5				
{HC(PPh ₂) ₃ } _{1/3} ^f	16.2		ca. –133				

^a Chemical shifts in CD₂Cl₂ (ppm downfield of 85% H₃PO₄; Values for L = etpb were measured relative to P(OMe)₃ and corrected for a downfield shift of 141 ppm relative to H₃PO₄). Coupling constants in Hz (following convention for signs as given in ref. 6). ^b Bis-radial, mono-axial isomer (–39°C). ^c Calculated values. ^d Ref. (–52°C). ^e Minor isomer (–39°C). ^f Necessarily tris-axial isomer (ref. 12).

measuring values of A_{∞} for the initial steps. As a result no kinetic studies were undertaken.

The ³¹P{¹H} NMR spectrum of Rh₄(CO)₉(etpb)₃

The room-temperature spectrum in CD₂Cl₂ shows two broad doublets centered at ca. 26 and 40 ppm upfield of P(OMe)₃. On cooling to –39°C these are resolved into a spectrum that is very similar (Table 2) to that of Rh₄(CO)₉{P(OPh)₃}₃ at –52°C [6]. This has two ligands in radial positions and attached to two different Rh atoms in the CO-bridged basal plane of the cluster, and a third attached in an axial position to the other Rh atom in the basal plane. The bands in the downfield region can be simulated according to an AA'XX' model (Table 2) and confirm that two of the etpb ligands are in radial positions [6]. The upfield axial bands show up as two doublets with very similar chemical shifts and with ¹J(Rh–P_{ax}) coupling constants of 208.4 and 216.5 Hz, the former doublet's being slightly downfield of the latter and having about twice the intensity. One of these doublets can be assigned to the bis-radial, mono-axial isomer discussed above. The other doublet could be assigned to the tris-axial isomer by analogy with the doublet observed for Rh₄(CO)₉{HC(PPh₂)₃} [12] or, possibly, to the mono-radial, bis-axial isomer in view of some additional weak bands observed in the radial part of the spectrum. The more intense doublet with the numerically slightly smaller coupling constant and greater intensity seems assignable to the bis-radial, mono-axial isomer on the grounds that all the coupling constants are then numerically smaller than those for the same isomer of Rh₄(CO)₉{P(OPh)₃}₃. It seems highly unlikely that the extra bands are due to an impurity since the cluster was purified by column chromatography and gave good analyses.

The kinetics of the reactions

The kinetics of all the reactions of Rh₄(CO)₉(etpb)₃ could conveniently be monitored with the Cary 210 spectrophotometer in the time drive mode or over the wave length range 340–400 nm. Reaction solutions were made up as follows. Stock solutions in dichloroethane of complex and nucleophile were deoxygenated and stored in septum-sealed flasks. 2.0–2.7 ml of complex were introduced, by syringe, through a septum cap into the UV-vis cell which was placed in the thermostated (25.0 ± 0.1°C) cell compartment of the spectrophotometer and left to attain thermal

Table 3

First and second order rate constants^a for reactions of Rh₄(CO)₉(etpb)₃ with nucleophiles, L, in 1,2-dichloroethane at 25.0 °C

L (pK _a , θ°)	λ (nm) ^b	10 ⁴ [L] (M)	N ^c	10 ⁵ k ₁ (s ⁻¹)	10 ² k ₂ (M ⁻¹ s ⁻¹)
P(OPh ₃) (-2, 128)	350	13–76	6	299 ± 27	80 ± 9
etpb(1.74, 101)	380	9–55	4	577 ± 100	405 ± 62
PPh ₃ (2.73, 145)	400	10–150	8	276 ± 47	94 ± 15
P(<i>p</i> -tolyl) ₃ (3.84, 145)	400	17–71	5	367 ± 22	131 ± 8
P(<i>p</i> -MeOC ₆ H ₄) ₃ (4.59, 145)	400	10–60	6	241 ± 48	244 ± 21
P(CH ₂ Ph) ₃ (6.0, 165)	380	7–62	5	209 ± 11	29 ± 5
PCy ₂ Ph (7.38, 161)	340	12–57	4	284 ± 12	65 ± 5
PCy ₃ (9.7, 170)	354	9–32	4	214 ± 14	78 ± 8

