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Structural characterization in solid state and solution of the hydridocarbonyl cluster anion $[Re_4(\mu\text{-}H)_4(CO)_{13}]^{2-}$

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Abstract

The salt $[AsPh_4]_2[Re_4(\mu\text{-}H)_4(CO)_{13}]$, obtained by pyrolysis of $[AsPh_4][ReH_2(CO)_4]$ in ethanol, has been investigated by X-ray analysis. The crystals are monoclinic, space group $P2_1/n$, with $a = 12.630(3)$, $b = 38.062(6)$, $c = 12.916(3)$ Å, $\beta = 105.94(2)°$ and $Z = 4$. The refinements, performed by full-matrix least-squares on the basis of 3389 significant reflections, gave final agreement indices R and R_w of 0.035 and 0.040, respectively. The anion contains a tetrahedron of rhenium atoms [Re–Re in the range 3.048(1)–3.126(1) Å], bearing thirteen terminal carbonyl groups and four edge-bridging hydride ligands. The variable temperature ^1H NMR investigation showed three hydridic resonances (ratio 1:2:1) at 153 K, in agreement with the C_s symmetry of the solid state structure. At higher temperatures, two different degenerate exchange processes concerning the hydride ligands are operative. The first, frozen only below 153 K, equalizes the three hydrides bridging the edges of the basal triangle. The second, frozen below 188 K, exchanges all the hydrides, leading to a single hydride resonance at room temperature. Band shape analysis provided an estimate of the rate constants and of the activation parameters of the two processes: intrabasal exchange, $E_a = 30.4 \pm 1.3$ kJ/mol, $\Delta H^\ddagger = 29.0 \pm 1.3$ kJ/mol, $\Delta S^\ddagger = -8.1 \pm 7.5$ J/K mol; overall scrambling, $E_a = 42.7 \pm 0.6$ kJ/mol, $\Delta H^\ddagger = 40.7 \pm 0.6$ kJ/mol, $\Delta S^\ddagger = -16.6 \pm 2.6$ J/K mol.

Introduction

In the chemistry of hydridocarbonyl cluster compounds of rhenium, few examples are known with a tetrahedral metal frame. Two of these are unsaturated species (possessing fewer valence electrons than the 60 expected for a tetrahedron), *i.e.* $[Re_4(\mu_3\text{-}H)_4(CO)_{12}]$ [1] and $[Re_4(\mu\text{-}H)_3(\mu_3\text{-}H)_2(CO)_{12}]^-$ [2], and the other two are saturated compounds, *i.e.* $[Re_4(\mu\text{-}H)_6(CO)_{12}]^{2-}$ [3] and $[Re_4(\mu\text{-}H)_4(CO)_{13}]^{2-}$ [4,5]. The latter anion possesses the highest number of CO ligands within this

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family. Additional carbonyl groups give rise to less compact cluster geometries, as, for instance, the butterfly $[Re_4(\mu\text{-}H)_5(CO)_{14}]^-$ [6] and the spiked-triangular $[Re_4H(\mu\text{-}H)_3(CO)_{15}]^{2-}$ species [7]. Thirteen CO ligands are relatively unusual in tetrahedral clusters and are present in some homonuclear or mixed-metal species containing metals of the iron triad, especially of the type $[M_4H_x(CO)_{13}]^{(2-x)-}$ (M = Fe, Ru, or Os; $x = 0$, 1, or 2) [8]. The presence at the same time in $[Re_4(\mu\text{-}H)_4(CO)_{13}]^{2-}$ of four hydrides to satisfy the electronic requirements of the rhenium atoms, makes a rather crowded cluster surface and the study of its stereochemistry is particularly interesting. The anion was isolated and characterized by some of us as its tetraethylammonium salt *via* reactions giving mixtures of products, and it was always impossible to obtain large quantities of the compound free of impurities [4,5]. The structural determination was performed on the NEt_4^+ salt; however, the poor quality of the diffraction data, mainly due to decay and high absorption, and the limited number of significant reflections prevented us from obtaining good bond parameters. We have therefore attempted to prepare the compound with a different cation and we report here the complete results of the X-ray analysis on the tetraphenylarsonium salt. The behaviour of the anion in solution, investigated by ^1H NMR spectroscopy at different temperatures, is also discussed.

Results and discussion

It was previously reported that upon refluxing an ethanol solution of $[NEt_4]_2[Re_4H(\mu\text{-}H)_3(CO)_{15}]$ for a few hours, mixtures were obtained containing *inter alia* the tetrahedral species $[NEt_4]_2[Re_4(\mu\text{-}H)_4(CO)_{13}]$ [4,5]. Alternatively, this compound was also obtained in poor yield by heating in ethanol a species at that time not yet characterized [5], and later shown to be $[NEt_4][ReH_2(CO)_4]$ [9]. Since then, a novel synthesis of the anion $[ReH_2(CO)_4]^-$ has been reported, by protonation of $[Re(CO)_4]^{3-}$ [10]. This allows the preparation of salts of this anion with cations different from NEt_4^+. We have therefore prepared the salt $[AsPh_4][ReH_2(CO)_4]$ according to [10], and then tried pyrolysis reactions in order to obtain $[AsPh_4]_2[Re_4(\mu\text{-}H)_4(CO)_{13}]$.

