Inorg. Chem. **1993,** *32,* 803–810

Addition Reactions of the Unsaturated Cluster Anion $[Re_4(\mu\text{-}H)_3(\mu_3\text{-}H)_2(CO)_{12}]^-$ with CO, PPh_3, and MeCN and Characterization of an Unstable Adduct with Water. X-ray Crystal Structure of the Tetraethylammonium Salt of the Derivative $[Re_4(\mu\text{-}H)_4(\mu_3\text{-}H)(CO)_{12}(PPh)_3]^-$

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Received July 20, 1992

The tetrahedral cluster anion $[Re_4(\mu\text{-}H)_3(\mu_3\text{-}H)_2(CO)_{12}]^-$ (**1**) easily adds donor molecules L, due to its unsaturation (58 cluster valence electrons). The reaction process changes significantly on varying the nature of L. In the presence of CO, two carbonyls are added, leading to the previously known butterfly derivative $[Re_4(\mu\text{-}H)_5(CO)_{14}]^-$ (**6**). Analogously, in the presence of MeCN, at 193 K, the novel $[Re_4(\mu\text{-}H)_5(CO)_{12}(NCMe)_2]^-$ (**4**) is formed, which, on the basis of the NMR data, is supposed to contain a butterfly cluster, with trans-diaxial nitriles coordinated on the wingtips of the butterfly. The reaction with PPh_3, at 193 K, leads on the contrary to a monoaddition derivative $[Re_4(\mu\text{-}H)_4(\mu_3\text{-}H)(CO)_{12}(PPh_3)]^-$ (**3**), containing a tetrahedral cluster, as shown by the X-ray analysis of its NEt_4^+ salt. Crystal data: triclinic, space group $P\bar{1}$ (No. 2), $a = 12.330$ (2) Å, $b = 13.202$ (2) Å, $c = 15.503$ (3) Å, $\alpha = 92.73$ (1)°, $\beta = 98.02$ (1)°, $\gamma = 96.92$ (1)°, $Z = 2$. The refinements, based on 3711 significant reflections, gave final R and R_w indices of 0.033 and 0.033. The same compound has also been obtained upon treating $[Re_4(\mu\text{-}H)_5(CO)_{12}(NCMe)_2]^-$ (**4**) with 1 equiv of PPh_3, at 243 K. Both compounds **3** and **4** decompose at room temperature, giving the previously known unsaturated triangular cluster anions $[Re_3(\mu\text{-}H)_4(CO)_9(PPh_3)]^-$ (**9**) and $[Re_3(\mu\text{-}H)_4(CO)_9(NCMe)]^-$ (**10**), respectively. ^1H NMR evidence has been obtained which shows that at low temperature compound **1** is able to reversibly coordinate one H_2O molecule, giving the adduct $[Re_4(\mu\text{-}H)_5(CO)_{12}(H_2O)]^-$ (**5**), in which water is supposed to act as a bridging ligand. On increasing the temperature, the equilibrium between compound **1** and the adduct with water progressively favors compound **1**. Approximate values of the equilibrium constants have been estimated from the NMR data at temperatures higher than 240 K (where the equilibrium is fast on the NMR time scale), allowing an evaluation of the thermodynamic parameters ($\Delta H^\circ = -59 \pm 2$ kJ mol^{-1}, $\Delta S^\circ = -215 \pm 8$ J K^{-1} mol^{-1}). The activation parameters for the dissociation of the aquo ligand ($\Delta H^\ddagger = 71 \pm 1$ kJ mol^{-1}, $\Delta S^\ddagger = 111 \pm 3$ J K^{-1} mol^{-1}) have been estimated from the rate constants obtained through a band-shape analysis in the range 202–234 K. The same computer simulations gave also the activation energy of the mutual exchange of the hydrides in the adduct with H_2O ($E_a = 52 \pm 1$ kJ mol^{-1}). Compound **1**, at T > 270 K, is unstable in solution in the presence of water and transforms slowly into the triangular cluster anion $[Re_3(\mu\text{-}H)_3(\mu_3\text{-}OH)(CO)_9]^-$ (**11**), likely via the unsaturated anion $[Re_3(\mu\text{-}H)_4(CO)_9(H_2O)]^-$ (**12**).

Introduction

Unsaturated carbonyl cluster species are of high current interest, because of their peculiar reactivity. The most extensively studied compound of this class is $[Os_3(\mu\text{-}H)_2(CO)_{10}]$, which gives rise to a variety of reactions leading to saturated derivatives.[1] Within the hydrido-carbonyl cluster compounds of rhenium some unsaturated species are known, exhibiting a triangular or a tetrahedral metallic frame, as $[Re_3(\mu\text{-}H)_3(CO)_{10}]^{2-}$ (**13**),[2] $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$ (**14**),[3] and $[Re_4(\mu_3\text{-}H)_4(CO)_{12}]$ (**8**).[4] The reactivity of these species, however, differs from that of the analogous unsaturated compounds of other metals, especially because they do not give additions of donor molecules. In fact $[Re_4(\mu_3\text{-}H)_4(CO)_{12}]$ (**8**) is reported[4] to undergoes a complete fragmentation in the presence of donor molecules and $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$ (**14**) reacts with 2-electron donor species L giving either substitution of two hydrides with two L molecules[5] or transfer of one hydride to the ligand.[6] We have previously reported[7] the synthesis and characterization of another unsaturated anion, $[Re_4(\mu\text{-}H)_3(\mu_3\text{-}H)_2(CO)_{12}]^-$ (**1**), possessing 58 cluster valence electrons (CVE) and containing a distorted tetrahedral metal atom frame, with the cluster unsaturation delocalized on two notably short edges. Its formula will be hereafter indicated simply as $[Re_4H_5(CO)_{12}]$, because in solution the hydrides are highly fluxional. This anion does give addition reactions leading to novel products, most of which are unstable and decompose to derivatives, which often are still unsaturated species. This reactivity is described here, together with the complete results of a single crystal X-ray investigation of the tetraethylammonium salt, diethyl ether solvated, of the unstable derivative $[Re_4(\mu\text{-}H)_4(\mu_3\text{-}H)(CO)_{12}(PPh_3)]^-$ (**3**).

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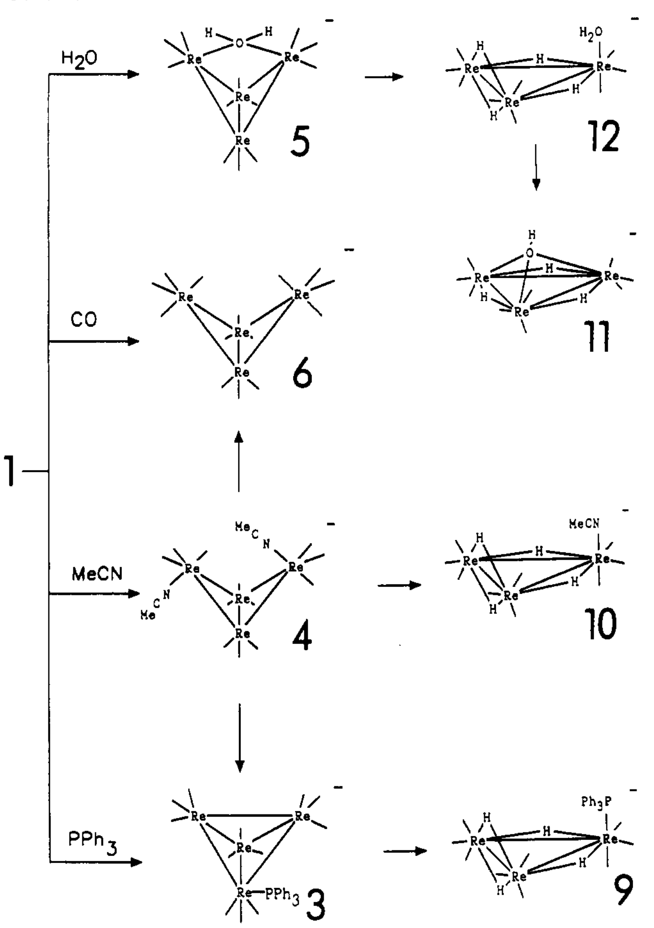
0020-1669/93/1332-0803$04.00/0