^a Uncertainties are based on a constant value of $\sigma(k_{\text{obs}}) = \pm 8.2\%$ obtained by the method of pooled variances. Initial concentration of complex = ca. $8 \times 10^{-5} M$. ^b Wavelength at which reactions were monitored. ^c Number of individual determinations of k_{obs} .

equilibrium. 1.0–0.3 ml of prethermostated solutions of nucleophile were then added in a similar way and the solutions mixed by vigorous shaking. Monitoring wavelengths were chosen so that increases or decreases of absorbance of at least 0.1 absorbance units were obtained for solutions with $[\text{Rh}_4] = \text{ca. } 8 \times 10^{-5} M$. Stable values of A_∞ were observed and rate constants were obtained by plotting $\ln(A_t - A_\infty)$ or $\ln(A_\infty - A_t)$ against the time, t . Rate constants were dependent on [L] and were all in accord with the two term rate equation 1. Values of k_1 and k_2 are shown in Table 3 and were obtained by a linear least squares analysis in which all values of k_{obs} were weighted according to the assumption of a constant percentage probable error in their measurement.

$$k_{\text{obs}} = k_1 + k_2[\text{L}] \quad (1)$$

The kinetics of the reactions of Rh₄(CO)₁₀(PCy₃)₂ with PCy₃ and P(OEt)₃ were monitored at 540 nm by stopped-flow techniques. Reactions with PPh₃ and P(OPh)₃ at lower concentrations were slow enough to be followed with the Cary 210 spectrophotometer set on the time-drive mode. In all cases UV-vis spectra were measured at the conclusion of the reactions over the range 300–600 nm. Reactions

Table 4

Second order rate constants^a for reactions of Rh₄(CO)₁₀(PCy₃)₂ in 1,2-dichloroethane with nucleophiles, L, at 25.0 °C

	L				
	P(OPh) ₃	PPh ₃	P(OEt) ₃	PCy ₃	AsPh ₃
N ^b	4	3	3	3	4
10 ⁴ [L] (M)	6–30	117–583	7–24	93–365	50–160
10k ₂ (M ⁻¹ s ⁻¹) ^c	455 ± 33	576 ± 46	760 ± 64	136 ± 12	2.9 ± 0.4

^a Uncertainties for P-donor nucleophiles correspond to a probable error of ±15% for each measurement of k_{obs} . Initial concentration of cluster = ca. $6 \times 10^{-4} M$. ^b Number of individual measurements of k_{obs} . ^c $k_2 = k_{\text{obs}}/[\text{L}]$ for P-donor nucleophiles. k_2 for L = AsPh₃ was obtained from eq. 1 ($10^4 k_1 = 4.3 \pm 2.7 \text{ s}^{-1}$, and the probable error for each measurement of k_{obs} was ±10%. Reactions were monitored continuously throughout reaction in an IR cell so the temperature of 25 °C is only approximate).

with AsPh_3 were slow enough to be monitored by IR measurements. Solutions were always made up in red light with particular care being taken to exclude oxygen at all stages of the procedure. Even so some runs showed erratic kinetic behavior and the data from these had to be discarded. The first order rate constants, obtained from plots of $\ln(A_t - A_\infty)$ vs. time, were clearly dependent on the concentration, $[\text{L}]$, of the nucleophiles. Reactions with P(OPh)_3 showed no evidence for any rate term independent of $[\text{P(OPh)}_3]$. Even reaction with AsPh_3 showed evidence for only a very small $[\text{AsPh}_3]$ -independent path with $k_1 = \text{ca. } 4 \times 10^{-4} \text{ s}^{-1}$, the majority of the reaction's proceeding via the $k_2[\text{L}]$ path. Values of k_2 for all the P-donor nucleophiles could therefore be obtained from $k_{\text{obs}}/[\text{L}]$ and the data are summarized in Table 4.