The salt $[AsPh_4][ReH_2(CO)_4]$ was dissolved in a minimum amount of ethanol and then heated under reflux for 3.5 h. A mixture was obtained, whose IR and NMR analyses showed it to be essentially composed of $[Re_3(\mu\text{-}H)_3(CO)_{10}]^{2-}$ [11] (*ca.* 70%) and $[Re_4(\mu\text{-}H)_4(CO)_{13}]^{2-}$ (*ca.* 20%). We have been unable to separate satisfactorily the components of this mixture. However, crystallization from acetone/EtOH gave a crop of yellow needles of $[AsPh_4]_2[Re_4(\mu\text{-}H)_4(CO)_{13}]$, which allowed X-ray and ^1H NMR investigations.

Structure of $[AsPh_4]_2[Re_4(\mu\text{-}H)_4(CO)_{13}]$

The crystal structure consists of the packing of discrete $[Re_4(\mu\text{-}H)_4(CO)_{13}]^{2-}$ anions and $[AsPh_4]^+$ cations in the ratio 1:2, separated by normal van der Waals' contacts. The anion, of overall idealized C_s symmetry, is illustrated in Fig. 1 and bond distances and angles are given in Table 1. It contains a tetrahedral metal cluster bearing 13 terminally bonded CO ligands, four to Re4 and three of each of the other rhenium atoms. The four hydride ligands, located indirectly (see later),

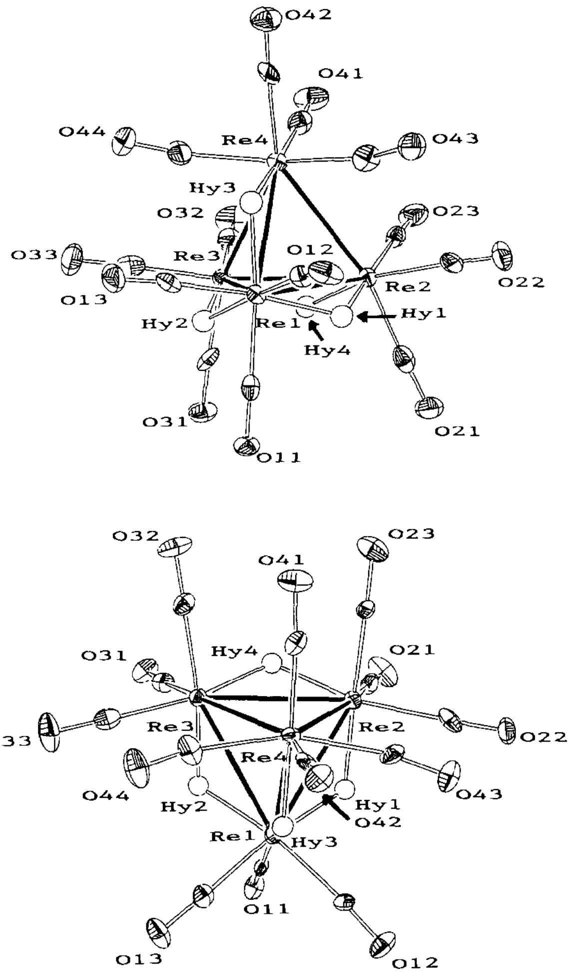

Fig. 1. Two views of the $[Re_4(\mu\text{-}H)_4(CO)_{13}]^{2-}$ anion. For clarity the numbering of the carbonyl groups is indicated only by the labels of their oxygen atoms.

are all edge-bridging, three on the edges of the basal $Re_3(CO)_9$ triangle and one on the Re1–Re4 edge.

The Re–Re bonds are in the range 3.048(1)–3.126(1) Å, with no net difference between hydrogen-bridged (4, mean 3.099 Å) and unbridged (2, mean 3.050 Å) edges. A similar and even less clear situation was previously observed for the same anion in its NEt_4^+ salt (see Table 1 for the individual Re–Re bond lengths), which exhibited an overall mean Re–Re bond distance of 3.088 Å, very close to the corresponding value in the present case (3.083 Å).

The $Re_3(\mu\text{-}H)_3(CO)_9$ basal triangular moiety is also common to $[Re_4(\mu\text{-}H)_6(CO)_{12}]^{2-}$ [3] and to many triangular cluster compounds of the formula $[Re_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}X)]^{n-}$: $n = 2$, X = O [11,12]; $n = 1$, X = OEt [13], X = S^tBu [14], X = $AuPPh_3$ [15], X = $\eta^2\text{-}CH_2O$ [16], X = η^2-CH(Me)O [17], X = $\eta^2\text{-}C(H)NC_6H_{11}$ [18]. The three rhenium atoms of this triangle exhibit distorted

Table 1

Bond distances (Å) and angles (deg) within $[AsPh_4]_2[Re_4(\mu\text{-}H)_4(CO)_{13}]$

