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# Reduction of unsaturated organic molecules by hydridocarbonyl cluster compounds of rhenium. Reaction of the anion $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$ with acetone: crystal structure of $[NEt_4][Re_3(\mu\text{-}H)_3(\mu\text{-}OCHMe_2)(CO)_{10}]$

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## Abstract

The reaction of the unsaturated anion $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$ in acetone affords the two saturated species $[Re_3(\mu\text{-}H)_3(\mu\text{-}OCHMe_2)(CO)_{10}]^-$ and $[Re_3(\mu\text{-}H)_3(\mu_3\text{-}OCHMe_2)(CO)_9]^-$ as a result of the attack of a hydride ligand of the parent anion on the ketonic carbon atom to give an isopropylate group. The structure of the former anion, as its $(NEt_4)^+$ salt, has been investigated by X-ray analysis. The crystals are monoclinic, space group $P2_1/c$, with $a$ 8.767(4), $b$ 25.913(6), $c$ 13.175(4) Å, $\beta$ 91.80(4)° and $Z = 4$. The refinements performed by full-matrix least-squares methods, on the basis of 2847 independent significant reflections, with $I > 3\sigma(I)$, gave final values of the conventional agreement indices $R$ and $R_w$ of 0.041 and 0.052, respectively. The anion contains an isosceles triangle of Re atoms, with two longer hydrogen-bridged Re–Re edges (mean 3.211 Å), and one shorter edge (2.930(1) Å) doubly bridged by a hydride and the isopropylate ligand. The mean value of the Re–O(alkoxy) bonds is 2.153 Å.

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## Introduction

We are currently investigating the reductive hydrogenation of organic molecules containing activated multiple bonds by use of hydridocarbonylrhenium complexes. The unsaturated anion $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$ (compound **1**) was shown to possess a high reactivity involving the hydrides of its $Re(\mu\text{-}H)_2Re$ moiety. These ligands exhibit a strong hydridic character since they readily undergo reactions with a variety of electrophilic reagents [1] and so they might be expected to attack the activated C atoms of species such as aldehydes, ketones, esters and so on. This

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prompted us to investigate as a first step the reaction of compound **1** with acetone and we report here the results of these studies, which led to the isolation and characterization of the anions $[Re_3(\mu\text{-}H)_3(\mu_3\text{-}OCHMe_2)(CO)_9]^-$ (compound **2**) and $[Re_3(\mu\text{-}H)_3(\mu\text{-}OCHMe_2)(CO)_{10}]^-$ (compound **3**). The results of an X-ray diffraction study of the $(NEt_4)^+$ salt of the latter anion are reported, and discussed in comparison with the structural parameters of related $[Re_3(\mu\text{-}H)_3(\mu\text{-}X)(CO)_{10}]^-$ anions.

## Results and discussion

### *Reactivity of compound 1 in acetone*

When a solution of the $NEt_4{}^+$ salt (**1**) of the unsaturated anion $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$ in acetone is refluxed a slow reaction occurs, as evidenced by the gradual fading of the yellow solution. Spectroscopic monitoring reveals the formation (complete after about 48 h) of a saturated derivative containing an isopropylate group, viz. the species $[Re_3(\mu\text{-}H)_3(\mu_3\text{-}OCHMe_2)(CO)_9]^-$ (compound **2**), which was previously obtained [2] by refluxing a solution of compound **1** in $Me_2CHOH$ (IR: $\nu$(CO) 2005s, 1915vs $cm^{-1}$, $^1H$ NMR; $\delta$ 3.95 (1, m, $J$ 6 Hz), 1.48 (6, d, $J$ 6 Hz), −11.47 (3, s) ppm).

