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Kinetic studies of some substituted hexarhodium carbonyl clusters†

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Reactions of the halides X^- (X^- = chloride, bromide or iodide) with the substituted cluster $Rh_6(CO)_{15}(PPh_3)$ in oxygen-free chloroform lead to $[Rh_5(CO)_{14}(PPh_3)]^-$, $Rh(CO)_2(PPh_3)_2X$ and $[Rh(CO)_2X_2]^-$ in the molar ratios 2 : 1 : ~13. Oxidation by the solvent is assumed to lead to most of the Rh(I) product, and the stoichiometry for reactions with I^- can be defined as $4Rh_6(CO)_{15}(PPh_3) + 27I^- + 12CHCl_3 \rightarrow 2[Rh_5(CO)_{14}(PPh_3)]^- + Rh(CO)_2(PPh_3)_2I + 13[Rh(CO)_2I_2]^- + 6C_2H_2Cl_4 + 4CO + 12Cl^-$. This can be rationalized quite simply with the aid of a few generally justifiable assumptions. Rate constants for reactions with bromide increase to a limiting value with increasing $[Br^-]$ in a way that shows that breaking of one Rh–Rh bond, with an unusual *closo* to *nido* structural change, is rate determining. This opening of the cluster might be spontaneous or solvent induced. To complete the reaction, the bromide has to compete with the reverse *nido* to *closo* change. The same *closo* to *nido* change is also a major rate determining step for reactions with $P(OPh)_3$ in oxygen-free solutions, and for reactions with bromide in oxygenated solutions in the presence of trifluoroacetic and some other acids. The limiting rates increase slightly with increasing basicity of the ligands $P(p\text{-}XC_6H_4)_3$ along the series X = F_3C, Cl, F, H and MeO. Activation parameters for these reactions are reported.

Introduction

The carbonyl cluster $Rh_6(CO)_{16}$ was the first binary carbonyl cluster[1] in which each metal atom was found to disobey the simple 18-electron rule,[2] and its two extra electrons appear to enable it to exhibit a rich redox chemistry that very often involves destruction or enlargement of the cluster framework.[3,4] Application of MO theory to M_6 clusters of this electron configuration showed that the extra electron pair can be accommodated in an $[A_{2g}]$ weakly anti-bonding cluster orbital[5] so that the 86-electrons form a closed shell arrangement. The octahedral *closo* Rh_6 core is fully consistent with PSEPT rules[2,6] for 86-electron clusters.

However, some features of its reactivity are poorly understood. It is, for instance, extremely resistant to simple substitution reactions such as CO exchange,[7] and no studies of kinetics of substitution by soft ligands such as P-donors have been reported. This contrasts with reactions of its smaller congener $Rh_4(CO)_{12}$ which undergoes substitution exceedingly rapidly.[8,9] Attempts to study such reactions of $Rh_6(CO)_{16}$ are complicated by their great sensitivity to oxygen and solvent impurities whereby trace amounts of impurities appear to give rise to irreproducible behaviour.[10]

So far the only successful kinetic studies of substitutions at the Rh_6 cluster core have involved the rapid displacement of labile ligands in such "lightly stabilized" clusters as $Rh_6(CO)_{15}NCMe$, *etc.*,[11] or the unusual chelation reactions in which a substituted P-bonded pyrrolyl ligand displaces a CO ligand from a neighbouring Rh atom.[12] Similar chelation reactions of P-donor ligands that contain more usual donor atoms in their pendant groups have also been described.[13] In an attempt to investigate the nature of substitution reactions at the Rh_6 cluster core more thoroughly we attempted to study reactions of $Rh_6(CO)_{16}$ with hard, activating nucleophiles that are known to attack other carbonyl clusters through carbon atoms of the CO ligands.[14] Me_3NO attacks $Rh_6(CO)_{16}$ quite effectively and is used in the synthesis of $Rh_6(CO)_{14}(NCMe)_2$.[15] Kinetic studies show that $Rh_6(CO)_{16}$ is also susceptible to rapid attack by hydroxide ions. (See the ESI† for a summary of these studies). Although $Rh_6(CO)_{15}{}^{2-}$ can be synthesized in nearly quantitative yield by addition of KOH to a slurry of $Rh_6(CO)_{16}$ in MeOH under nitrogen,[16] the kinetic runs have to be carried out in chlorinated solvents, for solubility reasons, and the products are not well defined. Halide ions turn out to be only very slightly reactive towards $Rh_6(CO)_{16}$ and the high susceptibility to traces of oxygen[10,17] makes kinetic studies unprofitable.

We have therefore examined reactions of some $Rh_6(CO)_{15}P(p\text{-}XC_6H_4)_3$ clusters with halide ions, thereby hoping to make use of the labilizing effect of the quite large $P(p\text{-}XC_6H_4)_3$ ligands,[18] as well as the nucleophilic character of halides towards other carbonyls.[17,19–23]

Experimental

General comments

$[NBu_4]Br$, CF_3COOH and phosphines (Strem), and $[NBu_4]I$ and [PPN]Cl (Aldrich), were used as received. The complexes $Rh_6(CO)_{15}(PPh_3)$,[24] $Rh_6(CO)_{15}P(p\text{-}XC_6H_4)_3$ (X = MeO, Cl, F and CF_3),[25] $Rh_4(CO)_{12}$,[26] and $[Rh_5(CO)_{14}(PPh_3)][NBu_4]$[27] were prepared according to published procedures. $Rh(CO)_2(PPh_3)_2I$[28,29] was prepared by a method to be described elsewhere,[30] and characterized by IR and NMR spectroscopy, and by crystallography.[30]

