Synthesis and Reactivity of $[NEt_4]_2[ReBr_3(CO)_3]$. Formation and Structural Characterization of the Clusters $[NEt_4][Re_3(\mu_3\text{-}OH)(\mu\text{-}OH)_3(CO)_9]$ and $[NEt_4][Re_2(\mu\text{-}OH)_3(CO)_6]$ by Alkaline Titration†

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The dianionic rhenium(I) complex $[ReBr_3(CO)_3]^{2-}$ has been synthesized and characterized. This complex is an important starting material for compounds containing the *fac*-$Re(CO)_3$ moiety since the three bromide ligands are very weakly bound. Particularly in co-ordinating solvents, the bromides are substituted by solvent molecules thus generating the strong $12e^-$ Lewis acid $[Re(H_2O)_3(CO)_3]^+$ **2**. This formula was confirmed, particularly in water, by IR spectroscopic methods. Complex **2** is stable in aqueous solution even when exposed to air for weeks. It has been titrated by NaOH solutions. The change in pH was detected potentiometrically and found to occur very slowly, indicating a reaction other than protonation/deprotonation. Depending on the rate of titration and the total concentration of OH^-, the two rhenium(I) hydroxo complexes $[NEt_4][Re_3(\mu_3\text{-}OH)(\mu\text{-}OH)_3(CO)_9]$ and $[NEt_4][Re_2(\mu\text{-}OH)_3(CO)_6]$ were isolated in good yield and structurally characterized. The former crystallizes in the orthorhombic space group *Pnma* with $a = 10.752(7)$, $b = 13.783(8)$ and $c = 18.254(12)$ Å. The skeletal framework is that of a cube lacking the $Re(CO)_3$ unit in one corner. The latter crystallizes in the orthorhombic space group *P2mm* with $Z = 1$, $a = 6.551(2)$, $b = 7.413(2)$ and $c = 12.084(2)$ Å. The two $Re(CO)_3$ moieties are bridged by three OH^- ligands which create a mirror plane. A second mirror plane is perpendicular to it along the Re–Re axis.

Rhenium-186 has been described as one of the most promising radionuclides for application in radioimmunotherapy.[1,2] Its decay characteristics suggest that a high dose deposition at the tumour site may be expected with a lower whole-body radiation burden than is observed with the frequently used nuclide ^{131}I. The chemistry of labelling antibodies with rhenium has been investigated following protocols worked out with the chemically related element technetium[3,4] where the procedures and the ligand systems have been extensively studied. Consequently the fundamental approaches are the same, *i.e.* bifunctional N,S-containing ligands are employed and metal ions are usual in the +V oxidation state.[5] Since perrhenate is more difficult to reduce than pertechnetate, the corresponding rhenium(V) complexes are less stable. For the above reasons we decided to focus our research on the +I oxidation state of rhenium for the labelling of proteins. A number of water-soluble rhenium(I) compounds such as $[Re(C_6H_6)(CO)_3]^+$ and $[Re([9]aneS_3)(CO)_3]^+$ ($[9]aneS_3$ = 1,4,7-trithiacyclononane) have been described as exceptionally stable in water, mainly due to kinetic rather than to thermodynamic stabilization.[6,7] We have investigated the synthesis of such compounds directly from aqueous solution under typical conditions suitable for use in the labelling of proteins. For the *in situ* generation of the '*fac*-$Re(CO)_3$' unit, $[ReBr_3(CO)_3]^{2-}$ **1** is a very convenient starting material. Its synthesis was first described some twenty years ago,[8,9] but its chemistry, especially in aqueous media, has scarcely been investigated in respect of its reactivity towards water. The three bromides are highly labilized by the strong *trans* influence of the carbonyl ligands and are thus expected to undergo at least partial substitution with solvent molecules. Precipitation of halides with Ag^+ for example results in activated complex moieties. However, these activations are often performed in acetonitrile, which itself can act as a good ligand due to its π-accepting ability.[10,11] Only a few examples are known where the activation of organometallic compounds has been performed in water.

We report here on the stability of $[ReBr_3(CO)_3]^{2-}$ in water and its reactivity towards OH^-. Precipitation of the halides creates an '*aqua-ion*' of '$Re(CO)_3^+$' with the tentative composition $[Re(H_2O)_3(CO)_3]^+$ **2**. Compared to other strong Lewis acids, such as $[Re(H_2O)(CO)_5]^+$,[12,13] this compound was found to be very stable to decomposition. It has been reported[14] that the alkaline hydrolysis/oxidation of the usual starting material $[Re_2(CO)_{10}]$ results in the formation of a very stable cubane cluster $[Re_4(\mu\text{-}OH)_4(CO)_{12}]$ **3**. There was however no reference as to whether any by-products or intermediates were found. A more detailed study on the carbonylation of $[ReO_4]^-$ in the presence of carbonate under different conditions revealed that polynuclear hydroxo- or alkoxo-bridged rhenium(I) intermediates are generated as the main products.[15]

