

A Novel Unsaturated Tetrahedral Hydrido-carbonyl Cluster Anion of Rhenium. Synthesis and X-Ray Characterization of $[\text{Re}_4(\mu\text{-H})_3(\mu_3\text{-H})_2(\text{CO})_{12}]^-$

Tiziana Beringhelli,^a Giuseppe D'Alfonso,^{*a} Gianfranco Ciani,^{*b} and Henriette Molinari^c

^a Centro C.N.R. Sintesi e Struttura Metalli di Transizione nei Bassi Stati di Ossidazione, Dipartimento di Chimica Inorganica e Metallorganica, Via G. Venezian 21, 20133 Milano, Italy

^b Istituto di Chimica Strutturistica Inorganica and Centro C.N.R., Via G. Venezian 21, 20133 Milano, Italy

^c Dipartimento di Chimica Organica e Industriale, Via Golgi 19, 20133 Milano, Italy

The reaction of the anion $[\text{Re}_4(\mu\text{-H})_6(\text{CO})_{12}]^{2-}$ with acids affords the unsaturated (58 valence electron) anion $[\text{Re}_4\text{H}_5(\text{CO})_{12}]^-$, which contains a distorted tetrahedral cluster, with Re-Re bond lengths in the range 2.857(1)—3.251(1) Å, bearing three edge-bridging and two face-capping hydride ligands, completely fluxional in solution down to -90°C .

Unsaturated carbonyl cluster compounds are interesting species owing to their peculiar reactivity,¹ but their number is at present quite limited. In the field of hydrido-carbonyl clusters of rhenium the only known tetrametal compound is the 56 valence-electron $[\text{Re}_4(\mu_3\text{-H})_4(\text{CO})_{12}]$.² We have now succeeded in isolating the novel tetrarhenium unsaturated (58 valence electron) anion $[\text{Re}_4(\mu\text{-H})_3(\mu_3\text{-H})_2(\text{CO})_{12}]^-$ and we

report here on its spectroscopic and structural characterization. It represents an intermediate between $[\text{Re}_4(\mu_3\text{-H})_4(\text{CO})_{12}]$ and $[\text{Re}_4(\mu\text{-H})_6(\text{CO})_{12}]^{2-}$,³ in terms of both the number of valence electrons and hydrides and the ligand stereochemistry.

Treatment of an acetone solution of the $[\text{NEt}_4]^+$ salt of the dianion $[\text{Re}_4(\mu\text{-H})_6(\text{CO})_{12}]^{2-}$ with the stoichiometric