Discussion

The kinetics of the reactions

Of the two clusters studied, the known [7] cluster $\text{Rh}_4(\text{CO})_9(\text{etpb})_3$ was quite stable and well characterized, and reactions with a wide variety of nucleophiles led to quite precise values for the rate constants k_1 and k_2 . Although its NMR behavior suggests that it exists as a labile mixture of two isomers these do not seem to be of very different stability. The analysis of the kinetic data that follows will not be affected in any way by this, the rate constants being the weighted average of those for the two isomers individually. The reactions of the much less stable $\text{Rh}_4(\text{CO})_{10}(\text{PCy}_3)_2$ were less extensively studied but led to reasonably precise values of k_2 for a few nucleophiles. Although the characterization of this cluster was difficult its ^{31}P NMR spectrum showed that it was a pure compound. The Rh analysis was much closer to that for $\text{Rh}_4(\text{CO})_{10}(\text{PCy}_3)_2$ than to those for other substituted Rh_4 clusters and its IR spectrum was characteristic of a substituted Rh_4 cluster and not of a substituted Rh_2 compound [7,8]. The reaction with AsPh_3 showed good isosbestic points in the IR spectrum and none of the kinetics of reactions with the P-donor ligands led to curved rate plots of the sort expected if reactions of mixtures were occurring.

The values of k_1 for reactions of $\text{Ru}_4(\text{CO})_9(\text{etpb})_3$ were in good agreement for most of the nucleophiles used, with the exception of those for reactions with etpb and $\text{P}(p\text{-tolyl})_3$ which were significantly higher. However, these involved reactions either with a large k_2 value or with values of $[\text{L}]$ which did not extend to such low concentrations, and we do not believe that these high values of k_1 have any mechanistic significance. The average of the other values, $(254 \pm 15) \times 10^{-5} \text{ s}^{-1}$ at 25°C can be compared (Table 5) with values for some analogous substituted Rh_4 and Ru_3 clusters that undergo substitution at the one unsubstituted $\text{M}(\text{CO})_n$ moiety. These show that the Rh_4 clusters are appreciably more labile towards what is presumably [10] a CO-dissociative process and that, in the case of the clusters with bridging P-donor ligands at least, this is due to more favourable ΔH_1^\ddagger and $T\Delta S_1^\ddagger$ terms. The greater lability of these substituted Rh_4 clusters is, however, far less pronounced than that shown by the unsubstituted clusters where the Rh_4 cluster is over 10^7 times more labile. This is because substitution increases the rates of CO dissociation from Ru_3 clusters whereas it greatly decreases it for the Rh_4 clusters. The value of k_1 for $\text{Rh}_4(\text{CO})_{10}(\text{PCy}_3)_2$ is considerably lower than that for $\text{Rh}_4(\text{CO})_9(\text{etpb})_3$. These trends are likely to be due to a number of structural, steric, and electronic substituent effects on both ground and transition states and the

Table 5

Rate parameters for dissociative reactions of some Rh₄ and Ru₃ carbonyl clusters at 25 °C

Cluster	10 ⁵ <i>k</i> ₁ (s ⁻¹)	Δ <i>H</i> ₁ [*] (kcal mol ⁻¹)	Δ <i>S</i> ₁ [*] (cal K ⁻¹ mol ⁻¹)	Ref.
Rh ₄ (CO) ₉ (etpb) ₃ ^a	250	–	–	This work
Ru ₃ (CO) ₁₀ (etpb) ₂ ^b	0.6	–	–	13
Rh ₄ (CO) ₉ {HC(PPh ₂) ₃ } ^c	5 × 10 ³	22.0 ± 0.4	8.9 ± 1.4	10
Ru ₃ (CO) ₁₀ (dppm) ^d	2	23.6 ± 0.2	–0.8 ± 0.7	14
Rh ₄ (CO) ₁₂ ^e	2 × 10 ⁶	–	–	9
Ru ₃ (CO) ₁₂ ^f	0.1	31.8 ± 0.2	20 ± 1	15

^a In 1,2-dichloroethane. ^b In hexane. ^c In dichloromethane at 20 °C. ^d In benzene. ^e In chlorobenzene at 28 °C. ^f In decalin.

available data are not yet sufficiently extensive for it to be possible to disentangle all these contributions.