Experimental

Materials.—All chemicals and solvents were obtained from Fluka and used without further purification. All preparations were carried out using standard Schlenk techniques. Although none of the complexes is sensitive to water or oxygen, the preparations were carried out under purified nitrogen.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Table 1 Crystallographic data and details of data collection and processing for complexes **4** and **5**

	4	**5**
Empirical formula	$C_{17}H_{24}NO_{13}Re_3$	$C_{14}H_{27}NO_{11}Re_2$
M	1027.0	746.5
Crystal size/mm	0.04 × 0.2 × 0.2	0.04 × 0.2 × 0.06
Space group	*Pnma*	*P2mm*
a/Å	10.752(7)	6.551(2)
b/Å	13.783(8)	7.413(2)
c/Å	18.254(12)	12.084(2)
U/Å^3	2705(3)	586.8(3)
Z	4	1
D_c/Mg m^{-3}	2.522	2.112
μ/mm^{-1}	13.454	10.356
F(000)	1888	337
Diffractometer	Syntex P21	Picker Stoe
2θ range/°	2.0–45.0	3–45.0
hkl ranges	0–11, 0–14, 0–13	0–7, 0–7, 0–13
Reflections collected	1860	485
Independent reflections	1860	485
Observed reflections [$F_o > 4\sigma(F_o)$]	1417	442
Number of parameters refined	175	69
Final R,R' (obs. data)	0.024, 0.024	0.051, 0.056
Goodness of fit	2.38	7.64

Details in common: colourless platelet crystal, orthorhombic; Mo-Kα radiation (λ = 0.710 73 Å); ambient temperature, highly oriented graphite-crystal monochromator; ω–2θ scans; scan speed 2.00–5.00° min^{-1}; stationary crystal and counter at beginning and end of scan; one standard reflection measured every 120; refinement by full-matrix least squares minimizing $\Sigma w(F_o - F_c)^2$, $w = 1/\sigma^2(F)$. High values of the goodness-of-fit parameter are due to systematic deviations in the low-order region of the reflections caused by disorder phenomena; particularly for species **5**, this disorder is confined to NEt_4 and H_2O and is therefore of minor relevance within the context of this paper.

Syntheses.—$[NEt_4]_2[ReBr_3(CO)_3]$ **1**. In a typical reaction, powdered NEt_4Br (1.69 g, 8.05 mmol) was slurried in 2,5,8-trioxanonane (diglyme) (300 cm^3) under dry nitrogen and heated to 80 °C. A suspension of $[ReBr(CO)_5]$ (1.5 g, 3.7 mmol) in warm diglyme (20 cm^3) was slowly added. The mixture was left at 115 °C for 4–5 h during which time a white precipitate formed. The reaction mixture was filtered whilst hot and washed with several portions of cold diglyme, diethyl ether and dried *in vacuo*. The resulting white powder was then slurried in ethanol (8–10 cm^3) to remove unreacted NEt_4Br. Filtration and drying *in vacuo* yielded the product as a white analytically pure powder (2.2 g, 80%). Extended reaction times gave better yields. Complex **1** is slightly soluble in ethanol so that a quantity of the product is lost during the washing procedure (Found: C, 29.75; H, 5.35; N, 3.80. $C_{19}H_{40}Br_3N_2O_3Re$ requires C, 29.60; H, 5.25; N, 3.65%).

$[NEt_4][Re_3(\mu_3\text{-}OH)(\mu\text{-}OH)_3(CO)_9]$ **4**. A solution of $AgNO_3$ (0.051 g, 0.3 mmol) in water (0.5 cm^3) was added at room temperature to a solution of complex **1** (0.077 g, 0.1 mmol) in water (0.5 cm^3), resulting in instantaneous loss of the three bromides and quantitative formation of a yellowish AgBr precipitate. After filtration, 1 mol dm^{-3} NaOH (0.133 mmol) was allowed to diffuse into the clear solution. After a few hours some crystals could be recognized and 1 week later colourless, thorn-like *crystals* of complex **4** were collected (0.02 g, 57%). More product can be obtained if the aqueous solution is extracted with CH_2Cl_2 (Found: C, 20.50; H, 2.75; N, 1.55. $C_{17}H_{24}NO_{13}Re_3$ requires C, 20.25; H, 2.40; N, 1.40%). The fast atom bombardment mass spectrum displayed typical Re_3 patterns at m/z = 1139.1 ($\{[NEt_4]_2[Re_3(OH)_4(CO)_9]\}^+$), 878.8 ($\{H_2[Re_3(OH)_4(CO)_9]\}^+$) and 861.9 ($\{H[Re_3(OH)_3(CO)_9]\}^+$). ν_{max} at 3622s, 3446(br), 2992w, 2004vs, 1906vs, 1880vs, 1856vs, 1846vs, 1636m, 1488m, 1396w, 1174w, 1002w, 882m, 786w, 652w, 512m and 484m cm^{-1} (KBr disc).