Chloroform (Fisher) for kinetic experiments was washed three times with equal volumes of distilled water, dried for 12 h over $CaCl_2$, and distilled over P_2O_5 under nitrogen. Other solvents were dried over appropriate reagents and distilled prior to use. IR spectra were recorded using a Nicolet Magna IR 550 FTIR spectrophotometer. UV-Vis spectra were recorded with Varian-Cary 2000 and Hewlett-Packard 8452A diode array spectrophotometers. Spectrometers were fitted with thermostated (± ~0.1 °C or better) cell holders for kinetic studies. Solutions for kinetic study were prepared under nitrogen, and the reactions were monitored by repetitive scanning of samples in the thermostated IR or UV cells. Rate constants were obtained by single or double exponential fitting of the changes of absorbances with

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† Electronic supplementary information (ESI) available: Tables of rate constants, and a description of the kinetics of reactions of $Rh_6(CO)_{16}$ with hydroxide. See http://www.rsc.org/suppdata/dt/b4/b408687b/

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time, making use of Grafit (v.3.09b) software. The ^{31}P NMR spectra were recorded on a Varian Gemini 300 MHz instrument, and referenced to external 85% H_3PO_4.

Results

Reaction of $Rh_6(CO)_{15}(PPh_3)$ with halide ions under an oxygen-free atmosphere

Analysis of reaction products and stoichiometry. Reactions of $Rh_6(CO)_{15}(PPh_3)$ with halide ions (as $[NBu_4]I$, $[NBu_4]Br$ and $[PPN]Cl$) in oxygen-free solutions gave three main products: $[Rh(CO)_2Hal_2]^-$, $[Rh_5(CO)_{14}(PPh_3)]^-$ and $[Rh(CO)_2(PPh_3)_2Hal]$. The first type of complex is stable indefinitely under any conditions, but the others are stable only in the absence of oxygen and in the presence of CO, the amount released during the reactions being sufficient. Otherwise, even under oxygen-free conditions, these complexes readily lose CO.[27–30]

The IR spectrum of the products of reaction with a large excess of bromide in $CHCl_3$ displayed strong CO stretching bands at 2069 and 1996 cm^{-1} of $[Rh(CO)_2Br_2]^-$, which are consistent with the previously reported data: 2068 and 1993 cm^{-1} in CH_2Cl_2.[31] The bands due to this compound were subtracted from the IR spectrum of the product mixture to give the spectrum shown in Fig. 1 and the remaining bands, and their relative intensities, correspond well with those reported for $[Rh_5(CO)_{14}(PPh_3)]^-$ in THF.[27]

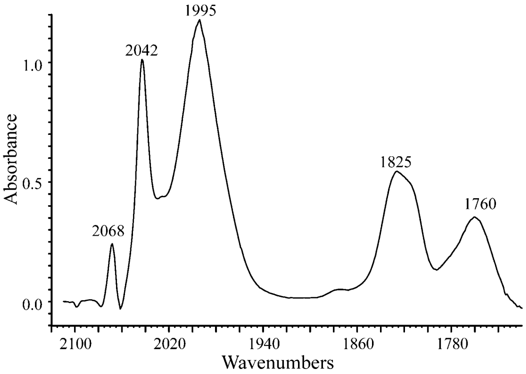


Fig. 1 An IR spectrum of the final product of the reaction of a large excess of bromide with $Rh_6(CO)_{15}(PPh_3)$ in oxygen-free $CHCl_3$ after subtraction of the IR spectrum of $[Rh(CO)_2Br_2]^-$.

The ^{31}P NMR spectrum of the final reaction mixture in $CDCl_3$ displayed two signals of equal intensity at 22.4 ppm [dm, ^1J(P–Rh) 183 Hz] and 31.2 ppm [d, ^1J(P–Rh) 95 Hz] when Hal = I. The high-field signal parameters are identical with the spectral data found for the independently synthesized cluster anion $[Rh_5(CO)_{14}(PPh_3)]^-$,[27] while the low-field signal corresponds to the independently synthesized[30] complex $Rh(CO)_2(PPh_3)_2I$ (31.2 [d, ^1J(P–Rh) 95 Hz]). Iodide was chosen as the halide for these experiments because of the higher stability of $[Rh(CO)_2(PPh_3)_2I]$ compared to its bromo and chloro analogues.

Characterization of products of the reaction of $Rh_6(CO)_{15}$(PPh$_3$) with P(OPh)$_3$. For comparative purposes, reactions of $Rh_6(CO)_{15}(PPh_3)$ with $P(OPh)_3$ in oxygen-free solutions were examined and the following products identified: $Rh_4(CO)_8\{P(OPh)_3\}_4$[32,33] and free PPh_3, together with a Rh_2 complex that is possibly $Rh\{P(OPh_3)\}_2(\mu\text{-}Cl)_2Rh\{P(OPh)_3\}_2$ (see below).

$Rh_6(CO)_{15}(PPh_3)$ (70 mg, 0.054 mmol) was dissolved in $CHCl_3$ (5 ml). The solution was degassed (three freeze-pump-thaw cycles) and was added to a degassed solution of $P(OPh)_3$ (260 mg, 0.839 mmol) in $CHCl_3$ (3 ml). The reaction mixture was left for 10–12 h until a TLC spot test showed complete consumption of the starting cluster. By this time the ^{31}P NMR spectrum of the reaction mixture displayed two signals that correspond to the rhodium complexes: a sharp doublet centered at 141.9 ppm (^1J(P–Rh) 239 Hz) and a broad resonance around 109 ppm. Solvent was removed under vacuum, and the residue dissolved in CH_2Cl_2 (2 ml), diluted with hexane (2 ml), and transferred onto a chromatographic column (2.5 × 7 cm). The following bands were obtained in the order of elution: (eluent CH_2Cl_2–hexane (3 : 4)), a broad red–orange band containing $Rh_4(CO)_8\{P(OPh)_3\}_4$, 83 mg; and (eluent CH_2Cl_2–THF (5 : 1)), a narrow yellow–orange band containing $RhCl\{P(OPh)_3\}_3$, 48 mg.