Distances

Re1–Re2	3.126(1)	[3.062(4)] [a]	Re3–C33	1.88(3)	C33–O33	1.19(3)
Re1–Re3	3.104(1)	[3.161(4)]	Re4–C41	1.85(3)	C41–O41	1.23(2)
Re1–Re4	3.098(1)	[3.126(4)]	Re4–C42	1.94(3)	C42–O42	1.15(2)
Re2–Re3	3.067(1)	[3.026(5)]	Re4–C43	1.97(3)	C43–O43	1.17(2)
Re2–Re4	3.052(1)	[3.098(5)]	Re4–C44	1.99(3)	C44–O44	1.13(2)
Re3–Re4	3.048(1)	[3.058(5)]	Re–H [b]	1.85	As1–C111	1.91(2)
Re1–C11	1.89(2)		C11–O11	1.17(2)	As1–C121	1.91(2)
Re1–C12	1.93(2)		C12–O12	1.12(2)	As1–C131	1.89(2)
Re1–C13	1.90(3)		C13–O13	1.16(2)	As1–C141	1.90(2)
Re2–C21	1.90(3)		C21–O21	1.16(3)	As2–C211	1.92(2)
Re2–C22	1.94(3)		C22–O22	1.12(3)	As2–C221	1.89(2)
Re2–C23	1.87(2)		C23–O23	1.19(2)	As2–C231	1.90(2)
Re3–C31	1.85(3)		C31–O31	1.21(2)	As2–C241	1.91(2)
Re3–C32	1.92(3)		C32–O32	1.13(2)		

Angles

Re2–Re1–C11	105.5(6)	C21–Re2–C23	94.2(9)	Re2–Re4–C43	65.3(7)
Re2–Re1–C12	103.5(6)	C22–Re2–C23	93.2(9)	Re2–Re4–C44	129.2(6)
Re2–Re1–C13	156.7(7)	C21–Re2–Hy1	87.0	Re3–Re4–C41	90.1(7)
Re3–Re1–C11	105.1(6)	C21–Re2–Hy4	78.7	Re3–Re4–C42	152.2(6)
Re3–Re1–C12	157.0(6)	C22–Re2–Hy1	84.3	Re3–Re4–C43	124.9(7)
Re3–Re1–C13	100.9(7)	C22–Re2–Hy4	161.7	Re3–Re4–C44	69.3(6)
Re4–Re1–C11	161.1(6)	C23–Re2–Hy1	177.2	C41–Re4–C42	88.8(9)
Re4–Re1–C12	100.0(6)	C23–Re2–Hy4	79.0	C41–Re4–C43	98.2(9)
Re4–Re1–C13	102.0(6)	Hy1–Re2–Hy4	103.7	C41–Re4–C44	96.6(10)
C11–Re1–C12	93.6(8)	Re1–Re3–C31	108.4(6)	C42–Re4–C43	82.7(10)
C11–Re1–C13	90.4(8)	Re1–Re3–C32	154.5(7)	C42–Re4–C44	83.2(9)
C12–Re1–C13	92.0(9)	Re1–Re3–C33	103.7(7)	C43–Re4–C44	159.2(10)
C11–Re1–Hy1	82.5	Re2–Re3–C31	105.8(6)	C41–Re4–Hy3	178.0
C11–Re1–Hy2	79.4	Re2–Re3–C32	100.6(7)	C42–Re4–Hy3	92.2
C11–Re1–Hy3	165.8	Re2–Re3–C33	161.7(6)	C43–Re4–Hy3	83.6
C12–Re1–Hy1	82.8	Re4–Re3–C31	164.4(7)	C44–Re4–Hy3	81.8
C12–Re1–Hy2	170.1	Re4–Re3–C32	95.8(7)	Re1–C11–O11	179(2)
C12–Re1–Hy3	77.6	Re4–Re3–C33	104.8(7)	Re1–C12–O12	171(2)
C13–Re1–Hy1	170.9	C31–Re3–C32	92.9(9)	Re1–C13–O13	177(2)
C13–Re1–Hy2	81.1	C31–Re3–C33	88.0(9)	Re2–C21–O21	177(2)
C13–Re1–Hy3	78.9	C32–Re3–C33	90.6(10)	Re2–C22–O22	176(2)
Hy1–Re1–Hy2	103.0	C31–Re3–Hy2	82.8	Re2–C23–O23	176(2)
Hy1–Re1–Hy3	107.1	C31–Re3–Hy4	77.6	Re3–C31–O31	176(2)
Hy2–Re1–Hy3	107.8	C32–Re3–Hy2	172.1	Re3–C32–O32	177(2)
Re1–Re2–C21	110.6(7)	C32–Re3–Hy4	83.7	Re3–C33–O33	178(2)
Re1–Re2–C22	107.6(7)	C33–Re3–Hy2	82.7	Re4–C41–O41	177(2)
Re1–Re2–C23	148.4(6)	C33–Re3–Hy4	164.1	Re4–C42–O42	177(2)
Re3–Re2–C21	107.4(7)	Hy2–Re3–Hy4	101.8	Re4–C43–O43	164(2)
Re3–Re2–C22	164.4(7)	Re1–Re4–C41	145.8(7)	Re4–C44–O44	166(2)
Re3–Re2–C23	94.5(6)	Re1–Re4–C42	125.4(6)	Re1–Hy1–Re2	115.3
Re4–Re2–C21	166.4(7)	Re1–Re4–C43	86.4(6)	Re1–Hy2–Re3	114.3
Re4–Re2–C22	106.5(7)	Re1–Re4–C44	89.5(8)	Re1–Hy3–Re4	113.7
Re4–Re2–C23	91.6(6)	Re2–Re4–C41	90.0(7)	Re2–Hy4–Re3	112.2
C21–Re2–C22	85.5(10)	Re2–Re4–C42	147.4(6)		