$[NEt_4][Re_2(\mu\text{-}OH)_3(CO)_6]$ **5**. An aqueous solution (2 cm^3) of $AgNO_3$ (0.051 g, 0.3 mmol) was added at room temperature to a solution of complex **1** (0.077 g, 0.1 mmol) in water (2 cm^3). After the AgBr had been filtered off, the solution was mixed with 1 mol dm^{-3} NaOH (0.300 mmol) and stirred immediately to prevent the formation of **4**. It was allowed to stand for about 2 weeks before colourless, strongly twinned square platelets were isolated. These were mechanically separable into untwinned fragments (0.022 g, 61%). If the reaction was performed with higher concentrations of NaOH, precipitation of **5** in similar yield and of analytically pure quality was obtained (Found: C, 22.30; H, 3.55; N, 1.90. $C_{14}H_{27}NO_{11}Re_2$ requires C, 22.20; H, 3.60; N, 1.85%). The fast atom bomardment mass spectrum displayed a Re_2 pattern at m/z = 851.1 corresponding to $\{[NEt_4]_2[Re_2(OH)_3(CO)_6]\}^+$; Other Re_2 peaks were found at m/z = 1149.3, 1042.3 and 986.2. ν_{max} at 3638m, 3316(br), 3146(br), 1998vs, 1858vs, 1484m, 1438w, 1172w, 996w, 786w, 650w, 516m and 476m cm^{-1} (KBr discs).

Crystallography.—Details of the crystal data, intensity measurement and data processing for complexes **4** and **5** are summarized in Table 1. For the calculation of the structure factors, corrections for Lorentz polarization effects and absorption (face-index numerical) were made. The structures were solved by direct methods. Subsequent Fourier-difference map analysis yielded the positions of the non-hydrogen atoms. The hydrogen atoms were included at calculated positions but not refined. Difference maps after the refinement showed the largest peak at 1.15 e Å^{-3} for **4** and 2.34 e Å^{-3} for **5** close to the Re atom. Atomic coordinates are summarized in Table 2. The SHELXTL program package[16] was employed for the solution and refinement.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Synthesis of $[NEt_4]_2[ReBr_3(CO)_3]$ **1**.—A different procedure for the synthesis of **1** yielded as the other main product the compound $[NEt_4][ReBr_2(CO)_4]$ **6**.[17] We used larger amounts of NEt_4Br and extended the reaction time to yield **1** almost quantitatively. Analysis of the diglyme solution or the raw products revealed no evidence for the presence of **6** or higher-nuclearity species. We assume that **6** is formed as a soluble intermediate which reacts further slowly to give $[NEt_4]_2[ReBr_3(CO)_3]$. Owing to its weak donating properties the Br^- is not expected to be very strongly bound and the only reason for the isolation of **1** is its complete insolubility even in refluxing diglyme. Several other complexes of general composition $[ReL_3(CO)_3]^+$, where L = NH_3,[18] MeCN[19] or Me_3NO,[20] have been prepared by similar procedures and structurally characterized. However the complexes with MeCN and Me_3NO are described as very stable in solution, due especially to the good π-accepting properties of these ligands. Thus their chemical reactivity can hardly be compared to that of compound **2** since its ligands have only weak σ-donating properties.

Behaviour in Water and Organic Solvents.—Complex **1** is very soluble in solvents with co-ordinating properties such as water, methanol or acetonitrile and slightly soluble in solvents with low tendency for metal co-ordination like tetrahydrofuran (thf), diglyme or dichloromethane. It is completely insoluble in non-co-ordinating solvents. As mentioned earlier, weakly binding anions like Br^- can often be exchanged in solution by solvent molecules. The resulting equilibrium is described in Scheme 1.

$$[ReBr_3(CO)_3]^{2-} + nH_2O \rightleftharpoons [ReBr_{3-n}(H_2O)_n(CO)_3]^{n-2} \rightleftharpoons [Re(H_2O)_3(CO)_3]^+$$

Scheme 1 Possible intermediates resulting from partial substitution of Br^- by water molecules

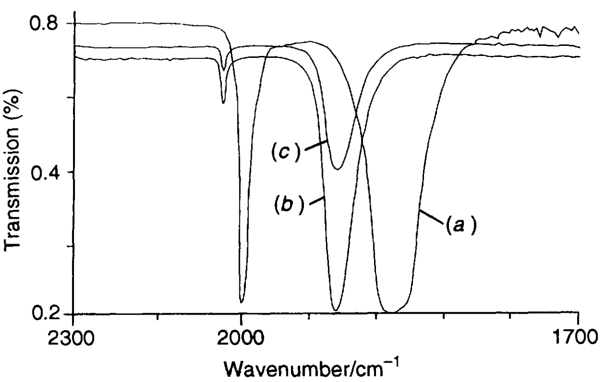

Fig. 1 Infrared spectra of complex **1** in the CO stretching region. (*a*) as solid in KBr disc; (*b*) as aqueous solution of **1** without precipitation of AgBr; (*c*) as aqueous soution after precipitation of AgBr

The proportions of the different species depends on the stability constants and the ligand concentration. Stability constants can often be determined in aqueous but not in organometallic chemistry, as the exchanged ligand in the latter case is often a volatile CO molecule.