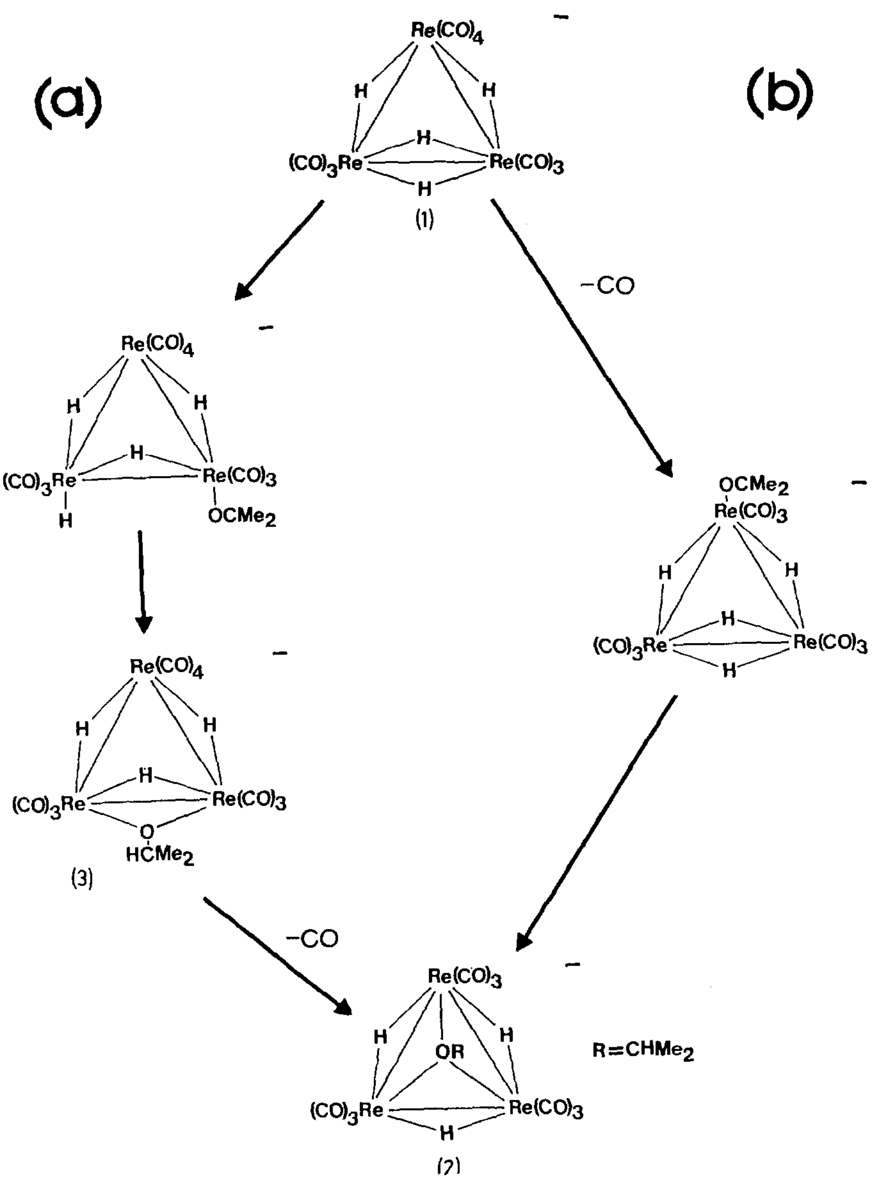
The possibility that compound **2** was formed from the reaction of **1** with the traces of isopropyl alcohol present in the solvent acetone, was ruled out in the following way. First careful GLC analysis of the acetone used for the reaction showed an $Me_2CHOH$ content far below that corresponding to the amount of compound **1**. Secondly, GLC analysis of the evolved gases revealed mainly the presence of CO, while the reaction of **1** with $Me_2CHOH$ to give compound **2** would involve the concomitant evolution of one equivalent of $H_2$. The experiments described below, in which deuterated acetone was used as solvent, permitted observation of the progressive growth of the $^1H$ NMR signal due to the $(CD_3)_2C\mathit{HO}$ group: this provided conclusive evidence that in the reaction a hydride ligand was transferred from compound **1** to the positively polarized ketonic carbon atom of an acetone molecule, giving the isopropylate group coordinated to the triangular metal cluster.

The transfer of the hydride probably takes place intramolecularly, in an unstable intermediate containing a coordinated acetone molecule. The coordination may either precede or follow the elimination of carbon monoxide. Accordingly, two main mechanistic pathways can be postulated (see Scheme 1), involving:

(a) addition of acetone to one of the metals of the $Re(\mu\text{-}H)_2Re$ edge, followed by H transfer, with formation of the isopropylate group, doubly-bridging this edge, and finally CO elimination and formation of **2**.

(b) elimination of one CO ligand *trans*-diaxially coordinated in the apical $Re(CO)_4$ moiety, with coordination of acetone at this site, followed by the H transfer, leading directly to compound **2**.

Addition reactions such as that postulated in the first step of the mechanism (a) are very easy with the related unsaturated triangular cluster of osmium $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ [3], but have never been observed in compound **1**. However this addition has been postulated as the first step in the reaction of **1** with donor species L, such as phosphines, CO or MeCN, leading eventually to the replacement of two H ligands by two L molecules [4]. The transformation of a doubly-bridging group



Scheme 1

into a triple-bridging one, that is the final step of (a), is a process often observed with triangular carbonyl cluster compounds, including compound **1** [5,6]. It generally requires the thermal activation for labilization of a CO ligand, but in the case of the anion $[Re_3(\mu\text{-}H)_3(\mu\text{-}AuPPh_3)(CO)_{10}]^-$ this was found to occur even at temperatures as low as 0 °C [6].

