Spectroscopic titration of $[Re_4(\mu_3\text{-}H)_4(CO)_{12}]$ with chloride ions. An electron-precise tetranuclear cluster as intermediate in the transformation of a tetranuclear unsaturated cluster into trinuclear unsaturated anions

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The unsaturated tetrahedral cluster $[Re_4(\mu_3\text{-}H)_4(CO)_{12}]$ easily added halide ions giving $[Re_4H_4X(CO)_{12}]^-$ anions, which in the presence of even poor donor species underwent fragmentation to unsaturated triangular cluster anions.

The reactivity of the tetrahedral cluster $[Re_4(\mu_3\text{-}H)_4(CO)_{12}]$[1] **1** is at present actively investigated[2,3] because of its high electronic unsaturation (56 valence electrons, v.e.s). Previous studies focused on the reactions of **1** with two-electron donors L, resulting in fragmentation to triangular clusters through an 'ionic' or a 'neutral' pathway: according to the nature of L, either unsaturated $[Re_3(\mu\text{-}H)_4(CO)_9L]^-$ anions (46 v.e.s) or saturated $[Re_3(\mu\text{-}H)_3(CO)_9L_3]$ neutral complexes have been obtained.[2e,3] For L = MeCN, the intermediate formation of $[Re_4H_4(CO)_{12}L_4]$ has been demonstrated (64 v.e.s and spiked-triangle structure), corresponding to the addition of double the number of ligands required to attain saturation.[3b] In the case of particularly labile ligands (such as methanol, acetone or tetrahydrofuran) the unsaturated anions $[Re_3(\mu\text{-}H)_4(CO)_9L]^-$ in non-donor solvents reversibly give a species **2**, which behaves as a *super*unsaturated '$[Re_3H_4(CO)_9]^-$' anion (44 v.e.s), even if its true formulation is still uncertain.[3a]

We report here the first results concerning the reactivity of cluster **1** with anions. Its titration with a solution of $[PPh_3(CH_2Ph)]Cl$, monitored by IR and NMR spectroscopy at room temperature in non-donor solvents, showed that upon addition of up to 1 equivalent of Cl^- the main reaction product was a novel species, exhibiting two hydridic resonances in the ratio 1 : 1 [Fig. 1(*a*) and (*b*), Table 1], which can be formulated as the addition derivative $[Re_4H_4Cl(CO)_{12}]^-$ **3**.

The most likely structure for cluster **3** can be derived from that (of C_2 symmetry) observed[4] in the solid state for the unsaturated (58 v.e.s) anion $[Re_4(\mu_3\text{-}H)_2(\mu\text{-}H)_3(CO)_{12}]^-$ **4**, by substituting the unique hydride of **4** with a halide ion (Scheme 1). The relationship between clusters **4** and **3** has been substantiated in two ways: (*i*) by obtaining **4** upon addition of H^- to **1** [equation (1), X = Cl or H]† or (*ii*) by converting **4** into **3**, according to reaction (2). In both cases (X = Cl or H) reaction (1) could be reversed by using appropriate electrophiles (CF_3SO_3H for **4**, $TlPF_6$ for **3**, CH_2Cl_2, room temperature)‡ [see equation (3); X = Cl, E = Tl; X = E = H].

$$[Re_4(\mu_3\text{-}H)_4(CO)_{12}] + X^- \longrightarrow [Re_4H_4X(CO)_{12}]^- \quad (1)$$

$$[Re_4H_5(CO)_{12}]^- + HCl \longrightarrow [Re_4H_4Cl(CO)_{12}]^- + H_2 \quad (2)$$

$$[Re_4H_4X(CO)_{12}]^- + E^+ \longrightarrow [Re_4(\mu_3\text{-}H)_4(CO)_{12}] + EX \quad (3)$$

The observation of two separate resonances for the two types of hydrides in **3** indicates that the presence of the halide freezes the scrambling of the hydrido ligands, which in **4** are in fast exchange even at 183 K. In the anion **3** the hydridic resonances begin to broaden only above 253 K and are almost collapsed at *ca.* 300 K [E_a = 59(4) kJ mol^{-1}, from the simulation of the spectra].

