

Preliminary communication

**A NOVEL TETRAHEDRAL HYDRIDOCARBONYLRHENIUM CLUSTER:
 PREPARATION AND X-RAY STRUCTURE OF $[\text{H}_4\text{Re}_4(\text{CO})_{13}]^{2-}$**

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Summary

The synthesis of the novel compound $(\text{NEt}_4)_2[\text{H}_4\text{Re}_4(\text{CO})_{13}]$ and its characterization by IR, NMR and X-ray analyses are described. The dianion contains a tetrahedral metal atom cluster bearing thirteen terminally-bonded carbonyl groups.

We are currently investigating the reactions of $\text{Re}_2(\text{CO})_{10}$ in methanolic KOH solutions and have already reported the synthesis and structure of some new hydridocarbonyl cluster derivatives, i.e. $[\text{H}_4\text{Re}_4(\text{CO})_{15}]^{2-}$ [1, 2], $[\text{H}_3\text{Re}_3(\text{CO})_{10}]^{2-}$ and $[\text{H}_3\text{Re}_3(\mu_3\text{-O})(\text{CO})_9]^{2-}$ [3].

Dilute solutions of $(\text{NEt}_4)_2[\text{H}_4\text{Re}_4(\text{CO})_{15}]$ in ethanol, upon refluxing for 4–5 h in the open air and cooling, give mixtures of crystals of the colourless $(\text{NEt}_4)_2[\text{H}_3\text{Re}_3(\mu_3\text{-O})(\text{CO})_9]$ and of an orange-yellow species [3]. (After filtration, the solution on standing gives crystals of the μ_3 -oxo species alone.) When the mixture of crystals is dissolved in acetone and ethanol, the less soluble orange-yellow compound precipitates first and can therefore be separated, although small amounts of the other species are always present. The new compound was shown to be the salt $(\text{NEt}_4)_2[\text{H}_4\text{Re}_4(\text{CO})_{13}]$. It is diamagnetic and the IR spectrum in acetone exhibits two strong and sharp bands at 2000 and 1980 cm^{-1} and a strong and rather broad band centered at 1910 cm^{-1} , all due to terminal CO groups. The NMR spectrum in CD_3COCD_3 at 37°C shows two singlets at τ 26.7 and 27.3 ppm (ratio 3:1) due to bridging hydrido ligands. The integrations relative to the cationic methylene hydrogens are incorrect because of impurity.

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Crystals of the salt have been investigated by X-ray diffraction. They are monoclinic, space group $P2_1/c$, with cell dimensions: a 11.830(4), b 20.847(6), c 16.148(5) Å, β 92.12(4)°, U 3979.7 Å³; D_m 2.30(2), D_c 2.29 g cm⁻³ for $Z = 4$. The intensity data were measured on a Philips PW 1100 four-circle diffractometer, using graphite monochromatized Mo- $K\alpha$ radiation (λ 0.7107 Å), within the interval $3^\circ < \theta < 22^\circ$. The accuracy of the data was limited by the decay of the sample upon X-ray irradiation (ca. 30% at the end of the collection) and by a high absorption ($\mu(\text{Mo-}K\alpha)$ 128.9 cm⁻¹), with transmission factors in the range 0.22–0.62. Corrections for these effects, as well as for the usual Lorentz and polarization factors, were applied. After rejection of all data having $\sigma(I)/I > 0.25$ a set of 1282 independent reflections was used. The structure was solved by Patterson and Fourier methods and refined by least-squares up to the actual conventional R value of 7.6%. Anisotropic thermal factors were assigned to the rhenium atoms only and all the C–O distances were kept constant, with the average value of 1.18 Å.

The structure of $[\text{H}_4\text{Re}_4(\text{CO})_{13}]^{2-}$ is shown in Fig. 1 and the main bonding parameters are summarized in Table 1. The anion contains a tetrahedral metal atom cluster; the carbonyl groups are all terminally bonded, four to Re(4) and three to each of the other rhenium atoms, with Re–C–O angles in the range 160–178°. The overall anion geometry does not show any symmetry, while the basal $\text{Re}_3(\text{CO})_9$ moiety possesses a distorted C_{3v} conformation.

The six Re–Re distances are rather scattered, with a mean value (3.09 Å) which is intermediate between the values of a normal single bond and of an hydrogen-bridged bond [4]. They do not fall distinctly into two classes and thus do not yield information on the hydridic atom positions. However, these positions can be derived from steric arguments based on the carbonyl arrangement. Computed maps of non-bonding energy interactions [5] indicate as possible locations of the hydrogen atoms denoted in Fig. 1 by four small black circles.