The first step of mechanism (b), the substitution of one CO ligand by a donor molecule L by thermal activation, is also a process already observed in the chemistry of compound **1**. For instance, upon refluxing of a solution of **1** in MeCN, one of the mutually *trans* CO groups of the Re(CO)$_4$ apex, labilized by the competition for the metal-to-ligand $\pi$-back donation, is selectively replaced by a solvent molecule [7]. A whole family of unsaturated species of general formula $[Re_3(\mu\text{-}H)_4(CO)_9L]^-$ has been prepared. Moreover, the intramolecular attack of one of the hydrides of the $Re(\mu\text{-}H)_2Re$ moiety on a L group coordinated in this way has previously been observed in the species with L = CHO [8] or ONMe$_3$ [9], leading to the formation of groups $\mu_3$-coordinated to the cluster.

To gain a better insight into the reaction mechanism, we studied the behaviour of **1** in acetone at lower temperatures, in order to suppress the thermal labilization of the carbonyl ligand. A solution of **1** in deuterated acetone was sealed under CO in a NMR tube and kept in an oil bath at 35 °C for several days. The progress of the reaction was monitored by recording the hydridic region of NMR spectra from day to day. The slow decrease in the heights of the two hydridic resonances of **1** at $\delta$ $-8.50$ and $-13.33$ ppm was accompanied by the growth of two new signals at $\delta$ $-9.34$ and $-13.74$ ppm, in the ratio 1/2. These data agree well with those previously observed [10] for the anion $[Re_3(\mu\text{-}H)_3(\mu\text{-}OMe)(CO)_{10}]^-$ ($\delta$ $-9.65$ and $-13.84$ ppm), and therefore suggest the formation of the anion $[Re_3(\mu\text{-}H)_3(\mu\text{-}OCHMe_2)(CO)_{10}]^-$ (compound **3**), postulated in mechanism (a). In accord with this, a broad signal (with the same integration as the signal at $-9.34$) grew progressively at $\delta$ 3.3 ppm, and is attributable to the hydride transferred to the carbon atom of the deuterated acetone (the coupling with 6 deuterium atoms being responsible for the observed broadening). After about 20 days, 90% of **1** had reacted, giving mainly **3**. The amount of **2**, as judged by the integrated signal at $-11.47$ ppm, was almost negligible (ca. 1–2%). When the experiment was repeated under N$_2$ atmosphere, the rate of decrease of **1** was about the same, but the amount of **2** was significantly higher (after 20 d, ca. 23% of **2** and 67% of **3**).

The reaction was repeated in non-deuterated acetone on a preparative scale. The mixture obtained after about 20 days at 35 °C under CO was crystallized, by slow diffusion of diethyl ether into a dichloromethane solution, allowing the isolation of pale yellow crystals, whose elemental analyses, and spectroscopic and finally X-ray diffraction data showed the product to be $[NEt_4][Re_3(\mu\text{-}H)_3(\mu\text{-}OCHMe_2)(CO)_{10}]$. (IR: $\nu$(CO) 2096 mw, 2022m, 2000vs, 1985sh, 1945m, 1909s, 1895vs cm$^{-1}$; $^1$H NMR: $\delta$ 3.27 (1, m, $J$ 6 Hz), 1.16 (6, d, $J$ 6 Hz), $-9.35$ (1, s), $-13.78$ (2, s) ppm).

Compound **3** was slowly converted in refluxing acetone into compound **2**, with loss of CO. This result clearly supports mechanism (a). In accord with this, when the reaction of **1** in boiling acetone, which gives **2**, was monitored by $^1$H NMR spectroscopy, the intermediate presence of a few percent of compound **3** was detected. This observation does not however, rule out the possibility that **2** was also formed by some other route.

In fact, other experiments gave some support to mechanism (b). The anion $[Re_3(\mu\text{-}H)_4(CO)_9(NCMe)]^-$ was prepared [7] and its solution in deuterated acetone, in an NMR tube kept at room temperature. Spectra recorded from time to time revealed the slow formation of **2**, confirming the validity of the process postulated in the second part of mechanism (b). Moreover, the thermal labilization of CO was shown to take place at temperatures as low as the boiling point of the acetone (56 °C). Thus the $^1$H NMR spectra of a solution of **1** in CD$_3$CN recorded over 10 h at 56 °C showed the formation of a relevant amount (ca. 30%) of $[Re_3(\mu\text{-}H)_4(CO)_9(NCMe)]^-$. Mechanism (b) must therefore also be assumed to operate, and kinetic measurements would be necessary to determine the relative importance of the two suggested pathways.

We note finally that the transformation of compound **2** into **3** by reaction with CO proved to be very difficult, in contrast to what was observed for the related phenoxy derivative $[Re_3(\mu\text{-}H)_3(\mu_3\text{-}OPh)(CO)_9]^-$ [5]; thus more than three days under 30 atm of CO at room temperature were necessary for conversion of 75% of **2** into **3**. The ability of CO to inhibit the formation of **2** observed in the experiments at 35 °C in the NMR tubes can thus be attributed to a kinetic effect, indicative of a dissociative mechanism for the transformation of compound **3** into compound **2**. At the temperature of these experiments (35 °C), the possible contribution of mechanism (b) to the formation of **2** from **1** can confidently be assumed to be negligible.