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[a] The corresponding bond lengths determined in the tetraethylammonium salt [4] are reported in brackets. [b] Imposed bond length.

octahedral coordination: Re1 is bound to three CO and three hydrides, Re2 and Re3 each to three CO, two hydrides and Re4.

In addition, the coordination about Re4 can be considered octahedral, with the lack of one coordination site, that *trans* to CO42, in the direction of the mid-point of the Re2–Re3 edge. Within the Re4(CO)$_4$ unit, two CO groups, CO43 and CO44, are mutually *trans*, the C43–Re4–C44 angle being 159.2(10)°, and exhibiting, as expected, longer Re–C bond lengths (mean 1.98 Å) than all the other carbonyl groups (mean 1.90 Å). These two CO groups are both slightly bent [Re–C–O 164(2) and 166(2)°] towards the basal triangle, different from the other eleven carbonyl ligands [Re–C–O in the range 171(2)–179(2)°]. The bends could be taken as indicative of some long range interactions of these groups with the basal metal atoms. Indeed a carbonyl stereochemistry similar to that of the present anion was found in [FeRu$_3$(μ-H)$_2$(CO)$_{13}$] [8f], [Ru$_4$(μ-H)$_2$(CO)$_{13}$] [8g] and [FeRu$_3$(μ-H)(CO)$_{13}$]$^-$ [8d], in which the two mutually *trans* CO groups of the apical M(CO)$_4$ unit are bent and semibridging, with rather long contacts toward the basal metal atoms. In [Re$_4$(μ-H)$_4$(CO)$_{13}$]$^{2-}$, however, the contacts of C43 and C44 with the basal rhenium atoms [Re2–C43 2.86(3) Å, Re3–C44 3.00(2) Å] are such as to rule out any bridging interaction.

Although the structure of the anion in the [AsPh$_4$]$^+$ salt is very similar to that previously obtained for the [NEt$_4$]$^+$ salt, there is a difference in the tilting of the apical Re(CO)$_4$ fragment with respect to the basal triangle. While in the present structure the disposition of the apex maintains one of the mirror planes of the basal Re$_3$(μ-H)$_3$(CO)$_9$ moiety, of idealized C_{3v} symmetry, thus resulting in an overall idealized C_s molecular symmetry (the mirror plane passing through Re1, Re4 and the mid-point of the Re2–Re3 edge), in the previous structure no symmetry plane was present, the apical fragment being rotated *ca.* 20° about an axis perpendicular to the basal Re$_3$ plane. This might suggest a low rotational barrier for the apex, in agreement with the fluxional process observed in solution for the anion (see below).

The four hydrido-ligands were not directly located. The indirect location of such ligands is often based on the analysis of the metal–metal bond lengths and on the presence of surface holes in the ligand envelope, shown by molecular graphics techniques. Both methods have limitations that have been discussed (see, for instance, ref. 19). As already outlined, the bond lengthening criterion does not furnish clear indications in the present case; hydrogen-bridged Re–Re edges in the literature exhibit a range of values (Δ range greater than 0.3 Å), which depends on the number and disposition of the ligands on the two bonded rhenium atoms. We have performed non-bonding potential energy calculations, using the program HYDEX [20], which clearly indicate the four reported edge-bridging locations.

Finally, as mentioned above, a variety of cluster compounds with the generalized formula [M$_4$H$_x$(CO)$_{13}$]$^{y-}$ (M$_4$ indicating a homonuclear or mixed metallic tetrahedral array) have been reported, which show many different ligand stereochemistries. Interest in the above clusters arises from two features: (a) the efforts to imitate the as yet unique species [Fe$_4$(μ-H)(CO)$_{13}$]$^-$ [21], containing a μ_4-η^2-CO ligand, and (b) the problem of ligand overcrowding on a tetrahedral cluster surface [22]. The anion [Re$_4$(μ-H)$_4$(CO)$_{13}$]$^{2-}$ is the only one within this cluster family containing only terminal groups. As for ligand crowding, we observe that, in spite of the presence of four hydrides in addition to the thirteen CO groups, there are no particularly short intramolecular contacts. The hydrido ligands play a complex role: they are in competition with the CO ligands for the volume around the cluster but, at the same time, they cause a cluster expansion, lengthening some metal–metal bonds. Due to these factors, the overall energetic balance is not easy to establish.