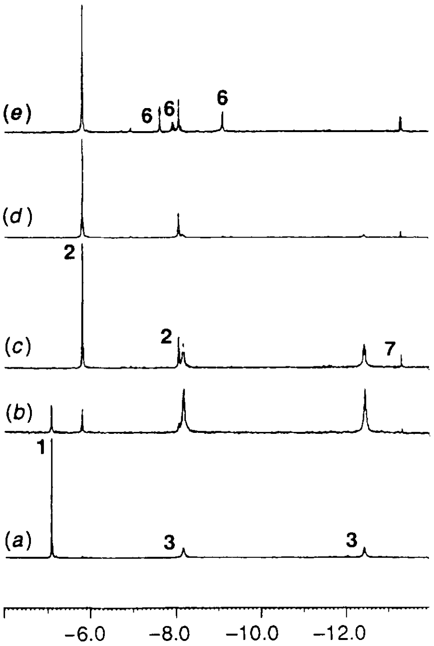

Fig. 1 Hydridic region of the 200 MHz ^1H NMR spectra of a sample of cluster **1** (4.2 μmol in 0.7 cm^3 of CD_2Cl_2) titrated, at room temperature, with a solution of $[PPh_3(CH_2Ph)]Cl$ (81 mmol dm^{-3}) in $CDCl_3$. Spectra recorded at 263 K, after addition of (*a*) 20 mm^3 (0.4 equivalent), (*b*) 45 (0.9), (*c*) 70 (1.4), (*d*) 95 (1.9) and (*e*) 145 (2.9). The resonances of **3** are broadened by the exchange of the hydrides. The vertical scale of spectrum (*d*) is half that of spectra (*a*)–(*c*) and (*e*)

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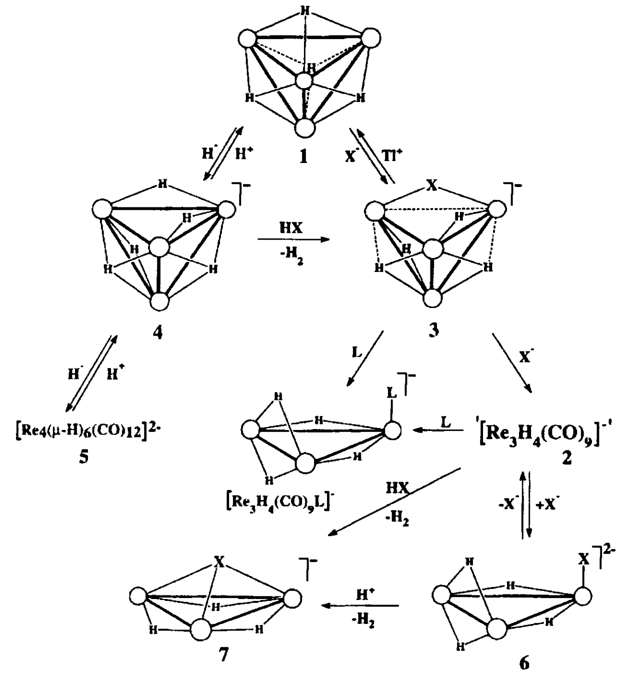
† It has been previously reported[1] that the treatment of cluster **1** with $NaBH_4$ gives the 60 v.e.s dianion $[Re_4(\mu\text{-}H)_6(CO)_{12}]^{2-}$ **5**. We have now recognized the intermediate formation of **4** (previously obtained[4] by treatment of **5** with strong acids), even if it is difficult to stop the reaction at the first H^- addition.

‡ Upon treatment of **3** (generated *in situ* by titration of **1** with 1 equivalent of Cl^-) with a slight excess of solid $TlPF_6$ the solution slowly acquired the red-brown colour of **1**. Infrared and NMR spectra also showed some fragmentation to **2** and other minor unidentified by-products.