Scheme I



Results and Discussion

All the addition reactions here reported have been studied spectroscopically (mainly via ^1H NMR), using as starting material samples of the unsaturated anion $[Re_4H_5(CO)_{12}]^-$ (**1**); see Scheme I. This anion is generated in situ by treatment of $[Re_4(\mu\text{-H})_6(CO)_{12}]^{2-}$ (**2**)[8] with CF_3SO_3H. At room temperature reaction 1 is instantaneous and the deep red color of **1** appears as soon as the acid is added.

$$\begin{array}{ll} [Re_4(\mu\text{-H})_6(CO)_{12}]^{2-} + H^+ \rightarrow & [Re_4H_5(CO)_{12}]^- + H_2 \quad (1) \\ \text{60 CVE } (\mathbf{2}) & \text{58 CVE } (\mathbf{1}) \end{array}$$

Upon treatment of **1** with KH or $NaBH_4$, at room temperature, the saturated derivative **2** can be easily re-obtained (eq 2).

$$\begin{array}{ll} [Re_4H_5(CO)_{12}]^- + H^- \rightarrow & [Re_4(\mu\text{-H})_6(CO)_{12}]^{2-} \quad (2) \\ \text{58 CVE } (\mathbf{1}) & \text{60 CVE } (\mathbf{2}) \end{array}$$

The formation of saturated derivatives $[Re_4H_5(CO)_{12}L]^-$ by addition of two-electron donor molecules L is more problematical, as will be discussed below.

Addition of Carbon Monoxide. Treatment of compound **1** with CO, at room temperature or below, results in an instantaneous color change of the solution from red to yellow. IR and ^1H NMR spectroscopic monitoring reveals the addition of *two* CO molecules, with quantitative formation of the 62 CVE butterfly cluster $[Re_4(\mu\text{-H})_5(CO)_{14}]^-$ (**6**), previously obtained[9] by reaction of $[ReH_2(CO)_4]^-$ with $[Re_3(\mu\text{-H})_3(CO)_{10}(NCMe)_2]$ (**15**). All attempts to obtain the hypothetical saturated (60 CVE) tetrahedral cluster $[Re_4H_5(CO)_{13}]^-$, by addition of only one CO molecule to compound **1**, failed, even using only 1 equiv of CO, at room temperature or at 193 K. We have also attempted the synthesis of $[Re_4H_5(CO)_{13}]^-$ by protonation of its conjugated base, i.e. the dianion $[Re_4(\mu\text{-H})_4(CO)_{13}]^{2-}$ (**7**),[10] but no stable product has been isolated.

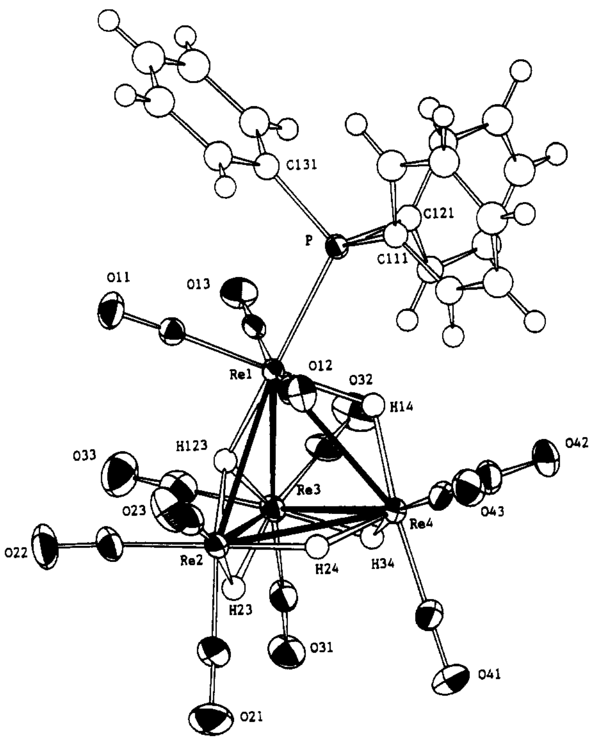


Figure 1. View of the anion $[Re_4(\mu\text{-H})_4(\mu_3\text{-H})(CO)_{12}(PPh_3)]^-$ (**3**). For clarity the numbering of the carbonyl groups is indicated only by the labels of their oxygen atoms. The H atoms are in calculated positions (see text).

Addition of PPh₃. The treatment with stoichiometric PPh_3, at low temperature, gives immediately a pale yellow solution. The ^1H NMR spectrum shows the essentially quantitative formation of a novel species, exhibiting three hydride resonances, at δ −14.20, −15.64, and −18.50 ppm, with intensity ratio 1:3:1, the upfield signal being a doublet with $J_{HP} = 14$ Hz. This spectrum suggests the formation of a saturated product of formula $[Re_4H_5(CO)_{12}(PPh_3)]^-$ (compound **3**), maintaining the tetrahedral Re_4 core, as confirmed by a single-crystal X-ray investigation (see below).

The location of the hydrides in solution is likely quite similar to that computed for the solid state structure (Figure 1), with two hydrides bound to the unique Re vertex and the other three bridging on the edges of the basal triangle. The observation of three hydridic resonances, instead of the five expected on the basis of the solid-state structure, indicates the presence of a dynamic process that equalizes three out of the five hydrides. The value of J_{HP} of the higher field resonance is typical of hydrides bound cis to PPh_3 on Re atoms (H14 in the solid state), the values of J_{HP} for trans hydrides being usually quite small in this class of compounds.[11] The observation of the coupling to the P atom of only one hydride indicates that the scrambling process, fast even at 193 K, does not change the relative positions of the six ligands bound to the unique Re vertex. In this hypothesis, therefore, the hydride triple-bridging in the solid state (H123) would be responsible for the resonance at lower field, and the

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[11] See for instance ref 5 or: Beringhelli, T.; D'Alfonso, G.; Minoja, A. P.; Freni, M. *Inorg. Chem.* **1991**, *30*, 2757.

signal of intensity 3 would be due to the averaged resonances of the basal hydrides. The mechanism of the scrambling could be either an edge–terminal–edge scrambling of these hydrides, or a rotation of the whole apical pseudooctahedral $[ReH_2(CO)_3\text{-}PPh_3]^-$ moiety with respect to the $Re_3(\mu\text{-}H)_3(CO)_9$ basal triangle, as already discussed for the isoelectronic moiety $[ReH(CO)_4]^{2-}$ in $[Re_4(\mu\text{-}H)_4(CO)_{13}]^{2-}$ (**7**).[10b] Indeed it is well-known that saturated 18-e species can act as ligands toward unsaturated fragments or even displace other weakly bound ligands.[12] Recently, the isoelectronic fragment $[ReH(CO)_5]$ has been proved able to replace COD or ethylene from platinum complexes like $[Pt(COD)_2]$[13a] or $[Pt(PPh_3)_2(C_2H_4)]$[13b] or the η^1-bound aldehyde in $[Mn_2(CO)_9(\eta^1\text{-tolualdehyde})]$.[13c]

The three hydride resonances remain sharp up to 273 K and then broaden all together, showing the onset of a new dynamic process together with the decomposition of compound **3**.

In fact, ^1H NMR and IR monitoring shows at room temperature the clean transformation (complete in about 12 h) of **3** into the unsaturated triangular cluster $[Re_3(\mu\text{-}H)_4(CO)_9(PPh_3)]^-$ (**9**), previously synthesized by a different route[14] and characterized by X-ray analysis (see Scheme I). The lost "$ReH(CO)_3$" fragment gives rise to various unidentified derivatives, as indicated by the presence in the ^1H NMR spectrum of several signals of very low intensity, whose attribution was not attempted.

