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Preliminary communication

SYNTHESIS AND X-RAY CHARACTERIZATION OF THE DIANIONS TRIHYDRIDODECACARBONYLTRIRHENATE(2–) AND TRIHYDRIDO-μ_3-OXO-ENNEACARBONYLTRIRHENATE(2–)

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Summary

The synthesis of the new anions $[H_3Re_3(CO)_{10}]^{2-}$ and $[H_3Re_3(\mu_3\text{-}O)(CO)_9]^{2-}$, obtained from $[H_4Re_4(CO)_{15}]^{2-}$, and their characterization by IR, NMR and X-ray analyses are reported; both species contain a triangular metal atom cluster and the former, which is electron deficient, contains a Re—Re double bond.

Decacarbonyldirhenium reacts with methanolic potassium hydroxide to give a variety of products such as μ-alcoxo species [1] and carbonylhydrido cluster compounds. We have recently reported the synthesis and structure of the dianion $[H_4Re_4(CO)_{15}]^{2-}$ [2], which has proved to be very useful for the preparation of other carbonylhydrido species. Concentrated ethanolic solutions of its NEt_4^+ salt, upon refluxing for ca. 3 h and cooling, give, by overall loss of a $HRe(CO)_5$ molecule, the red compound $(NEt_4)_2[H_3Re_3(CO)_{10}]$ (I). More dilute ethanol solutions of the parent salt, upon boiling for a prolonged time and cooling, give a mixture containing the colourless compound $(NEt_4)_2[H_3Re_3(\mu_3\text{-}O)(CO)_9]$ (II) and an orange-yellow species not yet identified. Both I and II are diamagnetic. They show IR bands (acetone solution) due to terminal CO groups as follows: 1990m, 1955m, 1920s, 1880m, 1860(sh) cm^{-1} (I) and 1980s, 1880s cm^{-1} (II). The high field NMR spectra in CD_3COCD_3 exhibit singlets at τ 18.4 and 21.1 ppm (ratio 2:1) for compound I, and at τ 22.8 ppm for II, due to the hydridic

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hydrogens. The integrations are in agreement with the proposed stoicheiometries.

Crystals of both compounds have been examined by X-ray diffraction*. The anion $[H_2Re_3(CO)_{10}]^{2-}$ (Fig. 1) lies at the intersection of two perpendicular mirror planes (the first one containing the Re_3 triangle and the other one passing through Re(1) and the middle of the Re(2)—Re(2') edge) and results disordered**. This species is an example of an electron deficient triangular cluster compound (46 valency electrons) [3], thus requiring the presence of a metal—metal double bond. The Re(2)—Re(2') bond [2.797(4) Å] is, in fact, ca. 0.2 Å shorter than a normal single bond; it is the shortest ever found in a rhenium carbonyl cluster, even shorter than the Re—Re double bond (2.896(3) Å) in $H_2Re_2(CO)_8$ (A) [4]. The shortening is comparable to that found in the isoelectronic species $H_2Os_3(CO)_{10}$ (B), which has a metal—metal double bond of 2.670 Å [5].

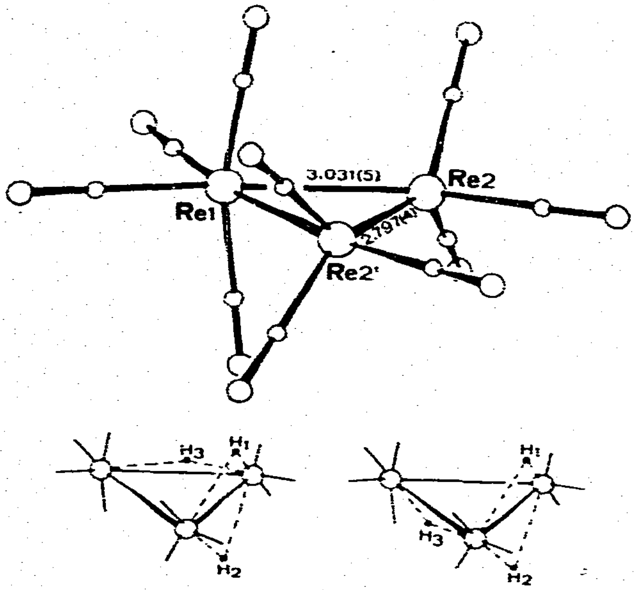

Fig. 1. Disordered structure of $[H_2Re_3(CO)_{10}]^{2-}$, probably derived from the average of the two lower structures.