In the case of low-valent metal centres the stability of a co-ordinated ligand is increased by its π-accepting properties. Solvent molecules with such properties should therefore easily substitute the bromides in the case of complex **1**. This assumption was confirmed by investigating an acetonitrile solution of **1** by IR spectroscopic methods. The carbonyl bands of **1** were readily replaced by those of $[Re(MeCN)_3(CO)_3]^+$ (2050 and 1948 cm^{-1}) and we could isolate this complex in quantitative yield. Attempts to grow crystals from water or methanol resulted in the isolation of NEt_4Br crystals and oily residues indicating the very low stability of the co-ordinated Br^- which prefers precipitation as NEt_4Br rather than co-ordination to the '$Re(CO)_3$' moiety. The equilibrium in Scheme 1 would be pushed towards the tribromide only when using a saturated $(NEt_4)Br$ solution, allowing us to isolate crystals of good quality.

Infrared spectroscopic studies of aqueous solutions of complex **1** confirmed that the equilibrium in water is completely to the right, thus the three Br^- ligands are quantitatively exchanged by water molecules. The spectrum in KBr was as shown in Fig. 1(*a*) with the typical *fac*-$M(CO)_3$ pattern for a complex with D_{3h} symmetry and carbonyl absorptions at 1870 (A_1) and 2001 cm^{-1} (E) when the complex was dissolved in water the spectrum showed the same pattern to be present but shifted to significantly higher wavenumbers, 1916 (A_1) and 2036 cm^{-1} (E) (CO), Fig. 1(*b*), a behaviour which is usually found on increasing the charge of carbonyl complexes to more positive values. Confirmation that the three bromide ligands are completely substituted by water molecules was obtained by precipitation of Br^- as AgBr and subsequent recording of the IR spectrum in water [Fig. 1(*c*)]. Spectra (*b*) and (*c*) are essentially the same in shape and wavenumbers in the carbonyl region, demonstrating clearly the identity of the two species present in aqueous solution before and after precipitation of Br^-

Aqueous solutions of complex **1** with or without precipitation of Br^- thus contain an organometallic 'aqua-ion' of tentative composition $[Re(H_2O)_3(CO)_3]^+$ **2**. Although up to 10 mol dm^{-3} NEt_4Br was added, with the exception of a slight broadening of the E band, no shift in wavenumbers was found. It seems that even at high bromide concentrations no $[ReBr_{3-n}(H_2O)_n(CO)_3]^{n-2}$ is formed ($0 < n < 3$). The aqua-ion **2** is exceptionally stable in aqueous media. We observed the intensity and the wavenumbers of the IR spectrum of solutions of **2** exposed to air for 3 weeks but could not detect any decomposition. On the other hand, complex **2** is very reactive towards *facial* co-ordinating tridentate compounds such as 1,4,7-triazacyclononane, 1,4,7-trithiacyclononane or even benzene. The nitrate of **2** is well soluble in polar organic solvents and reacts readily and quantitatively under ambient conditions with the aforementioned compounds to form complexes of general composition $[ReL(CO)_3]^+$ according to IR spectroscopy.[6,7,21,22]

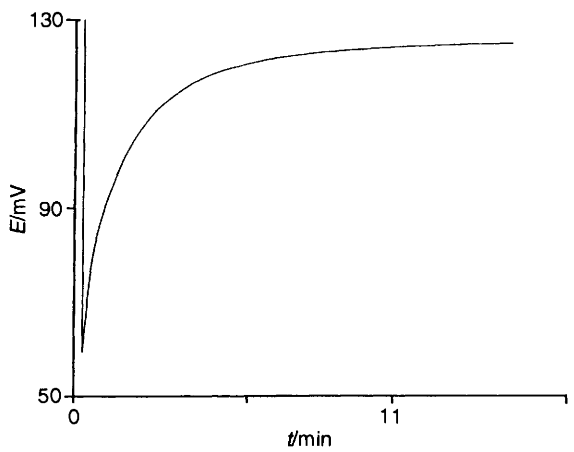

Fig. 2 Course of the pH (mV) as a function of time after addition of a small amount of 1 mol dm^{-3} NaOH to an aqueous solution of complex **1** (I = 0.05 mol dm^{-3} NEt_4ClO_4)