Some crystals of **3** suitable for X-ray analysis have been obtained (together with crystals of $[Re_3(\mu\text{-}H)_4(CO)_9(PPh_3)]^-$ (**9**)) by slow diffusion of diethyl ether into a concentrated dichloromethane solution at 253 K.

Structure of $[Re_4(\mu\text{-}H)_4(\mu_3\text{-}H)(CO)_{12}(PPh_3)]^-$ (3). The crystal structure consists of the packing of discrete $[Re_4(\mu\text{-}H)_4(\mu_3\text{-}H)\text{-}(CO)_{12}(PPh_3)]^-$ anions, tetraethylammonium cations, and solvate diethyl ether molecules in the ratio 1:1:1, separated by normal van der Waals' contacts. Bond distances and angles for the anion (see Figure 1) are given in Table I. Though no symmetry element can be easily envisaged, a rough mirror plane might be assumed to pass through Re1, Re4, P and the midpoint of the Re2–Re3 edge.

The metal atoms form a distorted tetrahedral cluster, which bears 12 terminally bonded CO ligands, three to each rhenium atom, a triphenylphosphine ligand, bound to Re1, and five bridging hydride ligands. These ligands, located indirectly by nonbonding potential energy calculations,[15] were found to occupy four edge bridging locations (three on the edges of the basal $Re_3(CO)_9$ triangle and one on the edge Re1–Re4) and one face bridging location, on the Re1, Re2, Re3 triangle.[16]

The stereochemistry of the anion can be related to that of $[Re_4(\mu\text{-}H)_4(CO)_{13}]^{2-}$ (**7**),[10] whose structure as been recently reinvestigated.[10b] In the monoanion, beside to the presence of an additional triple bridging hydride, a CO group is substituted by the phosphine ligand. In spite of the similarity of these two structures, all the attempts to obtain the corresponding $[Re_4(\mu\text{-}H)_4(\mu_3\text{-}H)(CO)_{13}]^-$ anion (see above), have failed up to now.

Table I. Bond Distances (Å) and Angles (deg) within $[Re_4(\mu\text{-}H)_4(\mu_3\text{-}H)(CO)_{12}(PPh_3)]^-$ (3)

Distances

Re1–Re2	3.177 (1)	Re4–C43	1.91 (2)
Re1–Re3	3.240 (1)	C11–O11	1.14 (2)
Re1–Re4	3.185 (1)	C12–O12	1.16 (2)
Re2–Re3	2.976 (1)	C13–O13	1.14 (2)
Re2–Re4	3.196 (1)	C21–O21	1.15 (2)
Re3–Re4	3.082 (1)	C22–O22	1.15 (2)
Re1–P	2.404 (4)	C23–O23	1.14 (2)
Re1–C11	1.93 (1)	C31–O31	1.18 (2)
Re1–C12	1.98 (2)	C32–O32	1.18 (2)
Re1–C13	1.97 (2)	C33–O33	1.18 (3)
Re2–C21	1.87 (2)	C41–O41	1.16 (2)
Re2–C22	1.89 (2)	C42–O42	1.17 (2)
Re2–C23	1.91 (2)	C43–O43	1.15 (3)
Re3–C31	1.86 (2)	P–C111	1.82 (2)
Re3–C32	1.86 (2)	P–C121	1.84 (1)
Re3–C33	1.85 (2)	P–C131	1.82 (1)
Re4–C41	1.87 (2)		
Re4–C42	1.91 (2)		

Angles

Re2–Re1–C11	90.2 (4)	Re2–Re3–C31	114.1 (5)
Re2–Re1–C12	74.5 (4)	Re2–Re3–C32	154.2 (6)
Re2–Re1–C13	116.6 (4)	Re2–Re3–C33	98.1 (6)
Re2–Re1–P	160.6 (1)	Re4–Re3–C31	110.5 (6)
Re3–Re1–C11	113.9 (5)	Re4–Re3–C32	99.6 (6)
Re3–Re1–C12	123.5 (4)	Re4–Re3–C33	157.0 (7)
Re3–Re1–C13	69.3 (4)	C31–Re3–C32	89.6 (7)
Re3–Re1–P	137.1 (1)	C31–Re3–C33	89.3 (9)
Re4–Re1–C11	149.4 (4)	C32–Re3–C33	91.8 (8)
Re4–Re1–C12	77.4 (4)	Re1–Re4–C41	157.0 (5)
Re4–Re1–C13	113.3 (4)	Re1–Re4–C42	110.0 (5)
Re4–Re1–P	110.6 (1)	Re1–Re4–C43	100.0 (5)
C11–Re1–C12	87.8 (6)	Re2–Re4–C41	97.4 (5)
C11–Re1–C13	85.8 (6)	Re2–Re4–C42	161.7 (6)
C11–Re1–P	94.8 (4)	Re2–Re4–C43	106.6 (4)
C12–Re1–C13	167.2 (6)	Re3–Re4–C41	104.5 (6)
C12–Re1–P	86.9 (4)	Re3–Re4–C42	105.7 (6)
C13–Re1–P	82.6 (4)	Re3–Re4–C43	159.4 (4)
Re1–Re2–C21	162.9 (6)	C41–Re4–C42	91.3 (7)
Re1–Re2–C22	104.8 (5)	C41–Re4–C43	88.4 (8)
Re1–Re2–C23	90.7 (5)	C42–Re4–C43	89.6 (8)
Re3–Re2–C21	114.9 (6)	Re1–C11–O11	178 (1)
Re3–Re2–C22	96.5 (5)	Re1–C12–O12	173 (1)
Re3–Re2–C23	154.0 (5)	Re1–C13–O13	171 (1)
Re4–Re2–C21	103.8 (5)	Re2–C21–O21	175 (2)
Re4–Re2–C22	155.3 (5)	Re2–C22–O22	177 (2)
Re4–Re2–C23	110.3 (5)	Re2–C23–O23	175 (1)
C21–Re2–C22	92.3 (8)	Re3–C31–O31	177 (1)
C21–Re2–C23	90.3 (8)	Re3–C32–O32	176 (2)
C22–Re2–C23	87.9 (8)	Re3–C33–O33	177 (2)
Re1–Re3–C31	170.8 (6)	Re4–C41–O41	179 (2)
Re1–Re3–C32	93.7 (6)	Re4–C42–O42	179 (2)
Re1–Re3–C33	99.2 (7)	Re4–C43–O43	179 (1)

The Re–Re bonds are scattered in the range 2.976 (1)–3.240 (1) Å. Rather surprisingly the shortest bond, Re2–Re3 = 2.976 (1) Å, corresponds to the unique tetrahedral edge which, according to the indirect location of the hydrides, supports, at the same time, a double-bridging hydride ligand and the triple-bridging hydride ligand. As observed in other cases,[17,18] the criterion of metal–metal bond lengthening due to the presence of bridging hydrides must be applied with caution. In particular, in the present case a lengthening of the Re2–Re3 edge should probably imply a shorter repulsive contact between the two hydrides (actual H23–H123 contact from the calculated positions: 2.21 Å). Similarly, in the triangular cluster $[Re_3(\mu\text{-}H)(\mu_3\text{-}H)(CO)_{10}(C_7H_7)]$, the unique Re–Re edge supposed to be bridged by both the hydrides is relatively short [3.076(1) Å] and shorter than the other two cluster edges [3.193 (1) and 3.160 (1) Å].[18]

The four rhenium atoms display distorted octahedral coordination: Re1 is bound to three CO groups, the phosphine

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(16) The hydride locations correspond to five quite clear potential minima, which are associated with evident holes among carbonyls on the cluster surfaces. Moreover, the simultaneous presence of five hydrides imposes geometrical restrictions, due to their mutual interactions, which lead to a unique unambiguous assignement.