The $Rh_4(CO)_8\{P(OPh)_3\}_4$ cluster was identified by its C–O stretching frequencies (2038w, 2023sh, 2011vs, 1832s; cf. 2036w, 2022sh, 2008vs, 1836s)[33] and by its ^{31}P NMR spectra in $CDCl_3$ (broad multiplet at δ 109.9 ppm). The latter fits well to dynamic averaging of the resonances observed in the low temperature limiting spectrum of this cluster.[32,33] The ^{31}P NMR spectral data of the mononuclear complex $Rh\{P(OPh)_3\}_3Cl$ ($CDCl_3$, δ 113.1, dd ^1J(P–Rh) 225 Hz, ^2J(P–P) 53 Hz; δ 119.8, dt, ^1J(P–Rh) 285 Hz, ^2J(P–P) 53 Hz) are consistent with previously reported data ($CDCl_3$, δ 112.5, dd, ^1J(P–Rh) 222 Hz, ^2J(P–P) 55 Hz, δ 118.9 (dt, ^1J(P–Rh) 281 Hz, ^2J(P–P) 55 Hz).[34] The composition of the mononuclear complex clearly indicates the oxidation of the reactive intermediates (Rh(0) species) by the chlorinated solvent. It is very probable that the interaction of the starting "Rh_6" cluster with the excess of $P(OPh)_3$ results in its splitting into "Rh_4" and "Rh_2" fragments, the latter being extremely reactive to give, for example, $Rh\{P(OPh_3\}_2(\mu\text{-}Cl)_2Rh\{POPh)_3\}_2$. An analogous binuclear Rh(I) complex containing $P(OMe)_3$ ligands has been characterized earlier[35] by ^{31}P NMR spectroscopy and displays the spectroscopic characteristics (δ 138.1 ppm, J(Rh–P) 295 Hz) which are quite similar to those found for the low-field signal presented in the reaction mixture. Thus, we suppose that this signal is generated by the $Rh\{P(OPh)_3\}_2(\mu\text{-}Cl)_2Rh\{P(OPh)_3\}_2$ complex, which transforms into the mononuclear $Rh\{P(OPh)_3\}_3Cl$ complex on silica in the presence of the ligand excess.

Reaction kinetics by FTIR monitoring. Rate constants were determined by monitoring the decreasing absorbance of the IR band of the starting cluster $Rh_6(CO)_{15}(PPh_3)$ at 2100 cm^{-1}, and fitting absorbance data to single-exponential curves. However, when lower concentrations of bromide were used, and rates were quite slow, initial rates of absorbance change were chosen together with A_∞ values inferred from other reactions. In a typical experiment, a solution (*ca.* 1.5 cm^3, *ca.* 1 mM) of $Rh_6(CO)_{15}(PPh_3)$ in chloroform was degassed (three freeze–pump–thaw cycles) using standard Schlenk techniques, and added by syringe to a degassed crystalline halide salt (chloride, bromide or iodide) or to a degassed solution of $P(OPh)_3$. After dissolution or complete mixing, the reaction mixture was degassed again by one freeze–pump–thaw cycle and transferred by syringe to an amalgamated NaCl cell (Wilmad Glass) with a water-thermostated jacket, and the spectra were scanned repetitively in the carbonyl stretching region. A typical set of spectra is shown in Fig. 2, and rate constants for a range of concentrations of nucleophile, and at various temperatures, are given in Table 1. The rate constants for reaction with bromide at 26.5 °C clearly increase with $[Br^-]$ towards a limiting rate, and the conditions for the other reactions are such that limiting rates are attained. The limiting rates all fit onto a common Eyring plot, irrespective of the nucleophile, as shown in Fig. 3. On the other hand, the rate constants for reactions with $P(OPh)_3$ increase linearly with $[P(OPh)_3]$ in a way that may suggest some contribution from an associative path. (See Fig. S1 in the ESI†).

Reactions of the $Rh_6(CO)_{15}P(p\text{-}XC_6H_4)_3$ (X = CF_3, Cl, F, H, MeO) clusters with bromide in the presence of oxygen and acid

Analysis of reaction products and stoichiometry. Reactions of $Rh_6(CO)_{15}(PPh_3)$ with bromide in the presence of oxygen alone are appreciably faster than in its absence, and lead mainly to $[Rh(CO)_2Br_2]^-$ and CO_2, together with small amounts of

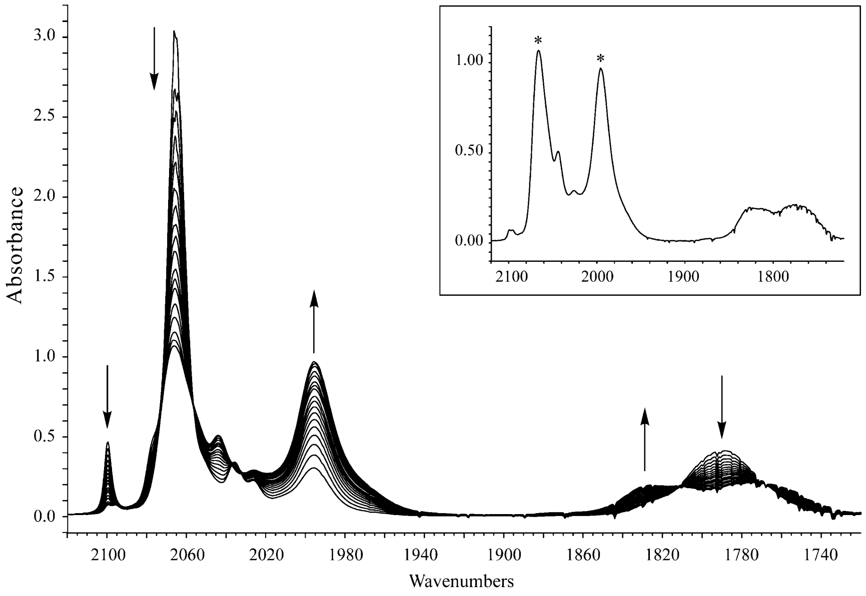


Fig. 2 Typical IR spectral changes for the oxygen-free reaction of bromide with $Rh_6(CO)_{15}(PPh_3)$ (T = 32 °C). The arrows denote increasing and decreasing absorbances. Inset: final spectrum of the reaction mixture; asterisks denote bands corresponding to $[Rh(CO)_2Br_2]^-$.