The X-ray structure of compound **2** was not determined since it is expected to be closely similar to that already known for $[Re_3(\mu\text{-}H)_3(\mu_3\text{-}OEt)(CO)_9]^-$, obtained by reaction of compound **1** with ethanol [2].

### *Description of the structure of compound 3*

The crystal structure consists of the packing of discrete anions and $(NEt_4)^+$ cations in the ratio 1/1. The anion, illustrated in Fig. 1, has an idealized $C_s$ symmetry, the mirror plane passing through the Re(1) atom, the middle point of the Re(2)–Re(3) edge and the oxygen atom of the isopropylate. It contains an isosceles triangle of rhenium atoms; Re(1) bears four terminal CO groups, while Re(2) and Re(3) each bear three such ligands. The isopropylate ligand bridges the short Re(2)–Re(3) edge. The three hydride ligands, not directly located, were placed in bridging positions on the $Re_3$ triangular edges on the basis of the Re–Re bond

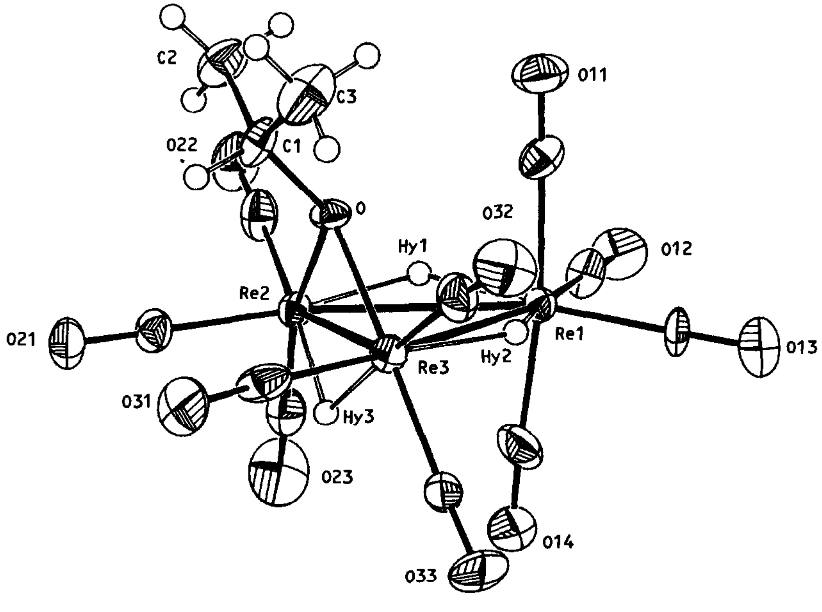


Fig. 1. A view of the anion $[Re_3(\mu\text{-}H)_3(\mu\text{-}OCHMe_2)(CO)_{10}]^-$, with the suggested positions of the hydridic hydrogens. The carbonyl carbon atoms bear the numbers of the oxygen to which they are attached.

Table 1

Bond distances and angles in $[\mathrm{NEt_4}][\mathrm{Re_3}(\mu\text{-H})_3(\mu\text{-OCHMe_2})(\mathrm{CO})_{10}]$