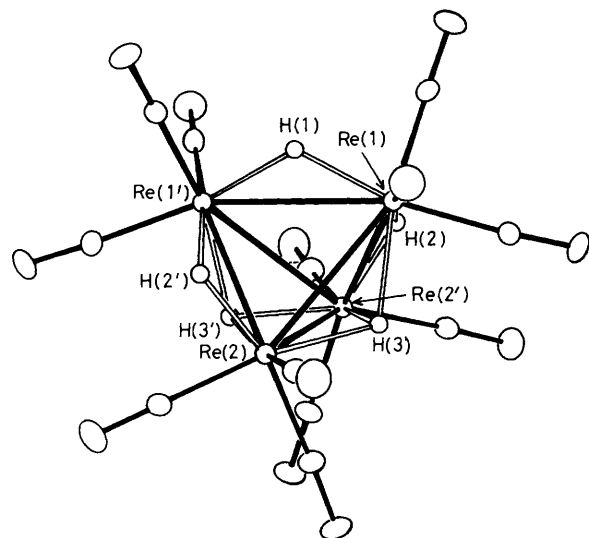


Figure 1. A view of one of the two independent anions $[\text{Re}_4(\mu\text{-H})_3(\mu_3\text{-H})_2(\text{CO})_{12}]^-$ [anion (A)]. A crystallographic two-fold axis passes through the middle points of edges $\text{Re}(1)\text{-Re}(1')$ and $\text{Re}(2)\text{-Re}(2')$. Relevant bond distances are as follows [with corresponding values for anion (B) in square brackets]: $\text{Re}(1)\text{-Re}(1')$ 3.118(1) [3.088(1)], $\text{Re}(1)\text{-Re}(2)$ 3.251(1) [3.241(1)], $\text{Re}(1)\text{-Re}(2')$ 2.857(1) [2.857(1)], $\text{Re}(2)\text{-Re}(2')$ 2.992(1) [2.994(1)], $\text{Re}(1)\text{-H}(1)$ 1.79(7) [1.80(6)], $\text{Re}(1)\text{-H}(2)$ 1.86(11) [1.72(10)], $\text{Re}(2)\text{-H}(2)$ 1.70(11) [1.94(10)], $\text{Re}(1)\text{-H}(3)$ 2.04(11) [2.17(11)], $\text{Re}(2)\text{-H}(3)$ 2.05(10) [2.06(10)], $\text{Re}(2')\text{-H}(3)$ 1.92(10) [2.03(10)] Å. The overall mean values for the Re-C and C-O interactions are 1.924 and 1.146 Å, respectively.

amount of $\text{CF}_3\text{SO}_3\text{H}$, at room temperature, resulted in an instantaneous colour change from yellow to deep red. Monitoring by i.r. spectroscopy showed the complete disappearance of the reagent, while H_2 evolution was indicated by gas chromatographic analysis. Recrystallization by slow diffusion of vapours of pentane into a CH_2Cl_2 solution allowed the isolation of a deep red crystalline product,† characterized as the salt $[\text{NET}_4][\text{Re}_4\text{H}_5(\text{CO})_{12}]$, on the basis of a single crystal X -ray analysis.‡ The reaction, which is almost quantitative, can be easily reverted using NaBH_4 .

† The i.r. spectrum in CH_2Cl_2 shows two $\nu(\text{CO})$ bands, at 2017 and 1941 cm^{-1} , indicative of the presence of $\text{Re}(\text{CO})_3$ groups only. ^1H N.m.r. spectra in $[\text{D}_6]\text{acetone}$ at room temperature reveal a single hydride resonance ($\delta = 10.35$, s, 5H by comparison of the integrated intensity with those of the cationic hydrogens); the signal remains unchanged down to -90°C .

‡ *Crystal data:* $\text{C}_{20}\text{H}_{25}\text{NO}_{12}\text{Re}_4$, $M = 1216.2$, monoclinic, space group $P2_1/a$ (non-standard setting of no. 13), $a = 17.974(4)$, $b = 8.764(3)$, $c = 18.412(4)$ Å, $\beta = 91.72(2)^\circ$, $Z = 4$, $D_c = 2.786$ g cm^{-3} , $\text{Mo-K}\alpha$ radiation, $\lambda = 0.71073$ Å, $\mu(\text{Mo-K}\alpha) = 169.3$ cm^{-1} . Intensity data were collected on a CAD4 Enraf-Nonius diffractometer by the ω -scan method within the limits $3 < \theta < 25^\circ$. The structure solution was performed by Patterson and Fourier methods, on the basis of 3076 absorption corrected independent significant [$I > 3\sigma(I)$] reflections. The anions were found to lie in special positions on two types of two-fold crystallographic axes [e and f in Wyckoff notation, for anion (A) and (B), respectively]. Refinements were carried out by full-matrix least-squares, assigning anisotropic thermal parameters to all the anionic atoms except to the hydrides. These were directly located and refined isotropically, while the cationic hydrogens were placed in idealized positions but not refined. The values of R and R_w are 0.023 and 0.029, respectively. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