Table 1 Kinetic data for the reaction of $Rh_6(CO)_{15}(PPh_3)$ with halide ions or $P(OPh)_3$ under an oxygen-free atmosphere in $CHCl_3$. Initial values of $[Rh_6(CO)_{15}(PPh_3)]$ were *ca.* 0.3 mM

Reactant	T/°C	[Reactant]/mM	$10^3k_{obs}/s^{-1}$
Cl^-	38.3	42	0.785
		53	0.827
		67	0.824
Br^-	26.5	5	0.075
		10	0.104
		26	0.119
		51	0.140
		86	0.149
		133	0.178
		217	0.176
	32.8	32	0.275
		48	0.337
		77	0.347
		107	0.371
	38.3	24	0.735
		38	0.897
		64	0.903
		87	0.860
		126	0.879
		165	0.900
	45.0	55	2.07
		59	2.03
		89	2.13
		92	2.15
		112	2.24
I^-	38.3	40	0.72
		86	1.03
		111	1.01
$P(OPh)_3$	25.5	22	0.131
		42	0.137
		187	0.144
		388	0.170
		546	0.167
$P(OPh)_3$/1 atm of CO	26.5	23	0.09

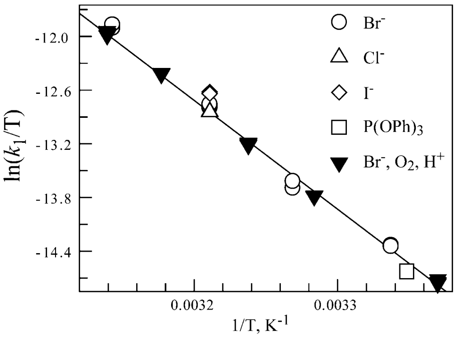


Fig. 3 Eyring plot for the reaction of bromide with $Rh_6(CO)_{15}(PPh_3)$ in oxygenated and acidified $CHCl_3$. Data for reactions in oxygen-free solution are superimposed on the Eyring plot.

$[Rh_6(CO)_{15}Br]^-$ and other unidentified products. These reactions are evidently catalytic and complex, and no easily interpretable kinetic data were obtained. The cluster is not sensitive to oxygen by itself. However, in the presence of trifluoroacetic acid (TFA), $Rh_6(CO)_{15}(PPh_3)$ and its congeners $Rh_6(CO)_{15}P(p\text{-}XC_6H_4)_3$ (X = CF_3, Cl, F or MeO), react smoothly with bromide, under an atmosphere of dry air or oxygen, to give essentially quantitative yields of $[Rh(CO)_2Br_2]^-$ and free $P(p\text{-}XC_6H_4)_3$. These subsequently react quite slowly to give some unidentified mononuclear phosphine-carbonyl complexes of Rh(I). Thus the presence of $[Rh(CO)_2Br_2]^-$ was confirmed by its CO stretching bands (see above), and the ^{31}P NMR spectrum of the final reaction mixture when X = H displays one signal, characteristic of coordinated PPh_3, at 29.7 ppm ($CDCl_3$, d, ^1J(Rh–P) 114.2 Hz). The addition of an excess of PPh_3 to this reaction mixture leads to the growth of intensity of this NMR signal and a decrease in the absorbance of the corresponding CO-stretching bands in the IR spectrum. These observations are indicative of CO substitution by PPh_3 in the slow reaction following $[Rh(CO)_2Br_2]^-$ formation.

Reaction kinetics. Typical sets of time-dependent IR spectra display quite sharp isosbestic points as shown in Fig. 4, and rate constants could be obtained by monitoring the absorbance changes of the most intense band in the IR spectrum of the $Rh_6(CO)_{15}(PPh_3)$ cluster.

However, the reactions in acidic solutions saturated with dry air or oxygen could also be monitored quite simply by continuous measurement of the absorbance at 420 nm. In a typical experiment, a solution (0.3 cm^3; *ca.* 10 mM) of the cluster in chloroform was transferred into a pre-thermostated 10 mm

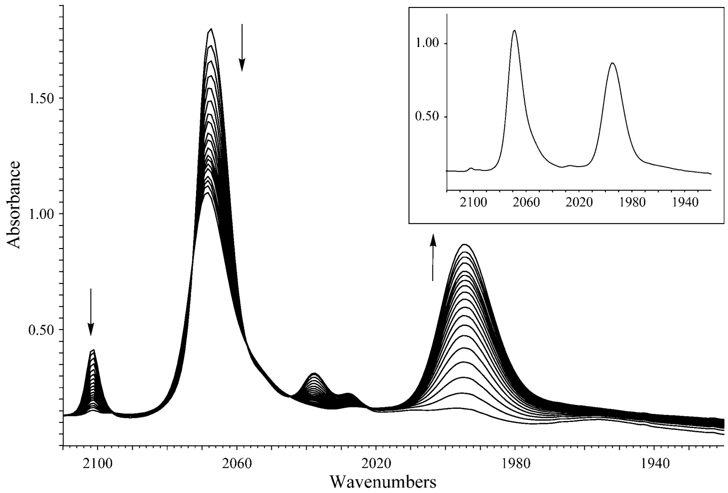


Fig. 4 Typical IR spectral changes for the reaction of $Rh_6(CO)_{15}P(p\text{-}XC_6H_4)_3$ with bromide in the presence of oxygen and trifluoroacetic acid (X = Cl). The arrows denote increasing and decreasing absorbances. Inset: final spectrum of the reaction mixture.