| | | | |
|---|---|---|---|
| *Distances (Å)* | | | |
| Re(1)-Re(2) | 3.202(1) | C(11)-O(11) | 1.11(2) |
| Re(1)-Re(3) | 3.219(1) | C(12)-O(12) | 1.15(2) |
| Re(2)-Re(3) | 2.930(1) | C(13)-O(13) | 1.12(2) |
| Re(2)-O | 2.168(8) | C(14)-O(14) | 1.14(2) |
| Re(3)-O | 2.137(9) | C(21)-O(21) | 1.16(2) |
| Re(1)-C(11) | 2.01(2) | C(22)-O(22) | 1.18(2) |
| Re(1)-C(12) | 1.92(2) | C(23)-O(23) | 1.15(2) |
| Re(1)-C(13) | 1.90(2) | C(31)-O(31) | 1.18(2) |
| Re(1)-C(14) | 1.93(2) | C(32)-O(32) | 1.17(2) |
| Re(2)-C(21) | 1.91(2) | C(33)-O(33) | 1.10(2) |
| Re(2)-C(22) | 1.88(2) | | |
| Re(2)-C(23) | 1.92(2) | O-C(1) | 1.44(2) |
| Re(3)-C(31) | 1.93(2) | C(1)-C(2) | 1.55(2) |
| Re(3)-C(32) | 1.89(2) | C(1)-C(3) | 1.44(2) |
| Re(3)-C(33) | 1.95(2) | | |
| | | $\mathrm{NEt_4}^+$ cation | |
| | | N-C | 1.46(3)-1.59(2) |
| | | C-C | 1.51(3)-1.69(4) |
| *Angles (deg.)* | | | |
| Re(2)-Re(1)-Re(3) | 54.29(2) | C(21)-Re(2)-C(22) | 91.4(7) |
| Re(1)-Re(2)-Re(3) | 63.14(2) | C(21)-Re(2)-C(23) | 90.0(6) |
| Re(1)-Re(3)-Re(2) | 62.57(2) | C(22)-Re(2)-C(23) | 88.9(8) |
| Re(2)-Re(1)-C(11) | 92.4(5) | C(21)-Re(2)-O | 95.7(5) |
| Re(2)-Re(1)-C(12) | 107.8(5) | C(22)-Re(2)-O | 102.6(6) |
| Re(2)-Re(1)-C(13) | 160.7(5) | C(23)-Re(2)-O | 166.9(6) |
| Re(2)-Re(1)-C(14) | 80.8(6) | C(31)-Re(3)-C(32) | 89.7(7) |
| Re(3)-Re(1)-C(11) | 88.5(5) | C(31)-Re(3)-C(33) | 89.0(6) |
| Re(3)-Re(1)-C(12) | 162.1(5) | C(32)-R(3)-C(33) | 89.6(8) |
| Re(3)-Re(1)-C(13) | 108.0(4) | C(31)-Re(3)-O | 96.2(5) |
| Re(3)-Re(1)-C(14) | 82.8(7) | C(32)-Re(3)-O | 100.1(6) |
| Re(1)-Re(2)-C(21) | 161.4(5) | C(33)-Re(3)-O | 169.0(6) |
| Re(1)-Re(2)-C(22) | 106.0(5) | Re(2)-O-Re(3) | 85.8(3) |
| Re(1)-Re(2)-C(23) | 96.6(5) | Re(2)-O-C(1) | 125.1(9) |
| Re(3)-Re(2)-C(21) | 98.6(5) | Re(3)-O-C(1) | 124.2(8) |
| Re(3)-Re(2)-C(22) | 148.3(5) | O-C(1)-C(2) | 108(1) |
| Re(3)-Re(2)-C(23) | 120.9(5) | O-C(1)-C(3) | 110(1) |
| Re(1)-Re(3)-C(31) | 163.2(5) | C(2)-C(1)-C(3) | 114(2) |
| Re(1)-Re(3)-C(32) | 105.5(5) | Re(1)-C(11)-O(11) | 178(2) |
| Re(1)-Re(3)-C(33) | 98.0(5) | Re(1)-C(12)-O(12) | 176(1) |
| Re(2)-Re(3)-C(31) | 100.8(5) | Re(1)-C(13)-O(13) | 179(2) |
| Re(2)-Re(3)-C(32) | 146.5(6) | Re(1)-C(14)-O(14) | 176(2) |
| Re(2)-Re(3)-C(33) | 122.0(5) | Re(2)-C(21)-O(21) | 180(2) |
| Re(1)-Re(2)-O | 74.5(2) | Re(2)-C(22)-O(22) | 176(2) |
| Re(1)-Re(3)-O | 74.5(2) | Re(2)-C(23)-O(23) | 178(2) |
| C(11)-Re(1)-C(12) | 92.6(7) | Re(3)-C(31)-O(31) | 175(2) |
| C(11)-Re(1)-C(13) | 94.9(7) | Re(3)-C(32)-O(32) | 176(2) |
| C(11)-Re(1)-C(14) | 171.0(8) | Re(3)-C(33)-O(33) | 176(2) |
| C(12)-Re(1)-C(13) | 89.7(6) | | |
| C(12)-Re(1)-C(14) | 95.1(8) | | |
| C(13)-Re(1)-C(14) | 89.8(8) | | |

Table 2

Relevant mean bond distances (Å) and angles (deg.) in the anions $[Re_3(\mu\text{-}H)_3(\mu\text{-}X)(CO)_{10}]^-$

| X | H | Cl | $OC_6F_5$ | $OCHMe_2$ |
|---|---|---|---|---|
| Re(1)–Re(2,3) | 3.190 | 3.207 | 3.229 | 3.211 |
| Re(2)–Re(3) | 2.789(1) | 2.995(2) | 2.975(1) | 2.930(1) |
| Re–X | – | 2.498 | 2.176 | 2.153 |
| Re(1)–C | 1.97 | 1.92 | 1.97 | 1.94 |
| Re(2,3)–C | 1.91 | 1.84 | 1.90 | 1.91 |
| Re(2)–X–Re(3) | – | 73.7(2) | 86.2(2) | 85.8(3) |
| Re(1)–Re(2,3)–C(*E*) [a] | 161.1 | 164 | 160.7 | 162.3 |
| Re(1)–Re(2,3)–C(*D*1) | 102.2 | 108 | 109.7 | 105.8 |
| Re(1)–Re(2,3)–C(*D*2) | | 93 | 93.4 | 97.3 |
| Re(2,3)–Re(3,2)–C(*E*) | 97.3 | 103 | 101.0 | 99.7 |
| Re(2,3)–Re(3,2)–C(*D*1) | 133.7 | 146 | 146.1 | 147.4 |
| Re(2,3)–Re(3,2)–C(*D*2) | | 119 | 123.2 | 121.5 |
| X–Re(2,3)–C(*E*) | – | 93 | 97.8 | 96.0 |
| X–Re(2,3)–C(*D*1) | – | 95 | 100.1 | 101.4 |
| X–Re(2,3)–C(*D*2) | – | 173 | 169.4 | 168.0 |
| Dihedral angle (Re(1),Re(2),Re(3))/(Re(2),Re(3),X)) | – | 102.1 | 100.4 | 93.8 |