By contrast the trends in the *k*₂ values are susceptible to a clear analysis in terms of the dependence of the rates on the nature of the attacking nucleophiles [11]. The dependence of the values of log *k*₂ on the p*K*_a values of nucleophiles of similar sizes can be concluded to be linear, on the basis of a large number of such studies [11], beginning with those of Schuster–Woldan and Basolo [16]. The gradients, β, have been proposed to be a function of the amount of bond-making in the transition states [11,15]. Values of log *k*₂⁰ = log *k*₂ – β (p*K*_a + 4) have been chosen [11,14] as indicating the values of log *k*₂ for a standard, weak nucleophile with the low p*K*_a value of –4, and values of log *k*₂⁰ can be plotted against the cone angles, θ, of the nucleophiles to provide steric profiles [4d,11,17]. A value of β (0.20) for reactions of Rh₄(CO)₉(etpb)₃ can be obtained from the plot (Fig. 1) of log *k*₂ vs. p*K*_a for the nucleophiles P(*p*-XC₆H₄)₃ (X = H, Me, and MeO) [18], all of which have identical cone angles of 145° [19]. Data are more often available for the nucleophiles P(OPh)₃ and P-*n*-Bu₃ (and, occasionally, P(O-*i*-Pr)₃) which have cone angles close to 130°. We assume here that values of β are not dependent on the cone angles of the sets of ligands chosen to measure them. The use of the P(*p*-XC₆H₄) nucleophiles to derive β is not as satisfactory because the range of p*K*_a values [18] and, therefore, of log *k*₂ values is not as great. However, data for the three nucleophiles fit very closely to the line drawn. A value of β (0.03) for reactions of Rh₄(CO)₁₀(PCy₃)₂ can be estimated from the dependence of log *k*₂ on p*K*_a for the nucleophiles P(OPh)₃, P(OEt)₃, and PPh₃ (Fig. 1). Although these do not have the same cone angles the steric effect in these reactions is evidently small. Thus the line drawn in Fig. 1 through the point for P(OPh)₃ (θ 128°) passes only ca. 0.05 log units above that for PPh₃ (θ 145°) and somewhat less below that for P(OEt)₃ (θ 109°). The corresponding steric profiles are shown in Fig. 2. * A steric profile for reactions of Rh₄(CO)₉{HC(PPh₂)₃} is also shown in Fig. 2 where the data were

* The data for reactions of Rh₄(CO)₉(etpb)₃ with all the nucleophiles apart from etpb evidently fall close to a straight line and can therefore be represented by the equation log *k*₂ = α + β p*K*_a + γθ. A double linear regression analysis of these data provides β = 0.20 ± 0.03 and γ = –0.059 ± 0.008 deg⁻¹ with a root mean square error of 0.09. These values are in excellent agreement with those obtained graphically, and confirm the validity of using the data in Fig. 1 to obtain a value for β.