Behaviour of the anion $[Re_4(\mu\text{-}H)_4(CO)_{13}]^{2-}$ *in solution*

At 298 K the ^1H NMR spectrum of $[Re_4(\mu\text{-}H)_4(CO)_{13}]^{2-}$ exhibits, in the hydridic region, only one signal at −16.95 ppm in $CD_2Cl_2/CDCl_3$ (−16.7 in acetone-d_6). A resonance at δ −17.5 (−17.3 in acetone-d_6) of much lower intensity, present in the sample used for the NMR studies, is attributable to traces of $[Re_4(\mu\text{-}H)_6(CO)_{12}]^{2-}$ [3]. The difficulty in obtaining samples of the product free from this impurity is responsible for the previous incorrect attribution of both these hydride resonances (at δ −16.7 and −17.3) to $[Re_4(\mu\text{-}H)_4(CO)_{13}]^{2-}$. The integrated intensities, however, were said not to be in very good agreement with the expected 3:1 ratio [5].

The equivalence of the four hydrides cannot be achieved in any structural arrangement of the $Re_4(CO)_{13}$ cluster and therefore fluxionality should be present, as confirmed by the variable temperature ^1H NMR spectra (Fig. 2a). Indeed on lowering the temperature below 273 K, the resonance broadens and collapses and at 198 K gives rise to two signals, at δ −14.99 and −17.97, respectively, with intensity ratio 1:3. On further decreasing the temperature, the high field resonance broadens again and eventually splits into two resonances (intensity ratio 2:1), at δ −17.57 and −19.64, respectively. This spectrum, consistent with the C_s symmetry of the solid state structure, was recorded at 153 K using as solvent a mixture of CD_2Cl_2 and $CDCl_3$; the two high field signals, however, appear still exchange-broadened, indicating that their interconversion has a low activation barrier. A spectrum recorded at *ca.* 148 K confirmed these results, even with significant deterioration of the spectrometer performances. Previous attempts with acetone solutions allowed only the observation (at *ca.* 180 K) of the collapse of the high field resonance. The signal at −14.99 ppm, which is the first to be resolved, can be attributed to H3 bridging the Re1–Re4 edge, while the other two resonances observed at lower temperature are due to the hydrides bridging the edges of the $Re_3(CO)_9$ basal triangle.

Two different degenerate exchange processes are therefore observable in $[Re_4(\mu\text{-}H)_4(CO)_{13}]^{2-}$: the first equalizes the three hydrides of the basal triangle, while the second exchanges all the hydrides. Computer simulations of the variable temperature spectra (Fig. 2b) allowed an estimation of the rate constants and of the activation parameters of the two processes: intrabasal exchange, $E_a = 30.4 \pm 1.3$ kJ/mol, $\Delta H^\ddagger = 29.0 \pm 1.3$ kJ/mol, $\Delta S^\ddagger = -8.1 \pm 7.5$ J/K mol; overall scrambling, $E_a = 42.7 \pm 0.6$ kJ/mol, $\Delta H^\ddagger = 40.7 \pm 0.6$ kJ/mol, $\Delta S^\ddagger = -16.6 \pm 2.6$ J/K mol.

To the best of our knowledge, the highest number of hydrides found in $M_4(CO)_{13}$ tetrahedral clusters until now was two (apart from the species $[ReOs_3H_3(CO)_{13}]$, not structurally characterized [23]) and therefore there are no previous examples of the dynamic behaviour of four hydrides on a $M_4(CO)_{13}$ cluster to compare with our results. However, several $H_4M_4(CO)_{12\text{-}n}L_n$ (L = two electron donors) tetrahedral clusters are known [24], with ground state symmetry T_d, D_{2d} or C_s, and hydride fluxionality *via* edge-terminal-edge scrambling has