[a] *E* = equatorial, *D*1 = diagonal by the side of X, *D*2 = diagonal by the opposite side of X (for X = H *D*1 = *D*2).

lengths (see below) and of the disposition of the other ligands. If the metal–metal interactions are neglected, each rhenium atom exhibits almost octahedral coordination. Bond distances and angles are listed in Table 1.

The stereochemistry of the anion is related to that in the parent compound **1** by replacement by the alkoxy ligand of one hydride bridging the short Re–Re bond. The ligand geometry is of a type present in related species which have been structurally characterized, such as $[Re_3(\mu\text{-}H)_3(\mu\text{-}Cl)(CO)_{10}]^-$ [11] and $[Re_3(\mu\text{-}H)_3(\mu\text{-}OC_6F_5)(CO)_{10}]^-$ [5]. In Table 2 the relevant mean bond lengths and angles within these species are compared. Other related $[Re_3(\mu\text{-}H)_3(\mu\text{-}X)(CO)_{10}]^-$ anions (X = carboxylate [12] or benzamido [13]) have been characterized, but in these the ligands are $\eta^2$-coordinated and the overall stereochemistry is significantly different.

Two of the Re–Re bond lengths are longer, mean 3.211 Å, with values typical of Re–H–Re hydrogen-bridged bonds. The third shorter edge, 2.930(1) Å, is doubly bridged by a hydride and the isopropylate ligand.

The CO ligands form three classes: (i) those *trans* to CO (2 groups), mean Re–C and C–O 1.97 and 1.12 Å; (ii) those *trans* to hydrides (6 groups), mean Re–C and C–O 1.90 and 1.16 Å; and (iii) those *trans* to the isopropylate (2 groups), mean Re–C and C–O 1.93 and 1.12 Å.

The isopropylate ligand bridges the edge of the metallic cluster in an almost perpendicular fashion. The dihedral angle between the plane of the $Re_3$ triangle and the Re(2),Re(3),O one is 93.8°. The Re–O–Re bridge is slightly asymmetric (difference 0.031 Å). The mean distance of the Re–O interactions, 2.153 Å, is comparable with corresponding distances in related triangular rhenium clusters. In particular, it is very similar to the Re–O bond lengths involving the bridging oxymethyl group (mean 2.146 Å) in $[Re_3(\mu\text{-}H)_3(\mu_3\text{-}\eta^2\text{-}OCH_2)(CO)_9]^{2-}$ [8]; it is slightly shorter than the mean Re–O distance in $[Re_3(\mu\text{-}H)_3(\mu\text{-}OC_6F_5)(CO)_{10}]^-$

(2.176 Å) [5], probably because of the lower basicity of the phenoxide ligand, and also slightly shorter than the mean Re–O bond distance for the triple bridging alkoxy group in $[Re_3(\mu\text{-}H)_3(\mu_3\text{-}OEt)(CO)_9]^-$ (2.17 Å) [2].

The bond parameters within the isopropylate ligand are normal.

An analysis of the data reported in Table 2 shows that the Re(1)–Re(2,3) edges are similar in all species and essentially unaffected by the change of the $\mu$-X ligand. On the other hand, owing to unsaturation, the Re(2)–Re(3) edge in compound **1** is shorter (by 0.14 to 0.21 Å) than that in the saturated species. This metal–metal bond shows a moderate shortening on passing from $\mu$-Cl, to $\mu$-$OC_6F_5$, to $\mu$-$OCHMe_2$, i.e. with increasing basicity of the ligand.

Except for those involving the $\mu$-X ligand the other bond parameters are similar in the three saturated species but somewhat different from those in compound **1**. The major differences, which arise from the substitution of a $\mu$-H ligand by a bridging ligand of greater steric hindrance, are associated with the diagonal carbonyl groups bound to Re(2) (CO(22) and CO(23)) and Re(3) (CO(32) and CO(33)), which are rotated away from the $\mu$-X ligand in order to minimize the intramolecular non-bonding repulsions.