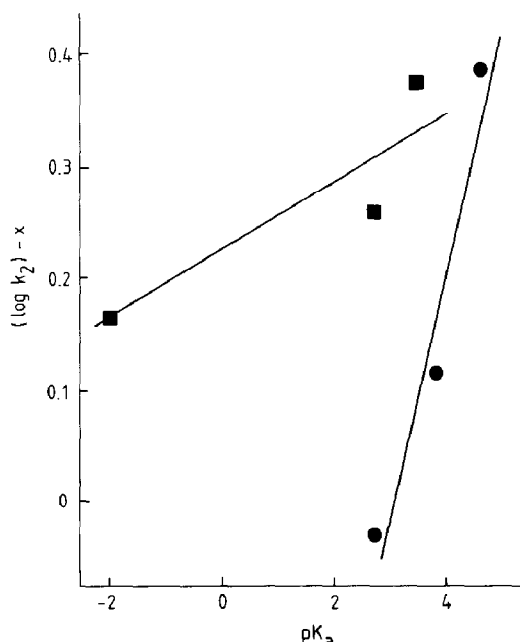


Fig. 1. Electronic profiles for associative reactions of $\text{Rh}_4(\text{CO})_9(\text{etpb})_3$ (●, $x = 0$, and nucleophiles are, from left to right, PPh_3 , $\text{P}(p\text{-MeC}_6\text{H}_4)_3$, and $\text{P}(p\text{-MeOC}_6\text{H}_4)_3$) and $\text{Rh}_4(\text{CO})_{10}(\text{PCy}_3)_2$ (■, $x = 1.5$, and nucleophiles are, from left to right, $\text{P}(\text{OPh})_3$, PPh_3 , and $\text{P}(\text{OEt})_3$).

taken from ref. 10. The value $\beta = 0.47$ was obtained from the data for P-n-Bu_3 and $\text{P}(\text{O-i-Pr})_3$ which have very similar cone angles [19].

The finite but low β value for $\text{Rh}_4(\text{CO})_{10}(\text{PCy}_3)_2$ suggests that there is little bond-making involved in the transition states for its reactions. This is supported by the rather late onset of steric retardation, the steric threshold [17] being $\geq 145^\circ$. The low value of k_2 for reaction of $\text{Rh}_4(\text{CO})_{10}(\text{PCy}_3)_2$ with AsPh_3 is consistent with the much lower nucleophilicity of this ligand although one might have supposed that this effect would have been smaller if bond-making were also small. The higher β value for $\text{Rh}_4(\text{CO})_9(\text{etpb})_3$, coupled with the lower steric threshold of ca. $110\text{--}120^\circ$, shows that bond making is considerably more pronounced. The steric effect defined by the gradient, $\gamma = -0.06 \text{ deg}^{-1}$, of the linear part of the steric profile [4d,11] is close to that for unsubstituted $\text{Ir}_4(\text{CO})_{12}$ [4d] which shows a higher degree of bond-making ($\beta = 0.3$) [11] although the steric threshold for $\text{Ir}_4(\text{CO})_{12}$ is lower ($< 100^\circ$). This suggests that, if a higher degree of bond-making were to occur for $\text{Rh}_4(\text{CO})_9(\text{etpb})_3$, the steric effect for this trisubstituted Rh_4 cluster would be greater than that for the unsubstituted Ir_4 cluster as would be expected. The value of β for $\text{Rh}_4(\text{CO})_9\{\text{HC}(\text{PPh}_2)_3\}$ (0.47) shows that bondmaking is even greater than for $\text{Rh}_4(\text{CO})_9(\text{etpb})_3$ and this is reflected in a considerably higher numerical value of γ (ca. -0.14 deg^{-1}) and a lower steric threshold, again as might be expected.

In all these clusters the horizontal parts of the steric profiles provide values of the standard reactivities, $\log k_2^0$ ($\theta \rightarrow 0$), of the clusters with respect to a small (zero steric effect) and weakly basic ($\text{p}K_a = -4$) nucleophile [11,14]. These values can be taken to approximate to a measure of the intrinsic reactivities of the clusters. The intrinsic reactivity of a cluster is related to the energy required for the cluster to