Table 2 Activation parameters for the reactions of the $Rh_6(CO)_{15}P(p\text{-}XC_6H_4)_3$ clusters with bromide in the presence of oxygen and acid in $CHCl_3$

X	pK_a'	$\Delta H^{\neq}$/kJ mol^{-1}	$\Delta S^{\neq}$/J mol^{-1} K^{-1}	σk_{obs}[a] (%)
CF_3	−1.39	101.3 ± 0.6	21.4 ± 1.9	2.1
Cl	0.87	95.0 ± 1.0	−3.3 ± 3.8	4.9
F	1.63	105.1 ± 0.9	32.2 ± 3.0	4.1
H	3.28	101.2 ± 0.7	20.6 ± 2.4	3.6
MeO	5.13	93.6 ± 0.7	−3.5 ± 2.3	3.6

[a] The standard error of an individual measurement of k_{obs}.

UV-vis cell, containing a solution of TFA (*ca.* 100 mM) and NBu_4Br (*ca.* 170 mM) in chloroform (3 cm^3). Rate constants were usually determined by fitting absorbance data to double-exponential curves. Double exponential analysis was needed because of the further reaction of the initial $[Rh(CO)_2Br_2]^-$ product mentioned above. Convenient temperature ranges were selected for each cluster and at least four runs were carried out over a 20 °C temperature range. Rate constants obtained in this way are given in Table S1 in the ESI,† and activation parameters are given in Table 2. The data show that the rate constants for each of these reactions all fall on a good Eyring plot (Fig. 3), irrespective of the concentrations of acid or bromide, and have satisfyingly small standard errors of measurement (Table 2). The rates were also independent of the nature and concentration of other acids. Thus reactions at 25.6 °C in $CHCl_3$ with bromide in the presence of 33.7 mM benzoylpropionic acid, 43.7 mM benzoic acid, and 86.5 mM trifluoroacetic acid led to values of $10^3 k_{obs}$ equal to 0.117, 0.113 and 0.112 s^{-1}, respectively. IR monitoring at ambient temperatures was carried out for each $Rh_6(CO)_{15}P(p\text{-}XC_6H_4)_3$ cluster to check that the reaction proceeded to give products analogous to those when X = H.

Fig. 3 shows that data for reactions of the halides or $P(OPh)_3$ in deoxygenated solutions, and for reactions with bromide in the presence of acid and oxygen, all fall on the same Eyring plot, *i.e.* their limiting rates are always the same.

Discussion

The course of the reactions

The reactions with bromide in chloroform and in the absence of oxygen and acid can be discussed in terms of the stoichiometric equation:

$$4Rh_6(CO)_{15}(PPh_3) + 27Br^- + 12CHCl_3 \rightarrow 2[Rh_5(CO)_{14}(PPh_3)]^- + Rh(CO)_2(PPh_3)_2Br + 13[Rh(CO)_2Br_2]^- + 6C_2H_2Cl_4 + 4CO + 12Cl^- \qquad (1)$$

This quite complicated equation incorporates the observation of *equal* intensities of the ^{31}P bands of the products $[Rh_5(CO)_{14}(PPh_3)]^-$ and $Rh(CO)_2(PPh_3)_2I$ in the NMR spectra of the products of reaction with I^-. By inference, it is concluded that the same would be true for reactions with Br^-. Eqn. (1) also takes account of the number of ligands needed to maintain the appropriate coordination numbers of the complexes, the disproportionation of the cluster, and the amount of $CHCl_3$ needed, in addition to disproportionation, to produce all the Rh(I) species. Since $Rh(CO)_2(PPh_3)_2Br$ contains two PPh_3 ligands compared with one in $[Rh_5(CO)_{14}(PPh_3)]^-$, its molar concentration must be half that of the former product. Further, the molar yield of $[Rh(CO)_2Br_2]^-$ can be estimated approximately as follows.

If it is assumed that the yield of $[Rh(CO)_2Br_2]^-$, after reactions under oxygen, is quantitative then the molar absorbance of $[Rh(CO)_2Br_2]^-$ at 1996 cm^{-1} can be estimated to be *ca.* 8.5% of that of $Rh_6(CO)_{15}(PPh_3)$ at 2065 cm^{-1} from data similar to those in Fig. 4. Data from four runs similar to those in Fig. 2, show that the absorbance of the $[Rh(CO)_2Br_2]^-$ at 1993 cm^{-1} is *ca.* 64, 66, 52 and 54% of that expected for quantitative formation, whereas the stoichiometry in eqn. (1) requires a yield of 100 × 13/24, *i.e.* 54%. However, the presence of some of the unstable minor product $[Rh_5(CO)_{14}(PPh_3)]^-$ would contribute somewhat to the absorbance at 1996 cm^{-1} and the two higher estimates for the yield might well be due to this factor. Thus, within the precision of the estimates, the observed yield of $[Rh(CO)_2Br_2]^-$ is consistent with that expected from the proposed stoichiometry.