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ligand and two hydrides, while the other metals are connected to three CO and three hydrides. Within the (Re1)(CO)$_3$(PPh$_3$) unit two CO groups, CO12 and CO13, are mutually trans, the C12-Re1-C13 angle being 167.2 (6)°, and exhibit, as expected, longer Re–C bond lengths (mean 1.98 Å) than all the other carbonyl groups (mean 1.89 Å).

The Re1–P bond length, 2.404 (4) Å, and the bond parameters within the triphenylphosphine ligand fall in the normal range of values for similar interactions.

The anion represents, as the parent unsaturated species $[Re_4(\mu-H)_3(\mu_3-H)_2(CO)_{12}]^-$ (**1**), a rare case of a cluster compound showing the contemporary presence of different types of hydride ligands. The structure, moreover, is of particular interest for the high number of ligands on a tetrahedral cluster surface; ligand overcrowding may be responsible for the instability of this species in solution at room temperature.

Addition of Acetonitrile. The treatment of **1** with MeCN, at 193 K, causes the selective formation of a novel species exhibiting three hydride resonances (δ −13.31, −14.47, and −14.61), in the ratio 2:1:2, and two resonances attributable to coordinated acetonitrile molecules (δ 2.64 and 2.45, each of relative intensity 3). The same species is obtained by protonation of **2** in the presence of MeCN, at 193 K. The product can be formulated as $[Re_4(\mu-H)_5(CO)_{12}(MeCN)_2]^-$ (**4**), with 62 CVE. The monoaddition product could not be observed, even on using only 1 equiv of MeCN.

On the basis of the NMR data, the most likely structure for compound **4** has both the nitriles axially coordinated on the wingtip positions of a butterfly cluster, one inward and the other outward with respect to the acute angle of the butterfly (see Scheme I, where the H atoms, bridging all the Re–Re bonds, have been omitted), with C_s symmetry.

When the temperature is raised, the hydride resonances of **4** broaden, indicating fluxionality. Also in this case, dynamic NMR analysis was impossible, because **4** is stable only at low temperatures. At $T > 243$ K, in fact, it transforms into an intermediate species as yet unidentified (see Experimental Section). Then, at still higher temperatures, the formation of the previously known[14] unsaturated triangular cluster anion $[Re_3(\mu-H)_4(CO)_9(MeCN)]^-$ (**10**) (see Scheme I) is observed. The same product is obtained if the reaction of **1** with MeCN is performed directly at room temperature.

Therefore, while the low temperature reaction of **1** with MeCN resembles that with CO (addition of *two* ligands), the room-temperature behavior is quite close to that of the PPh$_3$ derivative **3**. The fate of the lost moiety is more evident in this case than in the decomposition of **3**. NMR and IR monitoring show the formation of compound **2** and of the cationic species $[Re(CO)_3(MeCN)_3]^+$, according to the idealized stoichiometry

$$\begin{aligned} &6\underset{\mathbf{4}}{[Re_4(\mu\text{-}H)_5(CO)_{12}(MeCN)_{12}]^-} \rightarrow \\ &\qquad 6\underset{\mathbf{10}}{[Re_3(\mu\text{-}H)_4(CO)_9(MeCN)]^-} + \\ &\qquad 2[Re(CO)_3(MeCN)_3]^+ + \underset{\mathbf{2}}{[Re_4(\mu\text{-}H)_6(CO)_{12}]^{2-}} \quad (3) \end{aligned}$$

Treatment of **4** with CO, at 243 K, results in the expected substitution of the two nitriles by two carbonyls, with formation of the butterfly derivatives $[Re_4(\mu-H)_5(CO)_{14}]^-$ (**6**). The reaction with stoichiometric PPh$_3$, at the same temperature, leads to the tetrahedral derivative **3**. Compound **4**, therefore, behaves like the tetrahedral parent compound **1** toward donor molecules, even if NMR monitoring at 193 K shows the formation of intermediates, whose characterization is in progress.

Addition of Water. The occurrence of this reaction has been serendipitously discovered while monitoring the above reactions via low-temperature ^{1}H NMR analysis. We observed that the red color of an acetone-d_6 solution of **1** disappeared simply upon immersion of the NMR tube in an acetone/solid CO$_2$ bath, at about 193 K. ^{1}H NMR, at 193 K, showed the presence of two novel hydride resonances, at δ −11.17 and −14.61 (intensity ratio 4:1), instead of the unique hydride resonance of **1** (δ −10.33 at 298 K). This change could not be attributed to the freezing of an intramolecular fluxional process, since both the novel signals were shifted upfield with respect to that of **1**. At room temperature, the red color as well as the resonance of **1** reappeared reversibly.

Table II. Values of the Approximate Constants *K* for Equilibrium 4 Calculated from the NMR Data, in the Presence of Different Amounts of Water

	experiment B[a]			experiment C[b]		
T	δ[c]	*K*[d]	*K'*[e]	δ[c]	*K*[d]	*K'*[e]
255	−11.080	6.3	140	−11.493	8.4	25
265	−10.776	2.3	50	−11.168	2.8	8
275	−10.554	0.85	20	−10.830	1.0	3
285				−10.577	0.37	1
298				−10.449	0.16	0.5

[a] Experiment with 3.8 equiv of H$_2$O. [b] Experiment with 10.3 equiv of H$_2$O. [c] Values of δ of the unique hydride resonance observed for fast exchanging equilibrium mixtures of compounds **1** and **5**. [d] Constants of the equilibrium 4. [e] Constants of the equilibrium between **1** and **5**, according to the hypothesis that **5** bears two water molecules.

We attribute this behavior to the reversible formation of an adduct between compound **1** and the water present in the deuterated solvent, according to eq 4.

$$[Re_4H_5(CO)_{12}]^- + H_2O \rightleftharpoons [Re_4H_5(CO)_{12}(H_2O)]^- \quad (4)$$

In fact, when acetone-d_6 dried over molecular sieves was used, the red color was observed also at low temperature and the ^{1}H NMR spectrum showed, as the main hydride signal, the resonance of **1** (δ −10.54 at 193 K). The hydride resonances of $[Re_4H_5(CO)_{12}(H_2O)]^-$ (**5**) were still present (but with much lower intensity), due to the difficulty in removing completely water from acetone. Upon addition of H$_2$O, the red color disappeared and the resonance of **1** was completely replaced by the two signals of the aquo complex **5**. The formation of **5** by reaction of **1** with water was observed also in THF.

The NMR resonance of coordinated H$_2$O in THF-d_8 appears at δ 8.42 (193 K), with intensity corresponding to one molecule of water per cluster. In acetone-d_6, the resonance of water has not been unambiguously assigned (see Experimental Section), but we confidently assume the presence of only one coordinated molecule of water also in this solvent, on the basis of the values of the equilibrium constants for reaction 4, as discussed in the following (see Table II).

The presence of two hydride resonances in the ratio 4:1 rules out the possibility that **5** maintains the tetrahedral metallic skeleton of the parent compound. The most likely structure of **5** contains the H$_2$O ligand coordinated in a bridging location and therefore acting as a 4-electron donor, giving a 62 CVE butterfly cluster anion, of idealized C_{2v} symmetry (see Scheme I, where the H atoms bridging all the Re–Re interactions have been omitted).

The aquo ligand is very labile, as expected, and NMR monitoring shows its easy substitution, even at 193 K, by CO, PPh$_3$, and MeCN, to give the same derivatives obtained from compound **1**. However, when mixtures of **1** and **5** are treated with a deficiency of a donor molecule, **1** is preferentially attacked. It is therefore likely that the substitution of H$_2$O occurs via compound **1** (dissociative mechanism), since the equilibrium **4** is quite fast also at 193 K.