## Experimental

The reactions were performed under nitrogen by Schlenk techniques, in solvents dried and deoxygenated by standard methods. $[NEt_4][Re_3(\mu\text{-}H)_4(CO)_{10}]$ was prepared as previously described [1]. Acetone (Merck) was simply distilled under $N_2$ because all the usual drying methods caused the formation of variable amounts of products of aldol condensation. Infrared spectra were recorded on a Perkin–Elmer 781 grating spectrophotometer, in 0.1 mm $CaF_2$ cells, and were calibrated against polystyrene film absorptions. NMR spectra were recorded on a Bruker WP 80 spectrometer. Gas analyses were performed on a Carlo Erba HRGC 5340 instrument, equipped with a 2 m molecular sieve column, with carrier Ar for $H_2$ and carrier He for CO detection. The $Me_2CHOH$ content of the acetone was determined with a Perkin–Elmer Sigma 115 Gaschromatograph, equipped with a 4 m column containing 4.4% of Carbowax 400 on Chromosorb G, used at 75 °C with $N_2$ as carrier gas.

### *Reactions of compound 1 in acetone*

(a) A solution of 50 mg (0.051 mmol) of $[NEt_4][Re_3(\mu\text{-}H)_4(CO)_{10}]$ in 5 ml of acetone was refluxed under $N_2$. Samples were removed at intervals for recording of the IR and NMR spectra. After 50 h, only $[NEt_4][Re_3(\mu\text{-}H)_3(\mu_3\text{-}OCHMe_2)(CO)_9]^-$ was present. The GLC analysis of the acetone used for the reaction showed an isopropyl alcohol content of < 50 ppm (i.e., in 5 ml, < 0.003 mmol).

(b) A solution of $[NEt_4][Re_3(\mu\text{-}H)_4(CO)_{10}]$ in 0.5 ml of deuteroacetone was sealed under CO in a 5 mm NMR tube. A similar solution was sealed under $N_2$. The tubes were kept in an oil bath at 35 °C and spectra were recorded at intervals during 20 days.

(c) A solution of 100 mg (0.103 mmol) of $[NEt_4][Re_3(\mu\text{-}H)_4(CO)_{10}]$ in 5 ml of acetone was sealed under CO. After 20 days in an oil bath at 35 °C, the mixture was evaporated and the residue crystallized from $CH_2Cl_2/Et_2O$ to give 47 mg (0.046 mmol, isolated yields 44%) of $[NEt_4][Re_3(\mu\text{-}H)_3(\mu\text{-}OCHMe_2)(CO)_{10}]$. (Found: C, 24.70; H, 2.75; N, 1.20. $C_{21}H_{30}NO_{11}Re_3$ calcd.: C, 24.44; H, 2.91; N, 1.36%.) Upon heating the solid compound decomposed progressively, and the dark residue melted at 245 °C.

### *X-Ray analysis*

*Crystal data.* $C_{21}H_{30}NO_{11}Re_3$, $M = 1031.1$, monoclinic, space group $P2_1/c$ (no. 14), $a$ 8.767(4), $b$ 25.913(6), $c$ 13.175(4) Å, $\beta$ 91.80(4)°, $U$ 2991.6 Å$^3$, $Z = 4$, $D_c = 2.289$ g cm$^{-3}$, $F(000) = 1904$, Mo-$K_\alpha$ radiation ($\lambda$ 0.71073 Å), $\mu$(Mo-$K_\alpha$) 123.26 cm$^{-1}$.

*Intensity measurements.* A crystal sample of dimensions 0.13 × 0.30 × 0.33 mm was mounted on a glass fibre in the air. Data were measured on an Enraf–Nonius CAD4 automatic diffractometer using graphite monochromatized Mo-$K_\alpha$ radiation. The setting angles of 25 random intense reflections ($16 < 2\theta < 25$°) were used in a least squares fit to determine accurate cell constants and the orientation matrix. The data collection was performed by the $\omega$-scan method, with the limits $3 < \theta < 25$°. A variable scan-speed (from 2 to 20°/min) and a variable scan-range of $(0.9 + 0.35 \tan\theta)$° were used, with a 25% extension at each end of the scan-range for background determination. The total number of reflections measured were 5247. Three standard intense reflections, monitored every three hours, revealed no significant decay. The intensities were corrected for Lorentz and polarization effects. An empirical absorption correction was applied to the data set, based on $\psi$-scans ($\psi$

Table 3

Atomic coordinates for $[NEt_4][Re_3(\mu\text{-}H)_3(\mu\text{-}OCHMe_2)(CO)_{10}]$