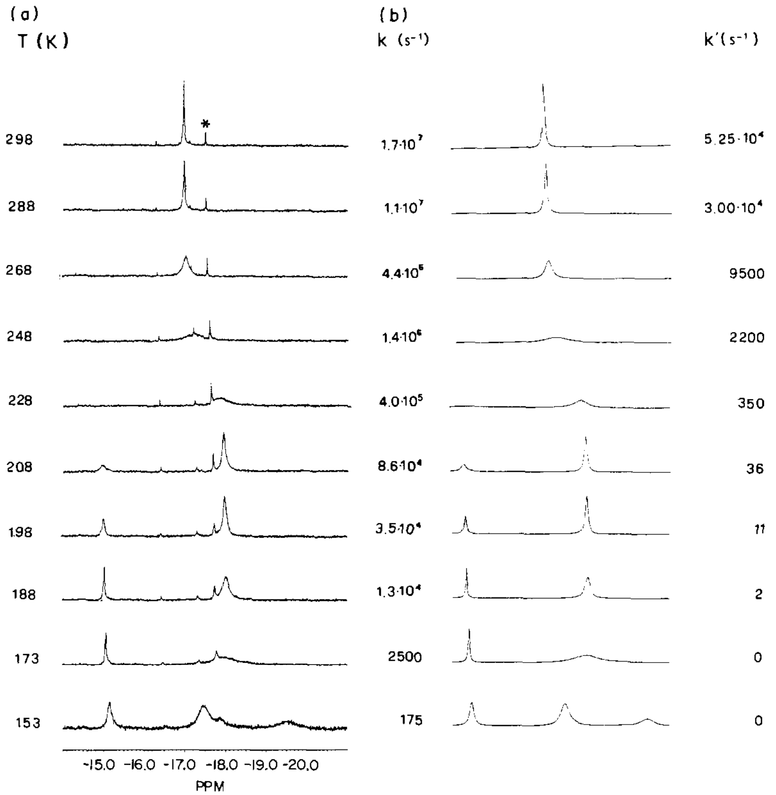

Fig. 2. Hydridic region of the ^{1}H NMR spectra of $[Re_4(\mu\text{-}H)_4(CO)_{13}]^{2-}$ at selected variable temperatures (200.13 MHz, $CD_2Cl_2/CDCl_3$): (a) experimental (T/K); (b) simulated (k/s^{-1} rate for intrabasal exchange from H4 to H1,H2; k'/s^{-1} rate for the overall scrambling from H4 to H3). The resonance marked with an asterisk is due to an impurity of $[Re_4(\mu\text{-}H)_6(CO)_{12}]^{2-}$.

been reported [25]. Similar mechanisms could also account for the processes observed in the present case. In fact, a transition state with one hydride terminally bound to each metal could give rise to the scrambling of the basal hydrides, while the equalization of all the hydrides could result from a different opening of the Re1–H3–Re4 bridge, leading to an intermediate with H3 and one basal hydride both terminally bound to Re1.

Other mechanisms, however, can be hypothesized. An attractive alternative for the lower energy process could be the rotation of the apical $HRe(CO)_4$ moiety with respect to the basal triangle. Indeed $[Re_4(\mu\text{-}H)_4(CO)_{13}]^{2-}$ can be thought of as arising from the interaction of the 18 valence electron $[HRe(CO)_4]^{2-}$ [10] with the electron-deficient $[H_3Re_3(CO)_9]$ species. The rotation of unsaturated fragments bound to metal centres is a well-established process in mononuclear compounds with coordinated alkenes or alkynes and similar mechanisms have also been suggested to explain the fluxional behaviour observed in trinuclear metal clusters [26]: see in particular the rotation of the same $HRe(CO)_4$ fragment about the "pseudo-acetylene" $[Re_2(\mu\text{-}H)_2(CO)_6]^{2-}$ [27]. This hypothesis may be supported by the different tilting of the $[HRe(CO)_4]$ moiety observed in the two X-ray structures of the anion.

Experimental

$[AsPh_4][ReH_2(CO)_4]$ was prepared by published methods [10]. The solvent ethanol (Merck) was deoxygenated and dried over molecular sieves. The IR spectra were recorded in 0.1-mm CaF_2 cells on a Perkin–Elmer 781 grating spectrophotometer, equipped with a data station using PE780 software. Elemental analysis was performed by the Microanalytical Laboratory of our Department.

Preparation of $[AsPh_4]_2[Re_4(\mu\text{-}H)_4(CO)_{13}]$ *and* $[AsPh_4]_2[Re_3(\mu\text{-}H)_3(CO)_{10}]$

A sample of $[AsPh_4][ReH_2(CO)_4]$ (200 mg, 0.29 mmol) was suspended in a small volume of refluxing ethanol (5 cm^3) under nitrogen for 3.5 h. The cream solution gradually became red, while a red precipitate separated. The precipitate was isolated and treated five times with boiling ethanol, leaving a residue (*ca.* 90 mg), shown by ^1H NMR analysis to contain mainly the anions $[Re_3(\mu\text{-}H)_3(CO)_{10}]^{2-}$ (*ca.* 70%) and $[Re_4(\mu\text{-}H)_4(CO)_{13}]^{2-}$ (20%), plus some $[Re_4(\mu\text{-}H)_6(CO)_{12}]^{2-}$. Attempts to separate the components by fractional precipitation or metathesis with different cations, such as $[NEt_4]^+$ or $[N(PPh_3)_2]^+$, were unsuccessful. Crystallization by slow diffusion of ethanol into a concentrated acetone solution gave a crop of yellow needles of $[AsPh_4]_2[Re_4(\mu\text{-}H)_4(CO)_{13}]$, which were used for the X-ray and the spectroscopic characterization. IR (acetone): $\nu(CO)$ 1994s, 1976vs, 1895s,br cm^{-1}. ^1H NMR of the anion (acetone-d_6, 298 K): δ -16.7 ppm, with the correct integrated intensity with respect to the cationic signals. Anal. Found: C, 39.0; H, 2.4. $C_{61}H_{44}As_2O_{13}Re_4$ calc.: C, 38.96; H, 2.34%.

Variable temperature NMR analysis

$[AsPh_4]_2[Re_4(\mu\text{-}H)_4(CO)_{13}]$ was dissolved in a mixture of CD_2Cl_2 and $CDCl_3$. The spectra were recorded on a Bruker AC 200 spectrometer operating at 200.13 MHz for protons. The temperature was controlled by the BVT-1000 unit of the spectrometer and calibrated down to 173 K with methanol solutions. Computer simulations were performed using a modified version of the QCPE program MSEX [28]. In the computer simulations, both the temperature dependence of the chemical shifts of all the resonances and the increase in the linewidth due to the increase of viscosity at very low temperatures have been accounted for. The activation parameters for the intrabasal exchange of the hydrides were obtained from the simulations of five spectra at 153, 163, 173, 180, 188 K (k = 175, 550, 2500, 6200, 13000 s^{-1}, respectively). These were used to calculate the rate constants at temperatures higher than 188 K to allow the simulations of the concerted exchange.