This stoichiometry can be accounted for by the following sequence of reactions,

$$\mathbf{2Rh_6(CO)_{15}L} + 4Br^- \rightarrow \mathbf{2[Rh_5(CO)_{14}L]^-} + [Br(CO)Rh(\mu\text{-}Br)_2Rh(CO)Br]^{2-} \qquad (2)$$

$$\mathbf{2Rh_6(CO)_{15}L} + 4Br^- \rightarrow 2[Rh_5(CO)_{14}Br]^{2-} + [L(CO)Rh(\mu\text{-}Br)_2Rh(CO)L] \qquad (3)$$

$$[L(CO)Rh(\mu\text{-}Br)_2Rh(CO)L] \rightarrow [L_2Rh(\mu\text{-}Br)_2Rh(CO)_2] \qquad (4)$$

$$2[Rh_5(CO)_{14}Br]^{2-} + 12CHCl_3 + 18Br^- \rightarrow \mathbf{10[Rh(CO)_2Br_2]^-} + 8CO + 12Cl^- + 6C_2H_2Cl_4 \qquad (5)$$

$$[Br(CO)Rh(\mu\text{-}Br)_2Rh(CO)Br]^{2-} + 2CO \rightarrow \mathbf{2[Rh(CO)_2Br_2]^-} \qquad (6)$$

$$L_2Rh(\mu\text{-}Br)_2Rh(CO)_2] + 2CO + Br^- \rightarrow \mathbf{[Rh(CO)_2Br_2]^-} + \mathbf{[Rh(CO)_2L_2Br]} \qquad (7)$$

where the known reactant cluster and products are shown in bold type. The presence of chloride in the product mixture suggests that some chloro carbonyl products might be formed. Some small spectral shifts, consistent with this, are in fact observed at low concentrations of bromide but this does not affect the following discussion.

The sequence of reactions in eqns. (2)–(7) assumes that:

(i) the original $Rh_6(CO)_{15}L$ cluster can be attacked by bromide in two ways, each of which results in abstraction of a Rh(I) moiety (*i.e.* $[Rh(CO)Br_2]^-$ and [Rh(CO)LBr]) which can dimerize in the usual way to form bridged complexes. (A mixed $[Br(CO)Rh(\mu\text{-}Br)_2Rh(CO)L]$ complex could also be formed but this does not affect the following discussion). In one case the Rh(I) carries a bromide ligand with it (eqn. (2)) and in the other (eqn. (3)) it carries a PPh_3 ligand. These two processes leave behind a Rh_5^- cluster, and must evidently occur with equal probability.

(ii) The $[Rh_5(CO)_{14}Br]^{2-}$ is unstable to oxidation by the solvent (eqn. (5)) by electron transfer to a chlorine atom, with subsequent dimerisation of the $CHCl_2$ radical.

(iii) $[L(CO)Rh(\mu\text{-}Br)_2Rh(CO)L]$ can isomerize quantitatively to $[L_2Rh(\mu\text{-}Br)_2Rh(CO)_2]$.

Assumption (i) is perfectly reasonable and fits with the kinetic indication of initial attack on an 'opened cluster' by bromide (see below). $[Rh_5(CO)_{14}L]^-$ is one of the characterized products, and $[Rh_5(CO)_{14}Br]^{2-}$ is a known cluster that is extremely sensitive to oxidation,[27] so supporting assumption (ii). Assumption (ii) is also in accordance with known oxidations of mononuclear carbonyl complexes[36] and clusters by chlorinated hydrocarbons,[37,38] and (iii) is absolutely essential to the formation of the completely characterized $[Rh(CO)_2L_2X]$ product. Such migrations are known in analogous polynuclear complexes.[39–42]

Reactions of $Rh_6(CO)_{15}(PPh_3)$ with bromide in the presence of oxygen are evidently complex and the sequence of compounds formed cannot even be speculated about. This makes the simplifying effect of added TFA difficult to explain as well, but protonation must evidently intervene at some stage in the catalytic sequence of reactions. However, even in the absence of any understanding of the detailed processes that occur, these reactions with bromide, oxygen and TFA are still useful. They allow for kinetic monitoring by UV-vis spectroscopy, something that is not possible for the reactions in the absence of oxygen where the UV-vis absorbance changes are not so simple. They lead to rate constants that are identical with those in the absence of oxygen and enable more rapid collection of precise kinetic data.

Kinetics and mechanism of the rate determining steps

The most important feature of the reactions with bromide in oxygen-free solutions is the rise of k_{obs} to a limiting value with increasing $[Br^-]$ as shown in Fig. 5. When a dissociation constant of 2.7×10^{-5} M is taken for $[NBu_4Br]$ in $CHCl_3$[43] a linear 'inverse plot' of $1/k_{obs}$ against $1/[Br^-]$ is obtained as shown in Fig. 6. This is characteristic of slow formation of a reactive intermediate which undergoes competitive reactions, either reverting to the original cluster or reacting with free bromide to proceed further along the reaction sequence as shown in eqn. (8).

$$Rh_6(CO)_{15}L \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Rh_6(CO)_{15}L^* \xrightarrow[k_2]{Br^-} \begin{array}{l} \{[Rh_5(CO)_{14}Br]^{2-} + Rh(CO)LBr\} \\ \\ \{[Rh_5(CO)_{14}L]^- + [Rh(CO)Br_2]^-\} \end{array} \tag{8}$$

$$k_{obs} = k_1k_2[Br^-]/(k_{-1} + k_2[Br^-]) \tag{9}$$

$Rh_6(CO)_{15}L^*$ is the reactive intermediate, and only the initial products of its reaction with bromide are given. The rate equation corresponding to this sequence of reactions is shown in eqn. (9) which leads to the linear inverse plot shown in Fig. 6. The intercept of this inverse plot is 1030 s, and the slope is 0.369 M s, and these lead to a value of 2.8×10^3 M^{-1} for k_2/k_{-1}. The rate constant k_2 is actually the sum of the individual rate constants for formation of the two pairs of products enclosed in brackets in eqn. (8).

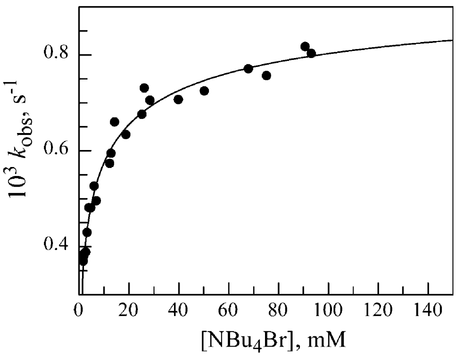


Fig. 5 Concentration dependence of k_{obs} for the reaction of $Rh_6(CO)_{15}(PPh_3)$ with bromide in oxygen-free $CHCl_3$ at 38.5 °C with widely varying values of [cluster] (see Table S2, ESI†). The line through the data was drawn using the parameters obtained from the 'inverse plot' in Fig. 6.