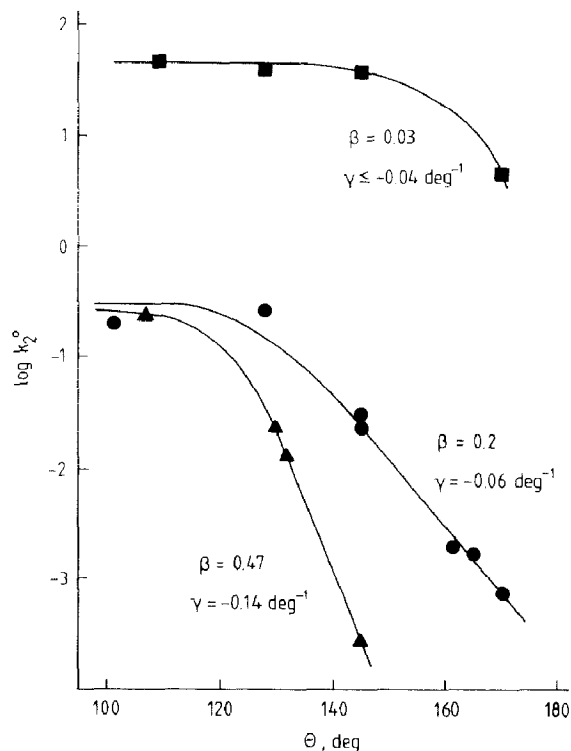


Fig. 2. Steric profiles for associative reactions of $\text{Rh}_4(\text{CO})_{10}(\text{PCy}_3)_2$ (■) and $\text{Rh}_4(\text{CO})_9(\text{etpb})_3$ (●) at 25°C in dichloroethane, and for $\text{Rh}_4(\text{CO})_9\{\text{HC}(\text{PPh}_2)_3\}$ (▲) at 20°C (data obtained from ref. 10). Values of β were obtained from gradients of plots as shown in Fig. 1 and values of γ represent the gradients of the linear, downward sloping, parts of the steric profiles. The form of the plot for $\text{Rh}_4(\text{CO})_9\{\text{HC}(\text{PPh}_2)_3\}$ depends slightly on the value taken for β . This cannot be greater than 0.47 and cannot be less than ca. 0.43. In the latter case the value of γ is hardly affected and the value of $\log k_2^0$ ($\theta \rightarrow 0$) (see text) is slightly larger but not greater than ca. 0. (The nucleophiles are from left to right, etpb, $\text{P}(\text{OMe})_3$, $\text{P}(\text{OEt})_3$, $\text{P}(\text{OPh})_3$, $\text{P}(\text{O-}i\text{-Pr})_3$, P-n-Bu_3 , $\text{P}(p\text{-XC}_6\text{H}_4)_3$, PCy_2Ph , $\text{P}(\text{CH}_2\text{Ph})_3$, and PCy_3).

rearrange in such a way as to provide access to the nucleophile present in the outer coordination sphere, rearrangement taking place before any substantial metal-nucleophile bond making occurs. The value, $\log k_2^0$ ($\theta \rightarrow 0$) = 1.6, for $\text{Rh}_4(\text{CO})_{10}(\text{PCy}_3)_2$ is the highest found from any such analyses [11,14] and, since it seems likely that an even higher value would be obtained for the unsubstituted $\text{Rh}_4(\text{CO})_{12}$, it seems clear that these Rh_4 carbonyl clusters can be quite exceptionally susceptible to nucleophilic attack.

The standard reactivities of $\text{Rh}_4(\text{CO})_9(\text{etpb})_3$ and $\text{Rh}_4(\text{CO})_9\{\text{HC}(\text{PPh}_2)_3\}$ are approximately the same. However, if an even weaker nucleophile were chosen as the standard reference, the standard reactivity of $\text{Rh}_4(\text{CO})_9\{\text{HC}(\text{PPh}_2)_3\}$ would be lower than that of $\text{Rh}_4(\text{CO})_9(\text{etpb})_3$ because of the higher β value for the former cluster. This suggests that the intrinsic reactivities of the clusters are in the order $\text{Rh}_4(\text{CO})_{10}(\text{PCy}_3)_2 > \text{Rh}_4(\text{CO})_9(\text{etpb})_3 > \text{Rh}_4(\text{CO})_9\{\text{HC}(\text{PPh}_2)_3\}$ so that the greater the intrinsic reactivity the less bond-making (lower β values and smaller steric effects) is needed in the transition states. This use of an even more weakly basic reference nucleophile would not appreciably affect the estimate, +1.6, of the