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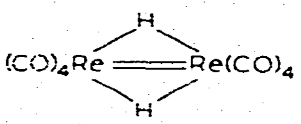
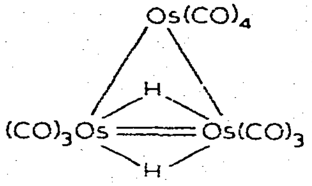
*Crystal data. Both species are orthorhombic. Compound I, $C_{26}H_{43}N_2O_{10}Re_3$, *M* 1102, *a* 9.96(1), *b* 22.78(2), *c* 15.16(2) Å, D_m 2.14(2), D_c 2.13 for $Z = 4$; $\mu(\text{Mo-}K_\alpha)$ 111.9 cm^{-1}. Space group *Cmcm* (No. 63). Compound II, $C_{25}H_{43}N_2O_{10}Re_3$, *M* 1090, *a* 15.05(2), *b* 12.32(1), *c* 18.35(2) Å, D_m 2.16(2), D_c 2.13 for $Z = 4$; $\mu(\text{Mo-}K_\alpha)$ 113.3 cm^{-1}. Space group *Pnma* (No. 62).

Intensity data were collected on a Pailred diffractometer with Mo-K_α (λ 0.7107 Å) graphite monochromatized radiation, within the limits $2\theta < 40°$ (I) and $< 42°$ (II). The intensities were corrected for Lorentz, polarization, absorption and decay (< 15%) effects. After rejection of reflections having $\sigma(I)/I >$ 0.30 (I) and > 0.25 (II), two sets of 384 and 1147 non-zero independent reflections were used, respectively. The structures were solved by conventional Patterson and Fourier methods and refined by least-squares. Anisotropic thermal factors were assigned to the rhenium atoms and, in compound I, the Re—C—O interactions were constrained to linearity, with fixed C—O distances of 1.16 Å. The current *R* values are 6.4% (I) and 3.8% (II), respectively.

**High thermal factors for all atoms, especially for the CO groups bound to Re(1) and lying in the Re_3 plane, and lack of observed reflections for θ above 20° are indicative of disorder, the mirror plane normal to the triangle being only statistical. Attempts to use disordered models or to assume as space group the possible non-centrosymmetric group $Cmc2_1$ led to high correlations or to complete divergence in the refinements.



(A)



(B)

In order to attain the EAN for the metal atoms in the anion, the two net negative charges should be mainly localized on the Re(2) and Re(2′) atoms. As a matter of fact the Re—C distances are shorter for Re(2) (mean value 1.83 Å) than for Re(1) (mean value 1.94 Å).

The low NMR signals of these bridging hydrides (τ 18.4 ppm for H(1) and H(2), and 21.1 ppm for H(3)) derive from the unsaturation of the compound [3]. Similar low values were found both in A (τ 19.04 ppm ($CDCl_3$)) [4] and in B (τ 20.9 ppm ($CDCl_3$)) [6].

The structure of $[H_3Re_3(\mu_3\text{-}O)(CO)_9]^{2-}$ is depicted in Fig. 2. It lies on a mirror plane passing through Re(1), O and the middle of the Re(2)—Re(2′) edge and possesses an overall idealized C_{3v} symmetry. The mean values of the Re—O(oxo), Re—C and C—O distances are 2.12, 1.84 and 1.20 Å, respectively. The dianion is electron precise (48 valency electrons). The disposition of the carbonyl groups implies that the hydrido ligands are in bridging positions on the three triangular edges, on the opposite side of the Re_3 plane from the μ_3-ligand, a situation very similar to that in $[H_3Ru_3(\mu_3\text{-}CMe)(CO)_9]$ [7]. The Re—Re bonds are normal single bonds, not lengthened, as is usually found [3], by the bridging hydrogen ligands. Normal bonds have been observed also in the Ru_3 species, and this seems to be a feature arising from the presence of the μ_3-bridging ligand, which might prevent a lengthening of the associated metal—metal bonds.

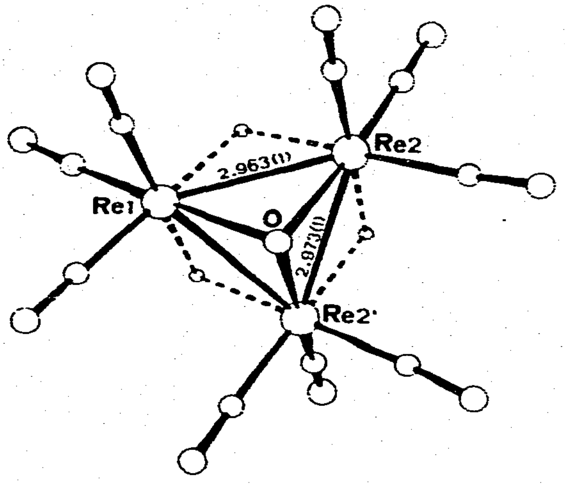


Fig. 2. View of the anion $[H_3Re_3(\mu_3\text{-}O)(CO)_9]^{2-}$ with the postulated hydridic atom positions.

The NMR signal from these hydrides is the lowest ever found for such bridging ligands on a Re—Re single bond; however, the situation in solution may be different from that in the solid state.

The reactions of compounds I and II are now under investigation. In particular, it is very likely that I, which is unsaturated, will undergo addition reactions of the kind recently observed for the isoelectronic $H_2Os_3(CO)_{10}$ [8].

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