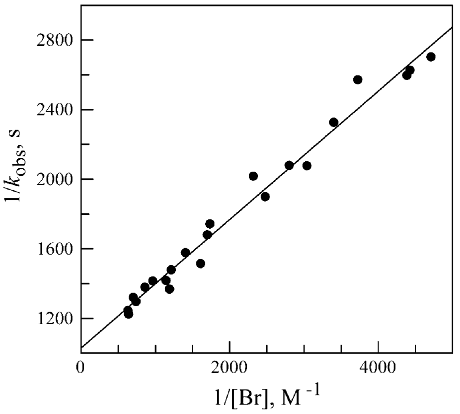


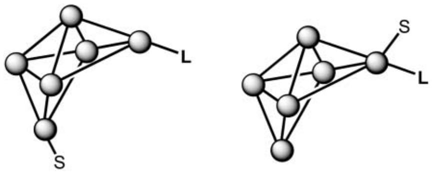
Fig. 6 The dependence of $1/k_{obs}$ on $1/[Br^-]$ for the reaction of $Rh_6(CO)_{15}(PPh_3)$ with bromide in oxygen-free $CHCl_3$ at 38.5 °C. The intercept and gradient give values of $1/k_1$ and k_{-1}/k_1k_2, respectively (see eqn. (9)).

This scheme implies that all the subsequent steps are relatively fast and the cleanness of the spectroscopic changes, as shown in Fig. 1, shows that the steps suggested in eqns. (2)–(7) are sufficient to account for the overall yields without complicating side reactions.

A crucial feature of Fig. 5 is that the rate constants were obtained using initial concentrations of complex that varied by a factor of over six (see data in Table S2, ESI†) This precludes the rate-determining step being CO-dissociation. Although CO is present as a product during the reactions its concentration varies from zero to only one equivalent of the initial cluster concentration as the reaction proceeds. This would lead to progressive retardation of the rates during the course of the reactions and, therefore, to non-linear rate plots, if the reverse of CO dissociation were occuring. In addition, this small average concentration of CO would vary by a factor of >6 as the initial concentration of cluster was varied by this factor. This would inevitably lead to less and less effective retardation as that concentration decreased, and to less and less curvature in plots such as that in Fig. 5. Such behaviour has been observed in substitution reactions that were sufficiently sensitive to released CO that retardation due to that CO occurred at higher concentrations of complex. Progressive diminution of the cluster concentration led eventually to the absence of any retardation.[44] It is also unlikely that the small amounts of CO released would be enough to compete to this extent with the reaction with bromide. Such retardation of CO-dissociative reactions are usually studied with applied pressures of CO, with [CO] constant at ~10^{-2} M. Attempts to do this with these reactions led to complications in the spectroscopic changes and severe irreproducibility of the rate constants. We attribute this to direct reactions of CO with the reactive intermediate, and major changes in the reaction sequence. Although a reaction with $P(OPh)_3$ under an atmosphere of CO did lead to a diminution of the rate constant, this is a necessary *but not sufficient* indication of a CO dissociative reaction.[45]

We therefore conclude that reaction does indeed proceed *via* the sequence shown in eqn. (8), and we propose that the reactive intermediate $Rh_6(CO)_{15}L^*$ is a form of the cluster that has undergone opening to a '*nido*' structure with one less Rh–Rh connectivity. This decreased connectivity involves loss of a 'bond' between the Rh atom to which the PPh_3 is attached and one other Rh atom, *i.e.* there is a decrease in the number of connectivities from 12 to 11. Although 86-electron clusters with six metal atoms and only 11 connectivities are quite well known as isolated and fully characterised clusters,[6] we believe that a vacant coordination site formed by heterolysis of that Rh–Rh bond would be filled by a solvent molecule, chlorocarbon ligands being perfectly capable of stabilising Rh_6 centres.[46] The charge separation that occurs on Rh–Rh bond heterolysis can be dissipated by formation of bridging CO groups between the three pairs of rhodium atoms involved in an opened Rh_4 moiety in a way that has been invoked before as being possible in associative reactions of metal carbonyl clusters.[9] However, such a repositioning of the CO ligands does not appear to be generally necessary as a means of dissipating the charge separation, no pronounced structural changes of that sort being observed when an acetonitrile ligand is added to the cluster $Ru_5(C)(CO)_{15}$.[47] Indeed the moderately polar nature of the $CHCl_3$ solvent could well help to stabilise a degree of charge separation that might remain if formation only of *semi*-bridging CO ligands occurred.

Without being specific about the exact positions of the CO ligands the structures below are simple and reasonable descriptions of two possible solvated forms of $Rh_6(CO)_{15}L^*$ where the solvent molecule can be coordinated to the Rh atom to which the P-donor is connected, or to a neighbouring Rh atom. This distinction must be related to the relative rates of formation of the two pairs of products in eqn. (8). There is no evidence as to when the $CHCl_3$ molecule (S) enters the coordination site, *i.e.* whether it enters after the vacant coordination site is completely formed, or during the process of homolysis. Further studies involving P-donors with different electronic and steric properties might help to answer these questions. These solvated $Rh_6(CO)_{15}L^*$ intermediates are capable of reacting with halides or, indeed, with $P(OPh)_3$ which leads to substitution and fragmentation instead of redox reactions.



A spontaneous opening of the Rh_6 cluster would be rather unusual, spontaneous breaking of Mn–Fe and Fe–Fe bonds in $Cp(CO)_2MnFe_2(CO)_6(\mu\text{-}PR)$ and $RPFe_3(CO)_{10}$ clusters, respectively, being two reported examples.[48,49] On the other hand, *induced* cluster opening by nucleophilic attack is thought to be a virtually universal mechanism for associative reactions of metal carbonyl clusters with P-donor and similar ligands.[50] Solvent assisted cluster opening might therefore be occuring in this case.