intrinsic reactivity of $\text{Rh}_4(\text{CO})_{10}(\text{PCy}_3)_2$ because its β value is so small.

The products of the reactions and the intimate mechanisms

The reactions of $\text{Rh}_4(\text{CO})_9(\text{etpb})_3$ with all the nucleophiles used led initially only to tetranuclear products so that the reactions all follow $S_{\text{N}}1$ and $S_{\text{N}}2$ paths. Subsequent fragmentation of the tetranuclear product appeared to occur with larger nucleophiles. By contrast all the reactions of $\text{Rh}_4(\text{CO})_{10}(\text{PCy}_3)_2$ with P-donor nucleophiles appeared to lead immediately to tetrasubstituted dinuclear products. These reactions all appear, therefore, to proceed only by $F_{\text{N}}2$ processes [11,20] since it seems unlikely that $\text{Rh}_4(\text{CO})_9(\text{PCy}_3)_2\text{L}$ products, formed by initial fast $S_{\text{N}}2$ processes, would undergo even more rapid associative fragmentation. Reactions of $\text{Rh}_4(\text{CO})_{10}(\text{PPh}_3)_2$ with PPh_3 lead very rapidly to $\text{Rh}_4(\text{CO})_9(\text{PPh}_3)_3$ at low $[\text{PPh}_3]$ whereas at higher concentrations of PPh_3 only fragmentation products are observed. This suggests strongly, both that an $S_{\text{N}}1$ process does occur, but that this is overwhelmed by an $F_{\text{N}}2$ process when $[\text{PPh}_3]$ is large enough. At higher concentrations of PCy_3 the major process is $F_{\text{N}}2$ in nature whereas etpb leads to substitution.

Although these results are qualitative it is clear that the more intrinsically reactive $\text{Rh}_4(\text{CO})_{10}(\text{PCy}_3)_2$ is very susceptible to associative fragmentation, even when attacked by relatively small and weakly basic phosphites. Although we do not know the intrinsic reactivity of $\text{Rh}_4(\text{CO})_{10}(\text{PPh}_3)_2$ it seems likely, from its qualitatively very rapid reactions, to be quite high and again it is very susceptible to fragmentation. The less intrinsically reactive $\text{Rh}_4(\text{CO})_9(\text{etpb})_3$ is much less susceptible to fragmentation so the three small substituents do not destabilize the cluster in this respect as much as the two much larger PCy_3 or PPh_3 substituents. The trisubstituted cluster with the $\text{HC}(\text{PPh}_2)_3$ ligand appears not to undergo any fragmentation either [10], presumably because of the bridging nature of the substituent which overcomes any effect due to its relatively large size.

These results are, therefore, generally in accord with the various possible intimate mechanisms all of which [4d,11,15,20b] involve an opening up of the cluster with a concomitant weakening of the metal-metal bonds within the cluster. This allows one of the metals to accept a pair of electrons from the incoming nucleophile without its having to exceed the 18-electron configuration characteristic of these relatively small clusters. With two large substituents this expansion of the cluster appears to be great enough for fragmentation to occur, whereas for the three small etpb substituents the weakening of the Rh_4 bonding is not so great and little or no fragmentation occurs.

Acknowledgements

The financial support of the Natural Science and Engineering Research Council is gratefully acknowledged as is the assistance of Dr. R.G.V. Hancock (of the University of Toronto's Slowpoke Reactor facility) with the neutron activation analyses. We are also indebted to Professors Fred Basolo and Bill Trogler for communicating their results [10] to us prior to publication, and to Professor R.J. Morris for providing several phosphorus donor ligands.