Water complexes of metals in low oxidation states are relatively uncommon,[19] and to the best of our knowledge, the detection of

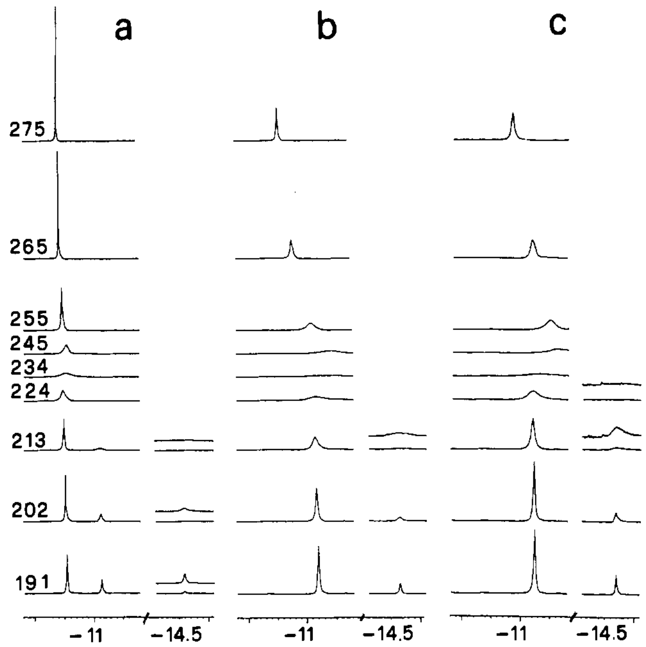

Figure 2. Variable-temperature ^1H NMR spectra (hydride regions) of acetone-d_6 solutions of $[Re_4H_5(CO)_{12}]^-$ (**1**), in the presence of different amount of water (see text). The intensities of the high-field resonance, shown in the insets, are four times the other ones.

an aquo ligand both in a carbonyl cluster species and in an anionic hydrido complex is unprecedented.

On raising the temperature, the ^1H NMR spectrum of a mixture of compounds **1** and **5** undergoes several changes (experiment A, Figure 2a). At first the two hydride resonances of **5** broaden and, at ca. 220 K, collapse, indicating the onset of a dynamic process equalizing the two types of hydrides of **5**. At 213 K, the resonance of compound **1** also broadens, suggesting that equilibrium 4 becomes fast on the NMR time scale. At temperatures higher than 245 K, only one resonance is present in the spectra, with a δ value resulting from the average of the chemical shifts of the two resonances of **5** and of the resonance of **1**, weighted according to their relative amounts. This δ value undergoes a downfield shift on raising the temperature, indicating the decrease of the amount of **5** in the equilibrium mixture. This shift is even more evident in the spectra of the samples containing added water (experiments B and C, Figure 2b,c), where a higher percentage of **5** is present at the lower temperatures.

From the averaged values of the chemical shifts, at temperatures corresponding to fast exchange between **1** and **5**, it is possible to obtain approximate values of the equilibrium constants K. This has been performed for experiments B and C, containing different amounts of water (Table II): the agreement between the values of K obtained in the two experiments is good, assuming that **5** bears one molecule of water only.

From the above data, it is easily computed that, in experiment B (water 0.15 M ca., corresponding to ca. 3 equiv), **5** is about 90% at 234 K, 30% at 265 K, and only 3% at room temperature. The variable amount of **1** accounts for the observed changes of the color of the solution with the temperature. The temperature at which the change of color occurs is a function of the concentration of water. Equilibrium 4, in principle, works therefore as a moisture indicator or a thermometer.

The formation of the adduct **5** is expected to be a slightly exothermic reaction, with negative entropy, and therefore is unfavorable at higher temperatures. This is in line with the increased dissociation of **5** at higher temperatures and with the values of the thermodynamic parameters calculated from the two sets of values of K for equilibrium 4 reported in Table II: $\Delta H° = -58 \pm 1$ and -59 ± 2 kJ mol^{-1}, $\Delta S° = -214 \pm 5$ and -215 ± 8 J K^{-1} mol^{-1}, in experiments B and C, respectively.

The band-shape analysis was employed in order to determine the kinetic parameters of the two processes responsible for the variable temperature spectral changes. At temperatures lower than 245 K the spectra of the two experiments with added water (Figure 2b,c) are affected only by the exchange of the hydrides within **5**, due to the very low amount of **1** in these conditions, and their simulations allowed the estimate of the rate constants for the intramolecular process (k_i). The rate constants for the exchange between **1** and **5** (k_d from **5** to **1**), at the same temperatures, were determined from the experiment without added water (Figure 2a). In this range of temperatures, similar sets of values for k_i and k_d gave satisfactory fittings of the spectra of all the experiments, leading to the following activation parameters: $E_a = 52 \pm 1$ kJ mol^{-1}, $\Delta H^{\ddagger} = 50 \pm 1$ kJ mol^{-1}, and $\Delta S^{\ddagger} = 38 \pm 5$ J K^{-1} mol^{-1} for the scrambling of the hydrides in **5**; $E_a = 72 \pm 1$ kJ mol^{-1}, $\Delta H^{\ddagger} = 71 \pm 1$ kJ mol^{-1}, and $\Delta S^{\ddagger} = 111 \pm 3$ J K^{-1} mol^{-1} for the transformation of **5** into **1**. The high positive $\Delta S^{\ddagger}$ value of the intermolecular exchange is typical of a dissociative process, while the relatively low (for a dissociative process) value of $\Delta H^{\ddagger}$ reflects the labile nature of the aquo ligand.

At temperatures higher than 234 K, all of the spectra are affected by both the processes and a separate evaluation of the two rate constants is not straightforward. Simulations using the values of k_i and k_d computed from the above Arrhenius parameters gave reasonable results only for the experiment of Figure 2a, while experiments B and C required much smaller rate constants for the intermolecular exchange. This could suggest that equilibrium 4 is not an elementary process. Indeed, at each temperature a better fit of all the three experiments was obtained using, for the intermolecular exchange, rate constants k_W depending on the concentration of water, [W], according to the relationship $k_W = k_d/(1 + k'[W])$. This expression is typical of two-step mechanisms, involving a first dissociative equilibrium with the forward reaction described by k_d. The constant k' represents the ratio between the rate constant for the equilibrium reverse reaction and that leading to the final products. A more detailed kinetic study of this process is needed, in order to verify this mechanicistical hypothesis and clarify the nature of the possible intermediate.

At temperatures higher than 275 K, compound **1** slowly decomposes in the presence of water, either in acetone or in tetrahydrofuran, leading finally to the triangular cluster anion $[Re_3(\mu\text{-}H)_3(\mu_3\text{-}OH)(CO)_9]^-$ (**11**),[20] identified by its hydridic resonance, at δ −11.71. This finding suggests that **5**, still present at room temperature, even if in quite low concentration, decomposes in the same way as the phosphine and nitrile derivatives **3** and **4**, giving an unsaturated intermediate $[Re_3(\mu\text{-}H)_4(CO)_9(H_2O)]^-$ (**12**) (see Scheme I). In this species the contemporary presence of the acidic water protons and of negatively polarized hydrides would result in H_2 evolution, as observed previously for the corresponding MeOH derivative,[14] with formation of the μ_3-OH group. The possible formation of $[Re_3(\mu\text{-}H)_3(\mu_3\text{-}OH)(CO)_9]^-$ (**11**) through this pathway has been previously discussed[20] in the reaction of $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$ (**14**) with Me_3NO in the presence of water.

Conclusions

Compound **1** has been found able to add the three donor molecules investigated (CO, PPh_3, MeCN) and also H_2O. However, the expected transformation of the unsaturated tetrahedral parent compound **1** (58 CVE) into a saturated tetrahedral derivative with 60 CVE has been obtained only with PPh_3. In the other cases, 62 CVE butterfly clusters were formed, by addition

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[19] Some recent examples of low-oxidation-state transition-metal water complexes are quoted in Agbossou, S. K.; Roger, C.; Igau, A.; Gladysz, J. A. *Inorg. Chem.* **1992**, *31*, 419.