Scheme 1 Reactions of $[Re_4(\mu_3\text{-}H)_4(CO)_{12}]$ **1** with anions X^- and H^-, and fragmentation paths of **3**. O = $Re(CO)_3$

Table 1 Proton NMR data (in CD_2Cl_2) of the tri- and tetra-nuclear anions obtained by treating cluster **1** with anions

Anion	Cl	Br	I
3	−8.30	−8.46	−9.08
	−12.57	−13.30	−14.37
6	−7.70	−7.58	−7.29
	−8.02	−7.86	−7.66
	−9.22*	−9.80*	−11.09*
7	−13.34	−14.34	−15.43

* Resonance of double-integrated intensity.

¶ The anion **3** has 60 valence electrons, as expected for saturated tetrahedral clusters.§ Nevertheless it readily reacts with any (even poor) donor species, with fragmentation to lower nuclearity species. So the titration with Cl^- ions beyond the equivalence point caused the disappearance of **3**, almost to completeness after addition of 2 equivalents of Cl^-. The reaction, slow at low temperatures [Fig. 2(*b*) and (*c*)], was instantaneous at room temperature and gave with good selectivity [Fig. 1(*d*)] the trinuclear 'superunsaturated' anion **2** (easily identified by its resonances at δ −5.83 and −8.09, 3 : 1). The Cl^- anions therefore cause the decomposition of **3** by stabilizing the $Re(CO)_3Cl$ moiety lost in the fragmentation. ¶

A related process took place upon treatment of **3** with neutral ligands L, such as CO or MeCN, affording the previously known[5] unsaturated (46 v.e.s) $[Re_3(\mu\text{-}H)_4(CO)_9L]^-$ anions (Scheme 1). Even an extremely poor donor molecule such as acetone was able to cause the fragmentation of **3**. The anion **2** was formed in this case, acetone being too labile a ligand to stabilize the 46 v.e.s $[Re_3(\mu\text{-}H)_4(CO)_9(Me_2CO)]^-$ anion [equation (4)].

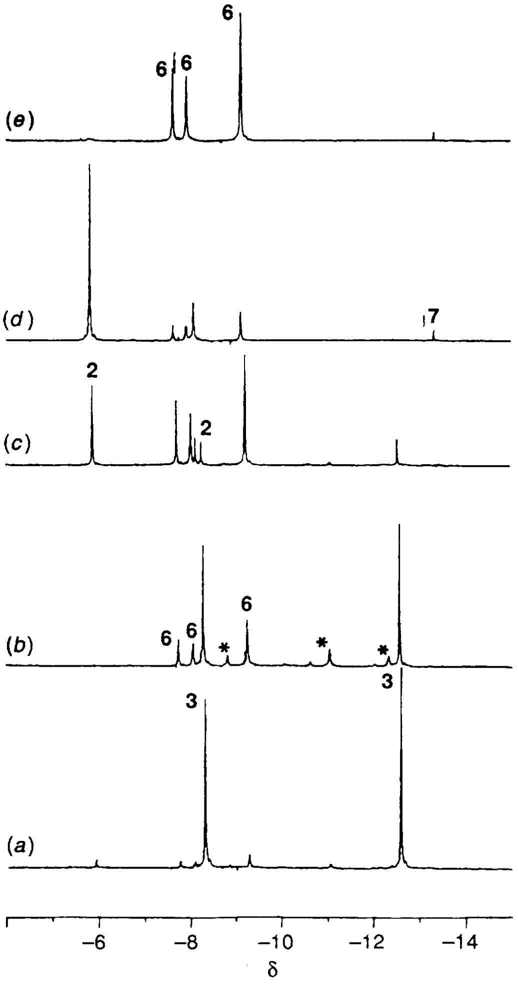


Fig. 2 Hydridic region of the 200 MHz ^1H NMR spectra of a sample of cluster **1** (11.3 μmol in 0.5 cm^3 of CD_2Cl_2) treated with increasing amounts of solid $[PPh_3(CH_2Ph)]Cl$ at 193 K. (*a*) Recorded at 203 K, after addition of 1 equivalent of Cl^-, (*b*) at 213 K after addition of a further equivalent of Cl^-, (*c*) at 233 K, after *ca.* 1 h, (*d*) at 273 K and (*e*) at 273 K, after addition of 2.5 equivalents of Cl^-. The minor peaks marked with an asterisk in spectrum (*b*) are due to unidentified intermediates

$$[Re_4H_4Cl(CO)_{12}]^- + 3L \longrightarrow [Re_3(\mu\text{-}H)_4(CO)_9L]^- + ReCl(CO)_3L_2 \quad (4)$$