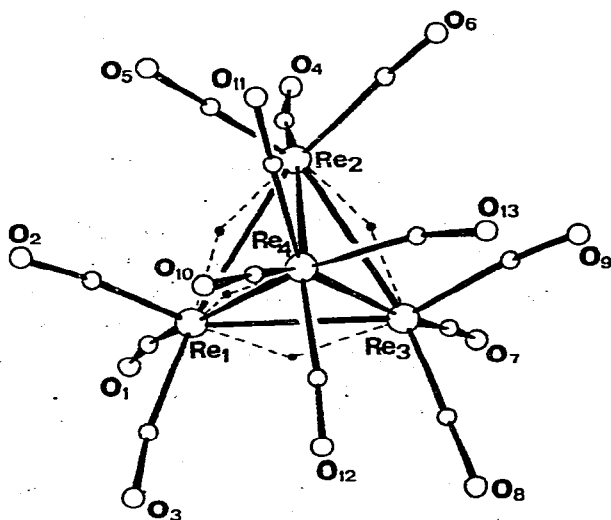


Fig. 1. View of the anion $[\text{H}_4\text{Re}_4(\text{CO})_{13}]^{2-}$ with the postulated hydridic atom.

TABLE 1
BOND PARAMETERS IN $[\text{H}_4\text{Re}_4(\text{CO})_{13}]^{2-}$

Distances (Å)		Re—Re—C angles in the basal triangle	
Re(1)—Re(2)	3.062(4)	Re—Re—C(<i>cis</i>) ^a	105(2)
Re(1)—Re(3)	3.161(4)	Re—Re—C(<i>trans</i>) ^a	154(3)
Re(1)—Re(4)	3.126(4)	Re—Re—C angles involving Re(4)	
Re(2)—Re(3)	3.026(5)	Re(4)—Re—C(<i>cis</i>) ^a	97(2)
Re(2)—Re(4)	3.098(5)	Re(4)—Re—C(<i>trans</i>) ^a	167(1)
Re(3)—Re(4)	3.058(5)	Re(1)—Re(4)—C(10)	121(2)
Re—C ^a	1.82(4)	Re(1)—Re(4)—C(11)	109(2)
C—Re—C angles (deg.)		Re(1)—Re(4)—C(12)	80(2)
C—Re(1)—C ^a	89(2)	Re(1)—Re(4)—C(13)	149(2)
C—Re(2)—C ^a	93(2)	Re(2)—Re(4)—C(10)	140(2)
C—Re(3)—C ^a	92(4)	Re(2)—Re(4)—C(11)	68(2)
C—Re(4)—C(<i>cis</i>) ^a	87(4)	Re(2)—Re(4)—C(12)	126(3)
C(11)—Re(4)—C(12)	166(3)	Re(2)—Re(4)—C(13)	101(2)
		Re(3)—Re(4)—C(10)	161(2)
		Re(3)—Re(4)—C(11)	122(2)
		Re(3)—Re(4)—C(12)	72(3)
		Re(3)—Re(4)—C(13)	88(2)

^a Mean value.

i.e. three are bridging on the basal triangular edges and the fourth is bridging on the Re(1)—Re(4) edge.

The coordination around Re(4) is of special interest. The carbonyl ligands approximately occupy four non-coplanar octahedral coordination sites and the orientation of the Re(4)(CO)₄ group, as a whole, is dictated by non-bonded intramolecular contacts. The values of all the Re—Re(4)—C angles are given in Table 1.

The anion is electron precise (60 valency electrons) [4]. The two net anionic charges should be unevenly distributed among the four rhenium atoms. This fact, together with the presence of asymmetric intramolecular contacts, may be responsible for the spreading of the metal—metal distances.

The carbonyl stereochemistry in $[\text{H}_4\text{Re}_4(\text{CO})_{13}]^{2-}$ is novel. Few structures of tetrahedral clusters bearing thirteen CO ligands are known, i.e. $[\text{Fe}_4(\text{CO})_{13}]^{2-}$ [6] and the two isostructural species $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$ [7] and $\text{H}_2\text{Ru}_4(\text{CO})_{13}$ [8]. In the first case one CO group is triple-bridging and the other three give highly asymmetric M—C—M bridges; in the latter structures two carbonyl ligands form asymmetric double bridges. The anion is the first containing only terminal CO groups, but this feature is normal for rhenium carbonyl clusters, in which bridging carbonyls have never been found [4].

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References

- 1 V.G. Albano, G. Ciani, M. Freni and P. Romiti, *J. Organometal. Chem.*, 96 (1975) 259.
- 2 G. Ciani, V.G. Albano and A. Immirzi, *J. Organometal. Chem.*, in press.
- 3 A. Bertolucci, M. Freni, P. Romiti, G. Ciani, A. Sironi and V.G. Albano, *J. Organometal. Chem.*, 113 (1976) C61.
- 4 H.D. Kaesz, *Chem. Brit.*, 9 (1973) 344.

- 5 See e.g. G. Ciani, D. Giusto, M. Manassero and A. Albinati, *J. Chem. Soc. Dalton*, (1976) in the press and refs. therein.
- 6 R.J. Doedens and L.F. Dahl, *J. Amer. Chem. Soc.*, 88 (1966) 4847.
- 7 C.J. Gilmore and P. Woodward, *J. Chem. Soc. A*, (1971) 3453.
- 8 D.B.W. Yawney and R.J. Doedens, *Inorg. Chem.*, 11 (1972) 838.