Alkaline Titration of Complex **2** *in Water*.—Many metal aqua-ions, especially from the first transition row, are known to act as Brönsted acids. Typical metal ions are Al^{3+} and Fe^{3+}, so called 'hard' metal centres which have pK_a values between 2 and 5.[23,24] The tendency to deprotonate co-ordinated water molecules mirrors the stability of the resulting hydroxo-complex. Acidity constants of co-ordinated water molecules in metallorganic complexes have scarcely been investigated, the reason being the almost negligible tendency of low-valent metal complexes to co-ordinate OH^-, thus resulting in a high pK_a value. In addition, organometallic compounds tend to decompose in water and to undergo undefined subsequent reactions. Based on the high stability of **2** we were interested to investigate whether an acidity constant could be determined. Since Re^I has a low affinity for strong σ-donating ligands we expected the acidity, if any, to be weak.

Addition of a standard NaOH solution to an aqueous solution of **2** (I = 0.05 mol dm^{-3} NEt_4ClO_4) revealed a rapid increase in the pH, followed by a very slow decrease almost to the original value within some 20 min. Fig. 2 presents a typical trend in the pH (potentiometric measurement) as a function of time after the addition of a small amount of NaOH solution. The change in the initially alkaline pH towards a more acidic value clearly indicates a slow consumption of OH^- ions. Each subsequent addition of NaOH showed the same characteristics in the shape of the curve of pH *vs.* time. A sharp change to alkaline pH values was found only after the addition of 1.34 ± 0.02 OH^- per Re (roughly four OH^- per three Re), indicating the end of hydroxide consumption. The second part of the curve follows that of a normal addition to water. A full titration curve is presented in Fig. 3. The time intervals between each addition are 20 min. Connecting the end points reached after each addition of OH^- in the titration curve yields a picture which corresponds qualitatively to the titration curve of a weak acid. The fact that the ratio between Re and OH^- is not 1 : 1 at the neutralization point, as could be expected for a single deprotonation to give $[Re(OH)(H_2O)_2(CO)_3]$, can be explained by a subsequent reaction without the consumption of additional OH^-. Therefore the reaction must consist in the substitution of terminal water ligands by μ_n-OH bridges, preventing deprotonation of the former as is often found for hard metal centres. By evaporation of the solution, and extraction of the residue with CH_2Cl_2, we were able to isolate almost quantitatively the trinuclear rhenium(I) cluster $[NEt_4]$-

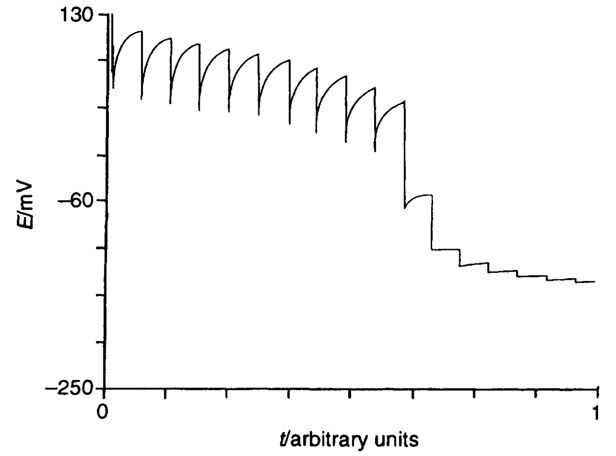

Fig. 3 Full titration curve of complex **1** with 0.1 mol dm^{-3} NaOH. Time interval between each addition is 20 min (I = 0.05 mol dm^{-3} NEt_4ClO_4)

$[Re_3(\mu_3\text{-}OH)(\mu\text{-}OH)_3(CO)_9]$. Its crystal structure could be elucidated (see below).

The occurrence of four μ_n-OH bridges (n = 2 or 3) in the structure explains the end-point after the addition of 1.34 OH^- per Re. The formation of such cluster complexes is well known for hard metal centres where further polymerization often takes place upon a second deprotonation leading to the formation of μ-O bridges. It seems that the negative charge of the incoming OH^- is best stabilized by delocalization over different rhenium centres so that the overall charge per rhenium atom is as low as possible, *i.e.* $\frac{1}{3}^-$ in our case.

The cubane cluster $[\{M(OH)(CO)_3\}_4]$ **3** (M = Re or Mn) was described some 15 years ago[14] as the thermodynamic end-product of thermal or photolytic decomposition and hydrolysis/oxidation of $[M_2(CO)_{10}]$ and was the subject of many studies.[25,26] Although the rate of addition of OH^- was varied over a wide range, neither mass nor IR spectroscopy gave evidence for the formation of **3**.