| Atom | *x* | *y* | *z* | Atom | *x* | *y* | *z* |
|---|---|---|---|---|---|---|---|
| Re(1) | −0.08155(8) | 0.14162(3) | 0.07797(5) | O | −0.038(1) | 0.0732(4) | 0.2930(7) |
| Re(2) | 0.17666(8) | 0.09084(3) | 0.22341(5) | C(1) | −0.059(2) | 0.0342(7) | 0.369(1) |
| Re(3) | −0.05344(9) | 0.15428(3) | 0.32087(5) | C(2) | −0.014(3) | −0.0185(8) | 0.324(2) |
| C(11) | −0.226(2) | 0.0823(8) | 0.098(1) | C(3) | −0.214(3) | 0.036(1) | 0.404(2) |
| O(11) | −0.302(2) | 0.0487(6) | 0.110(1) | N | 0.483(2) | 0.1465(7) | 0.740(1) |
| C(12) | −0.043(2) | 0.1211(8) | −0.059(1) | CT(1) [a] | 0.438(3) | 0.111(1) | 0.0649(2) |
| O(12) | −0.029(2) | 0.1099(6) | −0.1430(9) | CT(2) | 0.488(3) | 0.118(1) | 0.847(2) |
| C(13) | −0.234(2) | 0.1877(8) | 0.028(1) | CT(3) | 0.638(4) | 0.166(1) | 0.743(2) |
| O(13) | −0.326(2) | 0.2145(7) | −0.000(1) | CT(4) | 0.364(4) | 0.188(2) | 0.723(3) |
| C(14) | 0.064(3) | 0.1974(9) | 0.081(2) | CT(5) | 0.552(3) | 0.066(1) | 0.645(2) |
| O(14) | 0.151(2) | 0.2300(6) | 0.076(1) | CT(6) | 0.362(4) | 0.083(1) | 0.883(3) |
| C(21) | 0.302(2) | 0.0755(8) | 0.341(1) | CT(7) | 0.718(5) | 0.178(2) | 0.642(3) |
| O(21) | 0.378(2) | 0.0659(6) | 0.412(1) | CT(8) | 0.355(4) | 0.224(1) | 0.831(3) |
| C(22) | 0.228(2) | 0.0278(8) | 0.163(1) | H(1) | 0.0040 | 0.0396 | 0.4274 |
| O(22) | 0.269(2) | −0.0101(6) | 0.123(1) | H(21) | 0.0889 | −0.0168 | 0.3023 |
| C(23) | 0.348(2) | 0.1220(9) | 0.160(1) | H(22) | −0.0220 | −0.0446 | 0.3737 |
| O(23) | 0.453(2) | 0.1408(8) | 0.125(1) | H(23) | −0.0791 | −0.0264 | 0.2670 |
| C(31) | 0.019(3) | 0.1516(7) | 0.461(1) | H(31) | −0.2332 | 0.0696 | 0.4302 |
| O(31) | 0.075(2) | 0.1508(6) | 0.5434(9) | H(32) | −0.2832 | 0.0293 | 0.3487 |
| C(32) | −0.257(2) | 0.1585(9) | 0.365(1) | H(33) | −0.2261 | 0.0111 | 0.4554 |
| O(32) | −0.382(2) | 0.1644(7) | 0.391(1) | Hy(1) [b] | 0.0676 | 0.0944 | 0.1036 |
| C(33) | −0.039(2) | 0.2293(7) | 0.326(1) | Hy(2) | −0.1464 | 0.1645 | 0.1979 |
| O(33) | −0.031(2) | 0.2718(5) | 0.323(1) | Hy(3) | 0.1423 | 0.1541 | 0.2813 |

[a] CT = cationic carbon atoms. [b] Hy = bridging hydrides.

0-360° every 10°) of suitable reflections with $\chi$ values close to 90°; the relative transmission factors had values in the range 1.00–0.42. A total of 2847 independent significant reflections, with $I > 3\sigma(I)$, were used in the structure solution and refinement.

*Structure solution and refinements.* All computations were performed on a PDP 11/34 computer, using the Enraf–Nonius Structure Determination Package (SDP).

A three-dimensional Patterson map, revealed the positions of the Re atoms. Successive difference-Fourier maps allowed location of all the non-hydrogen atoms. The refinements were carried out by full-matrix least squares. Anisotropic thermal factors were assigned to all atoms except those in the cation. Rather high isotropic thermal factors indicated some disorder in the cation. The hydrogen atoms of the isopropylate ligand were placed in their idealized positions (C–H 0.95 Å, $B$ 5.0 Å$^2$), after each cycle of refinement, and not refined. The hydrogens in the cation were ignored. The final difference-Fourier maps were rather flat showing residual peaks not exceeding ca. 1 e Å$^{-3}$. No peaks corresponding with hydrides in bridging positions were observed. These hydride ligands were placed in ideal positions (mean Re–H of 1.81 Å) and not refined.

Weights were assigned according to the formula $w = 4F_0^2/\sigma(F_0^2)^2$, where $\sigma(F_0^2 = [\sigma(I)^2 + (pI)^2]^{1/2}/L_p$ ($I$ and $L_p$ being the integrated intensity and the Lorentz-polarization correction, respectively); $p$ was optimized to 0.04. The final values of the conventional agreement indices $R$ and $R_w$ were 0.041 and 0.052, respectively. The atomic coordinates are listed in Table 3. A final list of observed and calculated structure factors moduli and a table of thermal parameters is available from the authors.

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