The NMR titration of **3** with a still higher excess of chloride led to the appearance of a novel species **6** [Fig. 1(*e*), Table 1], whose NMR data support the formulation as the 46 v.e.s triangular cluster dianion $[Re_3(\mu\text{-}H)_4Cl(CO)_9]^{2-}$ [Scheme 1, equation (5)], analogous to the $[Re_3(\mu\text{-}H)_4(CO)_9L]^-$ anions

$$\text{'}[Re_3H_4(CO)_9]^-\text{'} + Cl^- \rightleftharpoons (Re_3(\mu\text{-}H)_4Cl(CO)_9]^{2-} \quad (5)$$

described above. Reaction (5) is reversible and the equilibrium can be driven to either side by varying the amount of chloride or the temperature [see Fig. 2(*c*)–(*e*)]. A similar behaviour was previously recognized in the equilibrium mixtures of **2** with methanol and acetone.[3a] In agreement with this, the low-temperature fragmentation of **3** in the presence of Cl^- gave **6** as the main product [Fig. 2(*b*) and (*c*)].

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§ The anion **3** could also be viewed as an unsaturated (two electrons short) butterfly species, in keeping with the low δ value of one of its hydridic resonances: in fact in rhenium clusters the presence of two hydrides μ or μ_3 bridging the same edge is usually associated with electronic unsaturation and with particularly low-field resonances.[4–6] In the present case there are no arguments to establish if these hydrides are face or edge bridging, and this is the reason for the dotted lines in Scheme 1.

The fate of this fragment has not been investigated in detail, but the stoichiometry of the reaction (⩾2 equivalents of Cl^-) suggests the formation of the previously known[7] anions $[Re_2(\mu\text{-}Cl)_2Cl_2(CO)_6]^{2-}$ and $[ReCl_3(CO)_3]^{2-}$. Infrared monitoring agrees with this, but it is not conclusive owing to the overlapping absorptions of the Re_3 anions.

The low-intensity resonance at δ −13.34, which appears in the NMR spectra at temperatures higher than 273 K, is attributable to the saturated anion $[Re_3(\mu\text{-}H)_3(\mu_3\text{-}Cl)(CO)_9]^-$ **7**, likely formed by reaction of **6** with traces of acidic species. The formation of this anion, indeed, is made quantitative by the addition of 1 equivalent of a strong acid, such as CF_3SO_3H, according to reaction (6).

$$[Re_3(\mu\text{-}H)_4Cl(CO)_9]^{2-} + H^+ \longrightarrow [Re_3(\mu\text{-}H)_3(\mu_3\text{-}Cl)(CO)_9]^- + H_2 \quad (6)$$

Preliminary experiments with bromide and iodide anions have given similar results (see Table 1) and the reactions will be investigated in detail in subsequent work. The key points we notice here are: (*i*) the reaction of compound **1** with halide ions affords monoaddition derivatives, with 60 v.e.s and is therefore completely different with respect to its reaction with neutral donors L, in which addition derivatives with 64 v.e.s and spiked-triangle clusters are formed; (*ii*) most importantly, these 60 v.e.s derivatives maintain the instability of the parent superunsaturated cluster **1** toward any substance with donor power; and (*iii*) the fragmentation of **3** gives unsaturated triangular anions whatever the ligand used, showing that halides are particularly effective in promoting the 'ionic' fragmentation with respect to the 'neutral' one, due to their ability to stabilize the $[Re(CO)_3]^+$ fragment lost in the 'ionic' cleavage.

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