X-Ray analysis of $[AsPh_4]_2[Re_4(\mu\text{-}H)_4(CO)_{13}]$

The relevant crystal data, together with details of the structure collection and refinement are given in Table 2.

Intensity measurements. The crystal sample was mounted on a glass fibre in air. The intensity data were collected on an Enraf–Nonius CAD4 automated diffractometer using graphite monochromatized Mo-K_α radiation. The setting angles of 25 random intense reflections ($16° < 2\theta < 25°$) were used to determine by least-squares fit accurate cell constants and orientation matrix. The collection was performed by the ω-scan method, within the limits $6° < 2\theta < 46°$. A variable scan

Table 2

Crystal data and intensity collection parameters for $[AsPh_4]_2[Re_4(\mu\text{-}H)_4(CO)_{13}]$

Formula	$C_{61}H_{44}As_2O_{13}Re_4$
FW (amu)	1879.67
System	Monoclinic
Space group	$P2_1/n$ (non-standard) $P2_1/c$ (no. 14)
a (Å)	12.630(3)
b (Å)	38.062(6)
c (Å)	12.916(3)
β (°)	105.94(2)
V (Å^3)	5970(4)
D_c (g cm^{-3})	2.086
Z	4
$F(000)$	3520
Radiation	Mo-K_α, $\lambda = 0.71073$ Å
μ(Mo-K_α)	93.31
Min. transmission factor	0.71
Crystal dimensions (mm)	$0.10 \times 0.19 \times 0.35$
Crystal decay (%)	15
Scan mode	ω
ω scan width (°)	$1.00 + 0.35 \tan \theta$
θ range (°)	3–23
Temperature (°C)	22 ± 2
Octants of reciprocal space	$\pm h, +k, +l$
Measured reflections	8243
No. of reflections with $I > 3\sigma(I)$	3389
Final R and R_w indices	0.035, 0.040
No. of refined variables	481
e.s.d.	1.211

e.s.d. $= [\Sigma w(|F_o| - k|F_c|)^2/(N_{obs} - N_{var})]^{1/2}$; $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma(F_o^2) = [\sigma^2(I) + (pI)^2]^{1/2}/L_p$; $R = \Sigma\|F_o| - k|F_c\|/\Sigma|F_o|$; $R_w = [\Sigma w(|F_o| - k|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

speed and a variable scan range were used, with a 25% extension at each end of the scan range for background determination. Three standard intense reflections, monitored every 2 h, showed some crystal decay of *ca.* 15% at the end of the collection. The intensities were corrected for Lorentz, polarization and decay effects. An empirical absorption correction was applied to the data, based on ψ-scans (ψ 0–360° every 10°) of three suitable reflections with χ values close to 90°. A set of 3389 significant $[I > 3\sigma(I)]$ independent reflections was used in the structure solution and refinement.

Structure solution and refinements. All computations were performed on a PDP 11/73 computer, using the Enraf–Nonius Structure Determination Package (SDP) and the physical constants tabulated therein.

The structure was solved by Patterson and Fourier methods, which revealed the locations of all the non-hydrogen atoms. The refinements were carried out by full-matrix least-squares. Anisotropic thermal parameters were assigned to all atoms except the carbon atoms of the cations. The hydrogen atoms of the phenyl groups were located in ideal positions (C–H 0.95 Å, with $B = 5.0$ Å^2) after each cycle of refinement and their contribution to the structure factors was kept into