[20] Beringhelli, T.; D'Alfonso, G.; Freni, M.; Ciani, G.; Molinari, H. *J. Organomet. Chem.* **1986**, *311*, 177.

of two CO or MeCN molecules, or by addition of one H_2O molecule acting as 4-electron donor.

It is worth noting that most of the addition derivatives are thermally unstable and decompose to give unsaturated triangular cluster anions $[Re_3(\mu\text{-}H)_4(CO)_9L]^-$. At room temperature, therefore, the reaction of the *unsaturated* $[Re_4H_5(CO)_{12}]^-$ anion (**1**) with donor molecules leads unexpectedly to other *unsaturated* species, of lower nuclearity, through *saturated* intermediates. These transformations reflect the peculiar stability of unsaturated species in rhenium hydrido–carbonyl cluster chemistry. This is possibly related to the high number of ligands required by rhenium to obey the 18-electron rule, which causes steric crowding also in clusters of nuclearity as low as 4.

It is likely that steric crowding is responsible also for the general preference for butterfly vs tetrahedral products. In fact, biaddition products (in spite of the presence of one more ligand) could be favored by the relief of ligand crowding due to the breaking of a Re–Re interaction of the tetrahedron to give a butterfly cluster. The isolation of the monoaddition product in the case of PPh_3 is likely due to kinetic factors, which make more difficult the addition of a second ligand.

In any case, as already pointed out for other systems,[21] the energy difference between butterfly and tetrahedral geometries appears small in many of these species. In fact, the unsaturated compound **1** (tetrahedral) and the "lightly stabilized" derivatives **4** and **5** (with the proposed butterfly structures) behave in the same way toward donor molecules as CO or PPh_3: particularly noteworthy is the transformation of the nitrile derivative **4** into the tetrahedral species **3**, upon treatment with PPh_3. It is also likely that the fluxional process responsible for the equalization of the hydrides in **5** occurs via an edge–terminal–edge scrambling of water, i.e. through a tetrahedral intermediate.

Experimental Section

Samples of $[Re_4(\mu\text{-}H)_6(CO)_{12}][NEt_4]_2$, hereafter indicated as **2**$[NEt_4]_2$, were obtained by fractional crystallization of mother liquors of the synthesis of $[Re_3(\mu\text{-}H)_3(CO)_{10}][NEt_4]_2$ (**13**).[3] Infrared spectra were recorded on a Perkin-Elmer 781 grating spectrophotometer in a 0.1-mm CaF_2 cell. NMR monitoring of the reaction progress was performed using a Bruker WP80 instrument.

The complete transformation of **2** into compound **1** requires a little excess of acid (20–30%), and the yields, as judged by the integrated intensity of the hydride resonance of **1** with respect to the cationic ones, are in the range 80–90%. Minor resonances are present at δ −7 to −9 ppm (193 K), likely due to decomposition of **1** at room temperature. To avoid the presence of excess acid in the experiments performed to study the reactivity of **1**, the protonation of **2** has been usually performed using 1 equiv of acid, thus leaving some unreacted starting material.

Reaction of $[Re_4H_5(CO)_{12}]^-$ (1) with CO. A sample (18 mg, 0.013 mmol) of **2**$[NEt_4]_2$, dissolved in acetone saturated with CO, was treated, under CO atmosphere, with 1.5 μL (0.017 mmol) of CF_3SO_3H. IR monitoring showed the quantitative formation of $[Re_4(\mu\text{-}H)_5(CO)_{14}]^-$ (**6**). The same result was obtained by treating **2**$[NEt_4]_2$ first with CF_3SO_3H (under N_2) and then with CO. The reaction was also monitored by NMR at low temperature: a sample of **2**$[NEt_4]_2$ (33 mg, 0.024 mmol) dissolved in a screw-cap NMR tube in dried acetone-d_6 was treated with 3 μL (0.034 mmol) of CF_3SO_3H. Four aliquots of 0.3 mL (about 0.012 mmol each) of CO were successively added, at 193 K. NMR monitoring at 193 K indicated that the reaction at this temperature was exceedingly slow, significant changes, after each CO addition, occurring only after the tube was shaken for a short time at room temperature or after the tube was kept in a bath at 233 K. The main process observed was the progressive formation of $[Re_4(\mu\text{-}H)_5(CO)_{14}]^-$ (**6**) (δ −15.27 and −16.33, 1:4), at the expense of **1**, at first, and then of the aquo complex **5**. A few unattributed resonances were observed (in particular at δ −14.78 and −16.21), but their intensities never became significant.

Reaction of $[Re_4H_5(CO)_{12}]^-$ (1) with $NaBH_4$. A sample (9 mg, 0.0066 mmol) of **2**$[NEt_4]_2$, dissolved in tetrahydrofuran, was treated with 1 μL of CF_3SO_3H (0.011 mmol). The red solution was then treated with $NaBH_4$ (1.7 mg, 0.045 mmol). The red color disappeared and IR monitoring showed the formation of $[Re_4(\mu\text{-}H)_6(CO)_{12}]^{2-}$ (**2**).

Reaction of $[Re_4H_5(CO)_{12}]$ (1) with PPh_3. A sample (15 mg, 0.011 mmol) of **2**$[NEt_4]_2$, dissolved in 0.5 mL of acetone-d_6, was treated at room temperature with 1 μL of CF_3SO_3H (0.011 mmol) and then, at about 193 K, with PPh_3 (3 mg, 0.011 mmol). ^1H NMR (193 K) showed the essentially quantitative formation of **3**: δ 7.6 (m, 15), −14.20 (s, 1), −15.64 (s, 3), and −18.50 (d, J_{HP} = 14 Hz, 1). As the temperature was increased, two of the three hydride resonances shifted significantly in opposite directions (at 273 K: δ −14.42, −15.45, and −18.46). At room temperature, all the resonances broaden, while the hydride signals of $[Re_3(\mu\text{-}H)_4(CO)_9(PPh_3)]^-$ (**9**)[14] were progressively growing, at δ −7.56 (d, J_{HP} = 5.5 Hz, 1), −8.70 (d, J_{HH} = 1.5 Hz, 1), and −12.17 (dd, J_{HP} = 16 Hz, J_{HH} = 1.5 Hz, 2). The reaction was repeated (using similar amounts of reagents) in a NMR tube at room temperature, showing the formation of $[Re_3(\mu\text{-}H)_4(CO)_9(PPh_3)]^-$ (**9**). The reaction was also performed in a Schlenk tube, in CH_2Cl_2, at ca. 193 K, and crystals of **3**$[NEt_4]$ were obtained by slow diffusion of Et_2O, at 253 K. IR (ν_{CO}, acetone, cm^{-1}): 2055 w, 2010 vs, 1952 m, 1935 sh, 1923 s, 1910 sh.

Reaction of $[Re_4H_5(CO)_{12}]^-$ (1) with MeCN. A sample (40 mg, 0.030 mmol) of **2**$[NEt_4]_2$, dissolved in 0.5 mL of acetone-d_6, was treated at room temperature with 2.6 μL of CF_3SO_3H (0.029 mmol) and then with 3.5 μL of MeCN (0.066 mmol), at ca. 193 K. The NMR spectrum, at the same temperature, showed the formation in high yields (>80%) of compound **4**, characterized by resonances at δ 2.64 (s, 3), 2.45 (s, 3), −13.31 (s, 2), −14.47 (s, 1), and −14.61 (s, 2). When the temperature was raised above 273 K, the resonances of compound **4** were completely substituted by those of $[Re_3(\mu\text{-}H)_4(CO)_9(NCMe)]^-$ (**10**) (δ 2.40, −7.97, −8.34, and −10.47; relative ratio 3:1:1:2),[14] $[Re(CO)_3(NCMe)_3]^+$ (δ 2.68), and compound **2**. The formation of an intermediate species, as yet uncharacterized, was observed at temperature higher than 253 K: δ 2.63 (3), −7.67 (1), −8.49 (1), −11.43 (1), −12.14 (1), and −12.21 (1).