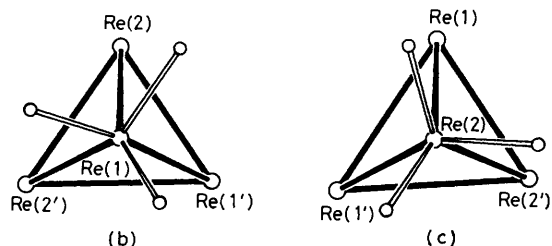
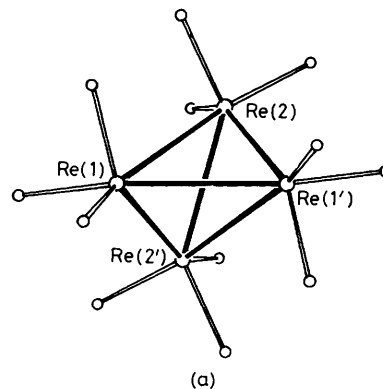


Figure 2. (a) The stereochemistry of the Re_4C_{12} moiety viewed down the two-fold axis, and the carbonyl geometry around (b) $\text{Re}(1)$ and (c) $\text{Re}(2)$ in anion (A). With respect to an ideal staggered orientation the carbonyl groups are rotated by ca. 25 and 38° about $\text{Re}(1)$ and $\text{Re}(2)$, respectively.

The unit contains two asymmetric but structurally independent 'half-anions', each anion (A) and (B) possessing crystallographically imposed C_2 symmetry and containing a distorted tetrahedron of rhenium atoms with the CO ligands terminally bonded, three to each metal (Figure 1). The distortion of the tetrahedral cluster geometry is noteworthy [see Figure 2a for anion (A)], owing to the presence of very different Re-Re bonds, and the angle between the two opposite edges $\text{Re}(1)\text{-Re}(1')$ and $\text{Re}(2)\text{-Re}(2')$, projected on the same plane, is ca. 75° (instead of the ideal 90°). The rhenium-rhenium edges are of four types [bond lengths averaged between anions (A) and (B)]: i, $\text{Re}(1)\text{-Re}(1')$, mean 3.103 Å; ii, $\text{Re}(2)\text{-Re}(2')$, mean 2.993 Å; iii, $\text{Re}(1)\text{-Re}(2)$ (and symmetry related bond), mean 3.246 Å; iv, $\text{Re}(1)\text{-Re}(2')$ (and symmetry related bond), mean 2.857 Å. Both the cluster unsaturation and the overall ligand stereochemistry can account for this variance.

The hydrides have been directly located and refined, and their positions have also been confirmed by potential energy calculations using the Orpen program.⁴ Three are double bridging, on the edges $\text{Re}(1)\text{-Re}(1')$, $\text{Re}(1)\text{-Re}(2')$, and $\text{Re}(1')\text{-Re}(2)$, while two are triple bridging, on the faces $\text{Re}(1,2,2')$ and $\text{Re}(1',2,2')$. Thus each Re atom attains a distorted octahedral co-ordination, with three CO and three hydride ligands. The Re-H bond lengths have mean values of 1.80 and 2.04 Å for double and triple bridges, respectively. The second value is somewhat higher than expected, but these parameters are affected by very high uncertainties. The presence in the same cluster of double and triple bridging hydrides is very unusual.⁵

The cluster unsaturation appears to be delocalized on the two short edges of type iv (2.857 Å). This finding is rather surprising since the known unsaturated compounds exhibit either a localized multiple bond, as for instance in $[\text{Re}_3(\mu-$

$\text{H})_4(\text{CO})_{10}]^-$ [short Re–Re bond length 2.789(1) Å, formal bond order 2],⁶ or a complete delocalization over all the cluster edges, as in $[\text{Re}_4(\mu_3\text{-H})_4(\text{CO})_{12}]^-$ (mean Re–Re 2.913 Å, formal bond order 1.33).² In the present anion the short Re–Re bonds, of formal bond order 1.5, have a mean length intermediate between these two cases (in all three species the edges are bridged by two hydrides).