There is also good structural evidence in favor of the nido species intermediacy. A detailed study of the structural parameters in mono-substituted $Rh_6(CO)_{16}$ derivatives[25] showed that there is considerable elongation of the Rh–Rh bonds in the immediate vicinity of the phosphorus donor ligands, exactly as required by our proposal. This ligand effect is statistically meaningful and essentially provides an enhanced tendency for *nido* cluster formation through a "pre-preparation" of the ground state of these molecules, thus lowering the energy gap between the ground and transition states. It is also worthwhile to note at this point that other distortions found in the solid state structures of $Rh_6(CO)_{15}(PR_3)$ clusters correlate well with the mechanisms of intramolecular CO scrambling reactions,[51,52] thus demonstrating again the close relations between ground state structural parameters of these molecules and their dynamic properties.

The limiting rate constants at high [halide] are a measure of k_1, the rate constant for the spontaneous or solvent induced cluster opening of the Rh_6 cluster in deoxygenated solvent, but reactions with bromide in oxygenated acidic solution are also governed by the same limiting rate constant k_1. Protonation of reactive intermediates, to form hydride clusters that are very unstable to oxidation, can presumably account for this.

The value of 2.8×10^3 M^{-1} for k_2/k_{-1} indicates that the reverse, *nido* to *closo*, reaction of the cluster is quite difficult in comparison to attack even by the weakly nucleophilic bromide ion. In the absence of the structural weakness induced by the substituent, and in the case of reactions with more nucleophilic ligands, such as P-donors, one would expect the reactions always to occur at the limiting rates. No evidence for reversible cluster opening would be obtained, and a CO dissociative mechanism might be supposed to be operating. In the same vein, the structural weakness due to the substituent might encourage a contribution from direct nucleophilic attack, even by the rather weak P-donor, $P(OPh)_3$, nucleophilic attack being accompanied by induced *closo* to *nido* cluster opening.

A plot of values of $\log k_1$ against pK_a', which is a useful measure of the sigma donicity of the $P(p\text{-}XC_6H_4)_3$ ligands,[53] is given in Fig. 7 The gradient of the linear plot is positive and significant, showing that cluster opening is facilitated by better sigma electron donors, but the effect is quite small and was not detected in the Rh–Rh bond lengthening mentioned above.[25] Because these ligands all have the same cone angle of 145°, no indication of steric effects is available although higher cone angles would also be expected to facilitate cluster opening. Thus, reactions of clusters substituted with large, highly donor ligands such as PCy_3 would be expected to undergo cluster opening even faster.

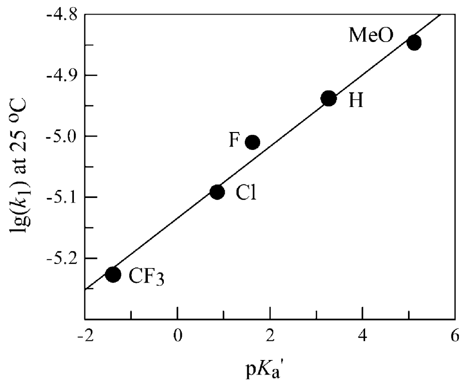


Fig. 7 Dependence of $\log(k_{obs})$ ($k_{obs} = k_1$) for the reactions of $Rh_6(CO)_{15}P(p\text{-}XC_6H_4)_3$ with bromide in oxygenated and acidified $CHCl_3$ at 25 °C on the sigma-donating ability of the phosphine ligands. The gradient is 0.059 ± 0.004, with $r^2 = 0.993$ and $\sigma(\log k_{obs}) = 0.2$.

The activation parameters in Table 2 show a very rough isokinetic, or compensation, plot of $\Delta H^‡$ against $\Delta S^‡$, and the gradient indicates that all the reactions would proceed at similar rates at *ca.* 40 °C. This is fairly close to the temperature at which the linear free energy plot of $\log k_1$ *vs.* pK_a' was plotted and this will lessen the observed dependence of $\log k_1$ on pK_a'. The activation parameters do not show any correlation with ligand basicity but all show low-to-moderate values of $\Delta S^{\ddagger}$ consistent with rather little, but variable, increases in the "flexibility" of the transition states as the *nido* structure is approached, or to variations in the contributions of Rh–S bond making. The values of *ca.* 100 kJ mol^{-1} for $\Delta H^{\ddagger}$ relate evidently to the 'ease of breaking' the Rh–Rh bond, but not to its intrinsic (or static) strength because Rh–Rh bond breaking is not necessarily near to completion in the transition states, and any contributions from Rh–S bond making would be important. Changes in other Rh–Rh and Rh–CO interactions as the *nido* structure is approached are to be expected.

Summary

These kinetic studies of some substituted Rh_6 carbonyl clusters show that the effects of the substituents on the structures of the clusters are also made manifest in their reactivity to the extent that they induce an opening up of the cluster which might be spontaneous or solvent induced. Usually such opening up of clusters is the result of photochemical activation, or is induced by direct nucleophilic attack. The participation of halide ions in these reactions does not, therefore, reflect any contributions from attack on the coordinated CO ligands such as is seen with other clusters' reactions with hard nucleophiles. Similar results would therefore have been obtained if only P-donor nucleophiles had been used, except for the fact that the weakness of bromide as a nucleophile allows for observation of the competition between bromide attack and reverse closure of the *nido* intermediate. This was the essential feature in demonstrating that the *closo* to *nido* cluster opening is rate determining. The complex stoichiometry of the reactions with halides and $P(OPh)_3$ is also illustrative of the very wide variety of redox, substitution and fragmentation chemistry that these Rh_6 clusters can undergo.

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