Structure of $[NEt_4][Re_3(\mu_3\text{-}OH)(\mu\text{-}OH)_3(CO)_9]$.—An ORTEP[27] plot of the complex anion is presented in Fig. 4. An asymmetric unit of the cell contains half of this complex anion since a mirror plane is formed by Re(2), O(6) and O(8). Fractional atomic coordinates are summarized in Table 2, important bond lengths and angles in Table 3. The structure can best be described as a pseudo cubane lacking one $Re(CO)_3{}^+$ unit in a corner which would normally complete the cubane framework. Each Re atom is surrounded by three CO ligands and three OH forming a distorted-octahedral geometry. The average OC–Re–CO angle is 89.1(5)°, thus close to octahedral geometry, but the angles between the bridging hydroxide ligands and the rhenium atoms are significantly contracted. The angle [μ-O(7)]–Re–[μ-O(8)] is 80.3(3)° while [μ_3-O(6)]–Re–[μ-O(7)] 73.8(2) and [μ_3-O(6)]–Re–[μ-O(8)] 74.0(3)° are much smaller. The angles between two Re atoms and the bridging oxygens O(6), O(7) and O(8) are almost those corresponding to an ideal tetrahedral geometry (109°). Angle Re(1)–[μ_3-O(6)]–Re(2) is 2.1° smaller than those of Re(1)–[μ-O(7)]–Re(2) and Re(1)–[μ-O(8)]–Re(1A). The Re–CO distances are within the range known for other rhenium(I) carbonyls. There is no significant difference in the bond lengths between Re and the CO ligands *trans* to μ- or μ_3-OH within the range of standard deviations. This is also true for the Re–[μ-O(7,8)] and Re–[μ_3-O(6)] distances. It is difficult to compare the Re–O bond lengths with other compounds containing CO and OH^- ligands since to our knowledge in the case of Re only the tetranuclear cluster $[\{Re(\mu_3\text{-}OH)(CO)_3\}_4]$ has been structurally characterized.[28] The bond length in the latter compound [2.207(8) Å] is comparable with 2.174(8) Å in the case of **4**. The angles Re–[μ_3-OH]–Re in complex **3** are 104.5° *versus* 104.3° (average) in **4** *i.e.* the same within the range of standard deviations. Comparison of the two skeletal frameworks of **4** and **3** reveals that they are very similar with the exception of the missing $Re(CO)_3$ unit in **4**.

Table 2 Fractional atomic coordinates ($\times 10^4$) with estimated standard deviations (e.s.d.s) in parentheses

Atom	x	y	z
(*a*) Compound **4**			
Re(1)	785(1)	3 748(1)	1 596(1)
Re(2)	−15(1)	2 500	52(1)
C(1)	208(12)	3 776(7)	2 579(6)
C(2)	1 947(13)	4 746(9)	1 842(6)
C(3)	−412(12)	4 698(8)	1 364(6)
C(4)	−1 209(10)	3 487(10)	−179(6)
C(5)	419(16)	2 500	−958(9)
O(1)	−179(10)	3 748(6)	3 172(4)
O(2)	2 623(10)	5 364(6)	1 982(5)
O(3)	−1 136(9)	5 286(6)	1 208(5)
O(4)	−1 914(8)	4 081(6)	− 304(5)
O(5)	645(13)	2 500	−1 566(6)
O(6)	−270(8)	2 500	1 233(4)
O(7)	1 346(6)	3 492(4)	484(3)
O(8)	1 988(8)	2 500	1 758(4)
O(1W)	−2 512(10)	2 500	1 782(5)
N	4 477(13)	2 500	−981(7)
C(6)	5 712(22)	2 500	−567(12)
C(7)	5 463(26)	2 500	236(11)
C(8)	4 998(31)	2 500	−1 716(15)
C(9)	3 830(54)	2 500	−2 241(14)
C(10)	3 620(15)	3 347(10)	−810(10)
C(11)	4 364(22)	4 279(13)	−946(18)
(*b*) Compound **5**			
Re	10 057	0	1 284(2)
O(1)	2 132(35)	2 784(2)	2 839(22)
O(2)	6 539(40)	0	2 699(30)
O(3)	9 117(35)	1 635(18)	0
O(4)	12 284(53)	0	0
O(1W)	4 896(45)	2 895(34)	0
O(2W)	950(51)	5 000	0
C(1)	11 457(39)	1 684(36)	2 279(22)
C(2)	7 903(50)	0	2 227(36)
N(1)	6 537	5 000	5 000
C(1N)	7 868	5 000	6 020
C(2N)	6 648	5 000	7 090
C(3N)	5 204	6 662	5 000
C(4N)	6 423	8 407	5 000