Reaction of $[Re_4H_5(CO)_{12}(NCMe)_2]^-$ (4) with CO. A sample of **4**$[NEt_4]$, prepared as above in an NMR tube from **2**$[NEt_4]_2$ (25 mg, 0.019 mmol), was treated at 193 K with 5 mL of CO (ca. 0.2 mmol). The NMR spectrum at 253 K showed that the resonances of **4** were substituted by those of $[Re_4(\mu\text{-}H)_5(CO)_{14}]^-$ (**6**) (δ −15.16, −16.28; 1:4).[9]

Reaction of $[Re_4H_5(CO)_{12}(NCMe)_2]^-$ (4) with PPh_3. A sample of **4**$[NEt_4]$, prepared as above in an NMR tube from **2**$[NEt_4]_2$ (43 mg, 0.032 mmol), was treated at 193 K with PPh_3 (9 mg, 0.34 mmol). The NMR spectrum at 243 K showed that the resonances of **4** were substituted by those of $[Re_4(\mu\text{-}H)_5(CO)_{12}(PPh_3)]^-$ (**3**). Also a minor amount of $[Re_3(\mu\text{-}H)_4(CO)_9(PPh_3)]^-$ (**9**) was present.[14]

Reaction of $[Re_4H_5(CO)_{12}]^-$ (1) with Water. (a) A sample (20 mg, 0.0148 mmol) of **2**$[NEt_4]_2$, dissolved in 0.5 mL of THF-d_8, was treated at room temperature with 1.5 μL of CF_3SO_3H (0.017 mmol). ^1H NMR at 193 K of the deep red solution showed (beside some unreacted **2**) the resonance of **1** at δ −10.61 and the resonances of **5**, at δ 8.42, −11.18, and −14.80 (relative ratio 2:4:1, using a relaxation delay 60 s). Upon addition of 1 μL of water, the red color and the resonance of **1** disappeared and the low-field resonance of **5** broadened and shifted at ca. δ 9, while the resonance of free water appeared at 3.9 ppm. Also the hydride resonances of **5** underwent a little shift (−11.27 and −14.75 ppm). After 2 days at room temperature, NMR analysis showed the complete disappearance of the signals of **1** and **5**, substituted mainly by a resonance at δ −11.84, attributable to $[Re_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}OH)]^-$ (**11**). Also the intensity of the resonance of **2** was increased.

(b) A sample (20 mg, 0.0148 mmol) of **2**$[NEt_4]_2$, dissolved in 0.5 mL of acetone-d_6, was treated at room temperature with CF_3SO_3H (1.3 μL, 0.0147 mmol). The deep red solution discolored when cooled at 193 K, and ^1H NMR at this temperature showed (beside unreacted **2**) only the resonances of **5**, at δ 9.16, −11.17, and −14.61 (relative ratio 2:4:1, using a relaxation delay of 60 s). A resonance at 5.3 ppm was attributed to free water. On using as solvent acetone-d_6 dried over 3A molecular sieves, the signal at low field attributed to coordinated H_2O showed much lower and erratic intensities, being often negligible. In these cases, only one averaged signal for free and coordinated water was usually detected, in the range δ 5.5–3.8 ppm.

Variable-Temperature ^1H-NMR Analysis of $[Re_4H_5(CO)_{12}(H_2O)]^-$ (5). (a) A sample (34 mg, 0.025 mmol) of **2**$[NEt_4]_2$, dissolved in 0.5 mL of acetone-d_6 dried over molecular sieves, was treated at room temperature with CF_3SO_3H (2.5 μL, 0.028 mmol). The solution became deep red, and ^1H NMR at 193 K showed in the hydridic region the resonances of **1** at δ −10.54 and of **5** at δ −11.14 (4) and −14.60 (1). A signal attributable to coordinated water was at δ 4.80 ppm. The variable-temperature spectra of this sample are reported in Figure 2a.

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[21] Mingos, D. M. P.; May, A. S. In *The Chemistry of Metal Cluster Complexes*; Shriver, D. F., Kaesz, H. D.; Adams, R. D., Eds.; VCH Publishers: New York, 1990.

Table III. Crystal Data and Intensity Collection Parameters for $[Re_4(\mu\text{-}H)_4(\mu_3\text{-}H)(CO)_{12}(PPh_3)]][NEt_4]\cdot OEt_2$ (**3**)

formula	$C_{42}H_{50}NO_{13}PRe_4$
fw, amu	1552.64
space group	$P\bar{1}$ (No. 2)
a, Å	12.330 (2)
b, Å	13.202 (2)
c, Å	15.503 (3)
α, deg	92.73 (1)
β, deg	98.02 (1)
γ, deg	96.92 (1)
V, Å^3	2475 (1)
D_c, g cm^{-3}	2.083
Z	2
radiation	Mo Kα, λ = 0.710 73 Å
μ(Mo Kα)	99.71
transm factors	0.65–1.00
temp, °C	22 ± 2
R^a	0.033
$R_w{}^b$	0.033

[a] $R = \sum F_o - kF_c/\sum F_o$. [b] $R_w = [\sum w(F_o - kF_c)^2/\sum wF_o^2]^{1/2}$.

(b) The reaction was repeated, using the same amount of reagents, and then water was added with a microsyringe (1.4 μL, 0.078 mmol). The solution became pale yellow and ^{1}H NMR showed only the resonances of **5**, slightly shifted (δ −11.20 (4), −14.67 (1)). Free and coordinated water gave an averaged signal at δ 4.57 (191 K). Variable-temperature spectra were acquired (Figure 2b), then a second aliquot of H_2O (2.5 μL, 0.14 mmol) was added (the hydride resonances shifted at δ −11.24 (4) and −14.70 (1) and the averaged resonance of water was at 4.53 ppm), and the variable-temperature monitoring was repeated (Figure 2c). The spectra were recorded on a Bruker AC-200 spectrometer operating at 200.13 MHz for ^{1}H. The temperature was controlled by the B-VT1000 equipment of the spectrometer that ensures a precision of ±1 K. The accuracy of the measurements was checked in all the experiments at 191, 234, 275, and 298 K by calibration with a MeOH/MeOD[22] solution. The ratio between water and compound **5** was determined from the integrated intensities of the corresponding signals in NMR spectra acquired at 191 K with a suitable relaxation delay (60 s).

At temperatures higher than 245 K, the hydride resonances of **1** and **5** are in fast exchange, and therefore the values of the chemical shift of their averaged resonance allow one to estimate the ratios r between **1** and **5**, through the relationship $r = (\delta_o - \delta_1)/(\delta_5 - \delta_o)$, where δ_o indicates the observed chemical shift and δ_1 and δ_5 stand for the chemical shifts of **1** and **5** (baricenter of its resonances), respectively, estimated from the values at 191 K, corrected linearly for their temperature dependence (+0.002 ppm/K). The values of K of equilibrium 4 so calculated are reported in Table II.

In the range 191–234 K the temperature behavior of the hydridic resonances of all the three experiments was simulated as a three-site exchange using the program MSEX (Multi Site EXchange)[23] modified to account for the different line widths of the resonances. At each temperature the chemical shifts of the three sites were changed as required by their temperature dependence while the populations were estimated from the values of the equilibrium constants computed through the Van't Hoff relationship. The goodness of the fit was judged by the comparison of the calculated and experimental intensities, line widths, and chemical shifts. The values of the rate constants obtained are as follows: for the intramolecular exchange, from the site with intensity 1 to the site with 4, k_i = 36, 200, 800, and 2500 s^{-1}, and for the intermolecular exchange from **5** to **1**, k_d = 1.5, 13, 100, and 500 s^{-1} at 202, 213, 224, and 234 K, respectively.