Another very interesting structural feature of this anion is its ligand stereochemistry. Various tetrahedral clusters of the type $[\text{M}_4\text{H}_x(\text{CO})_{12}]^{y-}$ are known, including $[\text{M}_4\text{H}_4(\text{CO})_{12}]^-$ (M = Ru,⁷ Os⁸), $[\text{M}_4\text{H}_3(\text{CO})_{12}]^-$ (M = Ru, Os),⁹ $[\text{Re}_4(\mu\text{-H})_6(\text{CO})_{12}]^{2-}$, $[\text{Re}_4(\mu_3\text{-H})_4(\text{CO})_{12}]$ and derivatives, which invariably show either staggered or eclipsed orientations of the CO groups (relative to the M–M edges). This implies, respectively, edge-bridging or face-capping locations for the hydrides, as confirmed also by theoretical calculations by Hoffmann *et al.*¹⁰ In the anion $[\text{Re}_4(\mu\text{-H})_3(\mu_3\text{-H})_2(\text{CO})_{12}]^-$ the presence of edge-bridging and face-capping hydrides determines a conformation of the CO groups intermediate between staggered and eclipsed (Figure 2b and c).

The fluxional behaviour of the hydrides in solution, resulting in an unique ¹H n.m.r. resonance even at –90 °C, might be related to two concurrent effects: the possibility of higher delocalization of the unsaturation on the cluster edges and a rapid interchange of the double and triple bridging hydrides, probably because of relatively low energy barriers to their movements.¹⁰

The reactivity of the anion is currently under investigation; it is expected to undergo easy addition reactions in order to achieve saturation. In fact, in the presence of CO it readily

adds two molecules giving the colourless (62 valence-electron) ‘butterfly’ anion $[\text{Re}_4(\mu\text{-H})_5(\text{CO})_{14}]^-$.¹¹

Received, 13th November 1986; Com. 1615

References

- 1 B. F. G. Johnson and J. Lewis, *Adv. Inorg. Chem. Radiochem.*, 1981, **24**, 225; E. L. Muetterties and M. J. Krause, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 135.
- 2 R. Saillant, G. Barcelo, and H. Kaesz, *J. Am. Chem. Soc.*, 1970, **92**, 5739; R. D. Wilson and R. Bau, *ibid.*, 1976, **98**, 4687.
- 3 H. D. Kaesz, B. Fontal, R. Bau, S. W. Kirtley, and M. R. Churchill, *J. Am. Chem. Soc.*, 1969, **91**, 1021; G. Ciani, A. Sironi, and V. G. Albano, *J. Organomet. Chem.*, 1977, **136**, 339.
- 4 A. G. Orpen, *J. Chem. Soc., Dalton Trans.*, 1980, 2509.
- 5 H. H. Wang and L. H. Pignolet, *Inorg. Chem.*, 1980, **19**, 1470; T. Beringhelli, G. Ciani, G. D’Alfonso, P. Romiti, A. Sironi, and M. Freni, *ibid.*, 1984, **23**, 2849.
- 6 T. Beringhelli, G. Ciani, G. D’Alfonso, H. Molinari, and A. Sironi, *Inorg. Chem.*, 1985, **24**, 2666.
- 7 R. D. Wilson, S. M. Wu, R. A. Love, and R. Bau, *Inorg. Chem.*, 1978, **17**, 1271.
- 8 B. F. G. Johnson, J. Lewis, P. R. Raithby, and C. Zuccaro, *Acta Crystallogr., Sect. B*, 1981, **37**, 1728.
- 9 M. McPartlin and W. H. Nelson, *J. Chem. Soc., Dalton Trans.*, 1986, 1557 and refs. therein.
- 10 R. Hoffmann, B. E. R. Schilling, R. Bau, H. D. Kaesz, and D. M. P. Mingos, *J. Am. Chem. Soc.*, 1978, **100**, 6088.
- 11 T. Beringhelli, G. Ciani, G. D’Alfonso, V. De Malde’, A. Sironi, and M. Freni, *J. Chem. Soc., Dalton Trans.*, 1986, 1051.