Table 3

Final positional parameters for $[AsPh_4]_2[Re_4(\mu\text{-}H)_4(CO)_{13}]$

Atom	*x*	*y*	*z*
Re1	0.26388(7)	0.13390(2)	−0.06031(6)
Re2	0.07360(7)	0.14732(2)	0.04667(6)
Re3	0.02345(7)	0.11206(2)	−0.17504(6)
Re4	0.15119(7)	0.07241(2)	0.02544(6)
As1	0.7081(2)	0.05253(6)	0.3455(2)
As2	0.5435(2)	0.26561(5)	0.9758(2)
O11	0.299(1)	0.2035(3)	−0.164(1)
O12	0.476(1)	0.1449(4)	0.118(1)
O13	0.389(1)	0.0968(4)	−0.201(1)
O21	−0.009(1)	0.2233(4)	0.017(1)
O22	0.176(1)	0.1707(4)	0.279(1)
O23	−0.140(1)	0.1225(4)	0.092(1)
O31	−0.084(1)	0.1697(4)	−0.334(1)
O32	−0.201(1)	0.0796(5)	−0.190(1)
O33	0.045(2)	0.0674(5)	−0.366(1)
O41	−0.068(1)	0.0433(4)	0.050(1)
O42	0.269(1)	0.0070(4)	0.144(1)
O43	0.265(1)	0.1002(4)	0.256(1)
O44	0.165(2)	0.0272(4)	−0.170(1)
C11	0.285(1)	0.1770(5)	−0.124(1)
C12	0.395(1)	0.1390(5)	0.058(2)
C13	0.342(2)	0.1100(6)	−0.146(2)
C21	0.024(2)	0.1946(6)	0.025(2)
C22	0.140(2)	0.1614(6)	0.194(2)
C23	−0.055(1)	0.1311(5)	0.076(1)
C31	−0.039(2)	0.1466(5)	−0.274(2)
C32	−0.116(2)	0.0909(6)	−0.183(2)
C33	0.037(2)	0.0844(6)	−0.291(2)
C41	0.020(2)	0.0551(6)	0.044(2)
C42	0.225(1)	0.0310(6)	0.097(1)
C43	0.210(2)	0.0936(6)	0.169(2)
C44	0.148(2)	0.0451(6)	−0.107(2)
C111	0.669(1)	0.0121(5)	0.414(1)
C112	0.667(2)	0.0130(6)	0.521(2)
C113	0.639(2)	−0.0153(6)	0.570(2)
C114	0.617(2)	−0.0448(6)	0.515(2)
C115	0.623(2)	−0.0481(6)	0.416(2)
C116	0.649(2)	−0.0193(6)	0.362(2)
C121	0.639(1)	0.0498(5)	0.194(1)
C122	0.528(1)	0.0427(5)	0.151(1)
C123	0.488(2)	0.0422(5)	0.042(1)
C124	0.553(2)	0.0486(5)	−0.024(2)
C125	0.667(2)	0.0550(6)	0.017(2)
C126	0.704(2)	0.0563(6)	0.127(2)
C131	0.658(1)	0.0923(5)	0.407(1)
C132	0.553(1)	0.1068(5)	0.355(1)
C133	0.518(2)	0.1347(6)	0.405(2)
C134	0.575(2)	0.1465(6)	0.498(2)
C135	0.677(2)	0.1333(6)	0.552(2)
C136	0.716(2)	0.1048(5)	0.506(2)
C141	0.863(1)	0.0557(5)	0.369(1)
C142	0.924(1)	0.0262(5)	0.376(1)
C143	1.032(2)	0.0288(6)	0.376(2)

Table 3 (continued)

Atom	x	y	z
C144	1.077(2)	0.0607(6)	0.368(2)
C145	1.021(2)	0.0899(6)	0.357(2)
C146	0.910(2)	0.0876(6)	0.357(2)
C211	0.496(1)	0.2509(5)	1.098(1)
C212	0.569(2)	0.2552(6)	1.199(2)
C213	0.531(2)	0.2442(7)	1.286(2)
C214	0.432(2)	0.2297(5)	1.273(2)
C215	0.360(2)	0.2262(7)	1.176(2)
C216	0.394(2)	0.2370(6)	1.085(2)
C221	0.597(1)	0.2263(5)	0.915(1)
C222	0.575(1)	0.1925(5)	0.944(1)
C223	0.624(2)	0.1644(6)	0.907(2)
C224	0.685(2)	0.1702(6)	0.840(2)
C225	0.707(2)	0.2034(7)	0.807(2)
C226	0.666(2)	0.2313(6)	0.851(2)
C231	0.425(1)	0.2868(5)	0.871(1)
C232	0.345(2)	0.3045(5)	0.907(2)
C233	0.257(2)	0.3204(5)	0.829(2)
C234	0.252(2)	0.3192(5)	0.723(2)
C235	0.331(2)	0.3012(5)	0.693(2)
C236	0.418(2)	0.2846(5)	0.762(2)
C241	0.661(1)	0.2984(5)	1.025(1)
C242	0.635(1)	0.3334(5)	1.035(1)
C243	0.731(2)	0.3561(6)	1.078(2)
C244	0.831(2)	0.3441(6)	1.108(2)
C245	0.856(2)	0.3092(6)	1.098(2)
C246	0.768(2)	0.2866(5)	1.052(2)
Hy1	0.2043	0.1628	0.0244
Hy2	0.1530	0.1315	−0.1879
Hy3	0.2791	0.0896	0.0020
Hy4	−0.0211	0.1448	−0.0905

account. Since no direct evidence was obtained from the difference Fourier maps, the four hydrido-ligands were located using Orpen's HYDEX program [20], assuming Re–H interactions of 1.85 Å. They were also included in the final structure factor calculation ($B = 5.0$ Å^2) but not refined. The final difference-Fourier map was flat, showing only some residual peaks not exceeding *ca.* 1.0 e Å^{-3}. Weights were assigned according to the formula $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma(F_o^2) = [\sigma^2(I) + (pI)^2]^{1/2}/L_p$ (I and L_p being the integrated intensity and the Lorentz-polarization correction, respectively); p was optimized to 0.040. The final values of the conventional agreement indices are reported in Table 2. The final positional parameters are given in Table 3.

The final list of observed and calculated structure factors moduli, a table of thermal factors and the calculated fractional coordinates of the phenyl hydrogen atoms are available from the authors.

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