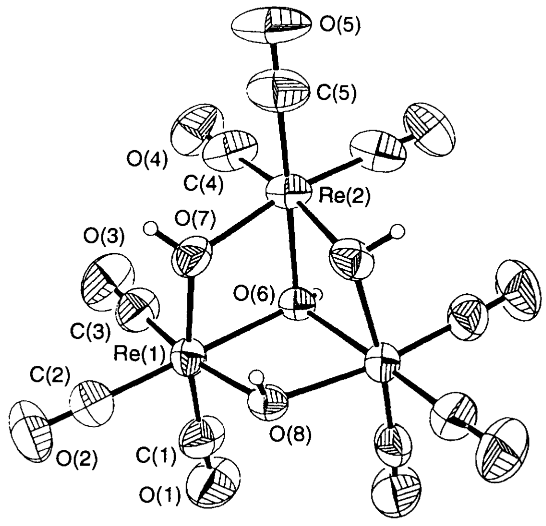

Fig. 4 Crystal structure of complex **4**

Table 3 Selected bond lengths (Å) and angles (°) for compound **4** with e.s.d.s in parentheses

Re(1)–C(1)	1.899(11)	Re(1)–C(2)	1.912(13)
Re(1)–C(3)	1.885(12)	Re(1)–O(6)	2.164(5)
Re(1)–O(7)	2.146(6)	Re(1)–O(8)	2.172(8)
Re(2)–C(4)	1.918(12)	Re(2)–C(5)	1.901(17)
Re(2)–O(6)	2.174(8)	Re(2)–O(7)	2.153(6)
C(1)–O(1)	1.161(14)	C(2)–O(2)	1.149(16)
C(3)–O(3)	1.159(15)	C(4)–O(4)	1.138(14)
C(5)–O(5)	1.136(20)		
C(1)–Re(1)–C(2)	88.7(5)	C(1)–Re(1)–C(3)	88.6(5)
C(2)–Re(1)–C(3)	88.9(5)	C(1)–Re(1)–O(6)	97.7(4)
C(2)–Re(1)–O(6)	170.5(4)	C(3)–Re(1)–O(6)	97.2(4)
C(1)–Re(1)–O(7)	171.4(3)	C(2)–Re(1)–O(7)	99.0(4)
C(3)–Re(1)–O(7)	95.3(4)	O(6)–Re(1)–O(7)	74.2(3)
C(1)–Re(1)–O(8)	94.7(4)	C(2)–Re(1)–O(8)	98.5(4)
C(3)–Re(1)–O(8)	170.9(4)	O(6)–Re(1)–O(8)	74.0(3)
O(7)–Re(1)–O(8)	80.3(3)	C(4)–Re(2)–C(5)	87.2(5)
C(4)–Re(2)–O(6)	97.7(4)	C(5)–Re(2)–O(6)	173.0(6)
C(4)–Re(2)–O(7)	94.7(4)	C(5)–Re(2)–O(7)	100.9(4)
O(6)–Re(2)–O(7)	73.8(2)	C(4)–Re(2)–C(4A)	90.4(7)
O(7)–Re(2)–O(7A)	78.9(3)	Re(1)–C(1)–O(1)	176.4(9)
Re(1)–C(2)–O(2)	178.1(10)	Re(1)–C(3)–O(3)	178.7(10)
Re(2)–C(4)–O(4)	178.7(11)	Re(2)–C(5)–O(5)	178.1(15)
Re(1)–O(6)–Re(2)	103.8(3)	Re(1)–O(6)–Re(1A)	105.2(4)
Re(1)–O(7)–Re(2)	105.1(3)	Re(1)–O(8)–Re(1A)	104.7(4)

Table 4 Selected bond lengths (Å) and angles (°) for compound **5** with e.s.d.s in parentheses

Re–O(3)	2.063(18)	Re–O(4)	2.130(61)
Re–C(1)	1.961(28)	Re–C(2)	1.814(37)
Re • • • Re(A)	3.104(4)	O(1)–C(1)	1.148(37)
O(2)–C(2)	1.060(46)		
O(3)–Re–O(4)	69.9(15)	O(3)–Re–C(1)	103.1(11)
O(4)–Re–C(1)	97.2(16)	O(3)–Re–C(2)	103.9(11)
O(4)–Re–C(2)	172.2(20)	C(1)–Re–C(2)	88.8(13)
O(3)–Re–Re(A)	41.2(6)	O(4)–Re–Re(A)	43.2(15)
C(1)–Re–Re(A)	127.8(9)	C(2)–Re–Re(A)	128.9(12)
O(3)–Re–O(3A)	72.0(13)	C(1)–Re–O(3A)	167.1(10)
Re–O(3)–Re(A)	97.6(11)	Re–O(4)–Re(A)	93.5(14)
Re–C(1)–O(1)	173.5(23)	Re–C(2)–O(2)	173.6(36)