References

- 1 A.J. Poë, in M. Moskovits (Ed.), *Metal Clusters*, Chapter 4, Wiley Interscience, New York, 1986, and ref. therein.

- 2 D.J. Darensbourg and M.J. Incorvia, *Inorg. Chem.*, 19 (1980) 2585;
D.J. Darensbourg, B.S. Peterson, and R.E. Schmidt, *Organometallics*, 1 (1982) 306.
- 3 G. Bor, U.K. Dietler, P. Pino, and A.J. Poë, *J. Organomet. Chem.*, 154 (1978) 301.
- 4 (a) K.J. Karel and J.R. Norton, *J. Am. Chem. Soc.*, 96 (1974) 6812;
(b) D.C. Sonnenberger and J.D. Atwood, *Inorg. Chem.*, 20 (1981) 3243;
(c) E.F. Stuntz and J.R. Shapley, *J. Organomet. Chem.*, 213 (1981) 389;
(d) K. Dahlinger, F. Falcone, and A.J. Poë, *Inorg. Chem.*, 25 (1986) 2654.
- 5 F. Oldani and G. Bor, *J. Organomet. Chem.*, 246 (1983) 309.
- 6 B.T. Heaton, L. Longhetti, D.M.P. Mingos, C.E. Briant, P.C. Minshall, B.R.C. Theobald, L. Garleshelli, and U. Sartorelli, *J. Organomet. Chem.*, 213 (1981) 333.
- 7 B.L. Booth, M.J. Else, R. Fields, and R.N. Haszeldine, *J. Organomet. Chem.*, 27 (1971) 119.
- 8 R.H. Whyman, *J. Chem. Soc., Dalton Trans.*, (1972) 1375.
- 9 J.R. Kennedy, F. Basolo, and W.C. Trogler, *Inorg. Chim. Acta*, 146 (1988) 75.
- 10 J.R. Kennedy, P. Selz, A.L. Rheingold, W.C. Trogler, and F. Basolo, *J. Am. Chem. Soc.*, 110 (1988) 3615.
- 11 A.J. Poë, *Pure and Appl. Chem.*, 60 (1988) 1209;
N.M.J. Brodie, L. Chen, and A.J. Poë, *Intl. J. Chem. Kin.*, 20 (1988) 467.
- 12 A.A. Bahsoun, J.A. Osborne, C. Voelker, J.J. Bonnet, and G. Lavigne, *Organometallics*, 1 (1982) 1114.
- 13 N.M.J. Brodie, Ph.D. Thesis, University of Toronto, 1989.
- 14 B. Ambwani, S.K. Chawla, and A.J. Poë, *Polyhedron*, 7 (1988) 1939.
- 15 A.J. Poë and M.V. Twigg, *J. Chem. Soc., Dalton Trans.*, (1974) 1860.
- 16 H.G. Schuster-Woldan and F. Basolo, *J. Am. Chem. Soc.*, 88 (1966) 1657;
F. Basolo, *Inorg. Chim. Acta*, 100 (1985) 33.
- 17 M.N. Golovin, M.M. Rahman, J.E. Belmonte, and W.P. Giering, *Organometallics*, 4 (1985) 1981.
- 18 M.M. Rahman, H.Y. Liu, A. Prock, and W.P. Giering, *Organometallics*, 6 (1987) 650.
- 19 C.A. Tolman, *Chem. Rev.*, 77 (1977) 313.
- 20 (a) N.M.J. Brodie, A.J. Poë, and V.C. Sekhar, *J. Chem. Soc., Chem. Commun.*, (1985) 1090;
(b) A.J. Poë and V.C. Sekhar, *Inorg. Chem.*, 24 (1985) 4376;
(c) N.M.J. Brodie and A.J. Poë, *ibid.*, 27 (1988) 3156.