Table IV. Atomic Fractional Coordinates for $[Re_4(\mu\text{-}H)_4(\mu_3\text{-}H)(CO)_{12}(PPh_3)]][NEt_4]\cdot OEt_2$ (**3**)

atom	x	y	z
Re1	0.36769 (4)	0.17114 (4)	0.22467 (4)
Re2	0.12430 (4)	0.22221 (5)	0.16490 (5)
Re3	0.23728 (5)	0.31578 (5)	0.33748 (5)
Re4	0.32977 (5)	0.39709 (4)	0.17577 (5)
C11	0.313 (1)	0.028 (1)	0.221 (1)
C12	0.347 (1)	0.159 (1)	0.096 (1)
C13	0.411 (1)	0.160 (1)	0.350 (1)
C21	0.005 (1)	0.285 (1)	0.116 (1)
C22	0.031 (1)	0.118 (1)	0.209 (1)
C23	0.113 (1)	0.136 (1)	0.061 (1)
C31	0.162 (1)	0.412 (1)	0.387 (1)
C32	0.359 (1)	0.355 (1)	0.422 (1)
C33	0.179 (2)	0.220 (2)	0.407 (1)
C41	0.250 (1)	0.505 (1)	0.145 (1)
C42	0.458 (1)	0.491 (1)	0.220 (1)
C43	0.375 (1)	0.397 (1)	0.063 (1)
O11	0.2779 (0)	−0.0566 (8)	0.2182 (8)
O12	0.3451 (9)	0.1501 (8)	0.0209 (8)
O13	0.441 (1)	0.141 (1)	0.4202 (9)
O21	−0.071 (1)	0.325 (1)	0.092 (1)
O22	−0.029 (1)	0.058 (1)	0.235 (1)
O23	0.097 (1)	0.085 (1)	−0.0026 (9)
O31	0.111 (1)	0.4701 (9)	0.4203 (9)
O32	0.433 (1)	0.382 (1)	0.479 (1)
O33	0.144 (1)	0.161 (1)	0.454 (1)
O41	0.200 (1)	0.572 (1)	0.127 (1)
O42	0.5357 (0)	0.5489 (9)	0.247 (1)
O43	0.401 (1)	0.398 (1)	−0.006 (1)
P	0.5562 (3)	0.1443 (3)	0.2195 (3)
C111	0.611 (1)	0.165 (1)	0.1180 (9)
C112	0.599 (1)	0.253 (1)	0.077 (1)
C113	0.644 (1)	0.275 (1)	0.003 (1)
C114	0.700 (1)	0.209 (1)	−0.031 (1)
C115	0.719 (1)	0.124 (1)	0.004 (1)
C116	0.675 (1)	0.096 (1)	0.081 (1)
C121	0.662 (1)	0.228 (1)	0.2940 (9)
C122	0.635 (1)	0.308 (1)	0.3436 (9)
C123	0.721 (1)	0.371 (1)	0.399 (1)
C124	0.830 (1)	0.352 (1)	0.403 (1)
C125	0.856 (1)	0.273 (1)	0.353 (1)
C126	0.774 (1)	0.210 (1)	0.297 (1)
C131	0.577 (1)	0.016 (1)	0.249 (1)
C132	0.535 (1)	−0.066 (1)	0.190 (1)
C133	0.540 (1)	−0.165 (1)	0.215 (1)
C134	0.587 (1)	−0.182 (1)	0.297 (1)
C135	0.628 (1)	−0.105 (1)	0.359 (1)
C136	0.622 (1)	−0.003 (1)	0.331 (1)
N	0.106 (2)	0.333 (2)	0.782 (1)
C1N	0.047 (3)	0.362 (2)	0.691 (2)
C2N	0.117 (2)	0.348 (2)	0.622 (2)
C3N	0.225 (3)	0.382 (3)	0.810 (2)
C4N	0.212 (3)	0.503 (3)	0.814 (2)
C5N	0.120 (4)	0.213 (4)	0.764 (3)
C6N	0.220 (4)	0.168 (4)	0.832 (3)
C7N	0.019 (5)	0.311 (4)	0.850 (4)
C8N	0.080 (3)	0.408 (3)	0.935 (3)
O	1.209 (1)	0.801 (1)	0.392 (1)
C1S	1.226 (2)	0.891 (2)	0.445 (2)
C2S	1.102 (2)	0.909 (2)	0.458 (2)
C3S	1.321 (2)	0.776 (2)	0.393 (2)
C4S	1.308 (2)	0.684 (2)	0.345 (1)
H14[a]	0.4241	0.3060	0.2176
H24	0.2107	0.3159	0.1106
H23	0.1078	0.3068	0.2594
H34	0.2941	0.4291	0.2848
H123	0.2325	0.1997	0.2591

[a] Calculated H atom positions.

X-ray Analysis of $[Re_4(\mu\text{-}H)_4(\mu_3\text{-}H)(CO)_{12}(PPh_3)][NEt_4]\cdot OEt_2$. Intensity Measurements. Crystal data are reported in Table III. The crystal sample, an irregular polyhedron, was mounted on a glass fiber in the air. The intensity data were collected on an Enraf-Nonius CAD4 automated diffractometer using graphite monochromatized Mo Kα radiation. The setting angles of 25 random intense reflections [16° < 2θ < 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° < 2θ < 48°. A variable scan-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 a marked crystal decay upon X-ray exposure, of ca. 35% 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 3 suitable reflections with χ values close to 90°. A set of 3711 significant [$I > 3\sigma(I)$] independent reflections was used in the structure solution and refinement.

Structure Solution and Refinements. The data reduction was performed

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on a PDP 11/73 computer, using the Enraf-Nonius Structure Determination Package (SDP) and the physical constants tabulated therein. All the other crystallographic computations were carried out by using the SHELX programs. Scattering factors for neutral atoms and anomalous dispersion corrections for scattering factors were taken from refs 24 and 25, respectively.

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 block-matrix least-squares (two blocks, one including all the parameters of the anion and the second one all those of the cation and solvent), minimizing the function $\Sigma w(F_o - k|F_c|)^2$. Anisotropic thermal parameters were assigned to all atoms of the anion except to the carbon atoms of the phenyl groups. The thermal parameters of the tetraethylammonium cation were rather high, probably indicative of some disorder which was not rationalized.

The hydrogen atoms of the phenyl groups were located in ideal positions (C–H 0.95 Å, $U = 0.08$ Å^2) after each cycle of refinement, and their contribution to the structure factors was taken into account. Since no direct evidence was obtained from the difference Fourier maps, the five hydrido ligands were located using Orpen's HYDEX program,[15] assuming Re–H interactions of 1.85 Å for double-bridging hydrides and 1.90 Å for the triple-bridging one. They were also included in the final structure factors calculation ($U = 0.05$ Å^2) but not refined. The final difference-Fourier map was flat, showing only some residual peaks not exceeding ca. 10 e Å^{-3}.

Weights were assigned according to the formula $w = k/[\sigma^2(F_o) + gF_o^2]$, with $k = 1.1537$ and $g = 3.87 \times 10^{-4}$. The final values of the conventional agreement indices R and R_w are reported in Table III. The final positional parameters are given in Table IV.

Acknowledgment. G.D. warmly thanks Mr. P. Illiano for the careful acquisition of countless low-temperature NMR spectra of the Bruker WP80 spectrometer.

Supplementary Material Available: Isotropic thermal factors (Table S1), anisotropic thermal factors (Table S2), the calculated fractional coordinates of the phenyl hydrogen atoms (Table S3), a complete table of the crystallographic data (Table S4), and a complete table of bond distances and angles (Table S5) (9 pages). Ordering information is given on any current masthead page.

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