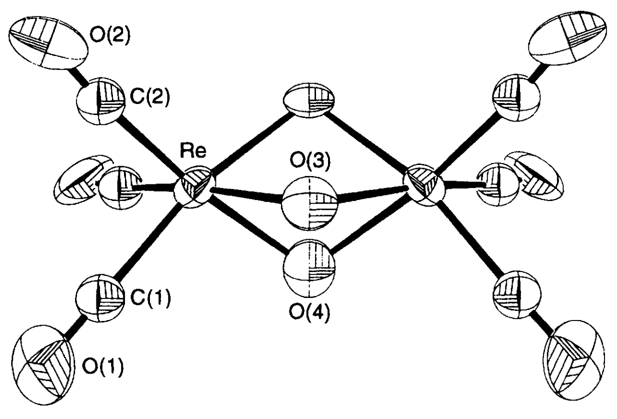

Fig. 5 Crystal structure of complex **5**

Formation of the Dimeric Complex [NEt$_4$][(OC)$_3$Re(μ-OH)$_3$Re(CO)$_3$].—As a result of the titration experiment the question arose as to whether much faster addition of OH$^-$ to a solution of complex **1** or the addition of the latter to a concentrated OH$^-$ solution would result in complexes with a higher ratio of OH$^-$: Re. This ratio can theoretically be increased to a maximum of 3 : 1 representing the formation of [Re(OH)$_3$(CO)$_3$]$^{2-}$. Faster addition of OH$^-$ to the aqueous solution displaced the jump in the titration curve slightly towards a higher OH$^-$: Re ratio and addition of 1–3 mol dm^{-3} NaOH solution to **1** resulted in the almost quantitative formation of dimeric compound **5**. It seems that very fast addition of OH$^-$ in high concentrations results in the initial formation of a mixture between [Re(OH)(H$_2$O)$_2$(CO)$_3$] and [Re(OH)$_2$(H$_2$O)(CO)$_3$]$^-$. This is reasonable from the thermodynamic point of view as the number of co-ordinated monodentate ligands primarily depends on the total ligand concentration (see Scheme 1). Subsequently these two compounds dimerize to the final product **5** which can be extracted into CH$_2$Cl$_2$. Analysis of the aqueous solution after the extraction showed no evidence for the formation of [Re(OH)$_3$(CO)$_3$]$^{2-}$. Crystals of X-ray quality could be grown by the slow diffusion technique using CH$_2$Cl$_2$ and hexane.

Structure of [NEt$_4$][(OC)$_3$Re(μ-OH)$_3$Re(CO)$_3$].—The crystal structure of the complex anion is depicted in Fig. 5 and important bond lengths and angles are summarized in Table 4. The two Re(CO)$_3$ fragments are bridged by three OH$^-$ ligands creating two mirror planes one perpendicular to the other. The first mirror plane is formed by the three oxygen atoms of the OH$^-$ bridges, the second by the Re–Re axis. The co-ordination sphere of each rhenium atom is distorted octahedral and thus fulfils the 18-electron rule. Consequently, no Re–Re bond can be assumed and the distance between the two metal centres, being 3.104 Å, is much too long for a Re–Re single bond. The angles at the μ-OH bridges Re–[μ-O(3)]–Re(A) and Re–[μ-O(4)]–Re(A) are 97.6(11) and 93.5(14)° respectively and thus significantly smaller than the corresponding ones in compounds **3** and **4**. Comparable angles have recently been found in the dimeric rhenium compound [(OC)$_3$Re(μ-OMe)$_3$Re(CO)$_3$]$^-$ (average 94.3°).[15] It seems that the electronic interaction of the three bridging oxygen atoms is strong enough to decrease the tetrahedral angle significantly. This phenomenon is accompanied by a decrease in the Re–Re distance. In the framework of the pseudo cubane system **4** the oxygens are sufficiently removed from each other so that there is no interaction and the tetrahedral angle at the bridging oxygens is almost ideal. The Re–[μ-O(3,4)] bond length is comparable within standard deviations to those in [(OC)$_3$Re(μ-OMe)$_3$Re(CO)$_3$]$^-$ as well as to the distances in **4**.

Conclusion

The complex [ReBr$_3$(CO)$_3$]$^{2-}$ can be used as an important and reactive starting material for the synthesis of cluster-like compounds. The bromide ligands are very weakly bound and thus can easily be substituted. The compound is presumably present in aqueous solution as a semi aqua-ion [Re(H$_2$O)$_3$(CO)$_3$]$^+$ which acts as a strong Lewis acid. Substitution reactions of low-valent metal centres having three weakly bound ligands such as acetonitrile or tetrahydrofuran have often been described. Activation with water ligands is quite new and will allow the development of ligand-substitution reactions also in aqueous solution, since the compound [Re(H$_2$O)$_3$(CO)$_3$]$^+$ is stable in this solvent even when exposed to air. Rhenium(I) is a d^6 centre and its kinetic behaviour often allows the isolation of intermediates which are not the thermodynamic end-products. Thermodynamic data for the formation of the described clusters **4** and **5** and substitution reactions in water with *facial* co-ordinating tridentate compounds are currently being investigated in our laboratories.

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