*Journal of Organometallic Chemistry*, 136 (1977) C49—C51

**Preliminary communication**

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# SYNTHESIS AND X-RAY STRUCTURE OF THE ANION TETRA-μ-HYDRIDO-DECACARBONYL-*triangulo*-TRIRHENATE(1–)

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(Received June 13th, 1977)

## Summary

The novel hydridocarbonyl cluster compound $(NEt_4)[H_4Re_3(CO)_{10}]$ has been characterized by IR, NMR and X-ray analyses. In the anion the three metal atoms form an isosceles triangle, with two long hydrogen-bridged Re—Re bonds and a short doubly hydrogen-bridged Re=Re double bond.

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We have recently reported [1] the synthesis and structure of the unsaturated red dianion $[H_3Re_3(CO)_{10}]^{2-}$ (I), and we have now begun to study its reactions with acids and bases. When a solution of its tetraethylammonium salt in acetone is treated with a strong acid such as HCl or $HClO_4$ at room temperature, and water is subsequently added, a yellow precipitate is obtained in good yield. The analysis of the product corresponds to the new species $(NEt_4)[H_4Re_3(CO)_{10}]$. The IR spectrum (in acetone) shows bands due to terminal carbonyl ligands at 2090w, 2025m, 1998vs, 1948m and 1915s $cm^{-1}$. The NMR spectrum (in $CD_3COCD_3$) at high field exhibits two singlets, at $\tau$ 18.5 and 23.4 ppm, in the ratio 1 : 1, whose integration with respect to the cationic methylene hydrogens is in good agreement with the proposed stoicheiometry. Reaction 1 seems not to

$$[H_3Re_3(CO)_{10}]^{2-} + H^+ \rightarrow [H_4Re_3(CO)_{10}]^- \qquad (1)$$

be reversed on treatment of the product with a strong base, probably for reasons similar to those outlined by Kaesz [2] for the case of the two species $[HRe_3(CO)_{12}]^{2}$ and $[H_2Re_3(CO)_{12}]^-$.

Recrystallization of the yellow precipitate from acetone/water or ethanol/water gives different crystallographic modifications of the same substance. We have investigated by X-ray diffraction an orthorhombic form, space group *Pbcn*, with cell constants *a* 13.09(1), *b* 11.83(1), *c* 34.29(2) Å, $Z = 8$. The structure was solved by Patterson and Fourier methods and refined by block-matrix least-squares to a conventional *R* value of 0.085 for 753 independent observed reflections. The Re—C—O interactions were constrained to linearity and the C—O distances were kept constant, with a value of 1.18 Å.

The structure of $[H_4Re_3(CO)_{10}]^-$ is illustrated in Fig. 1 and the bond parameters are listed in Table 1. The anion contains an isosceles metal atoms triangle and exhibits an overall idealized $C_{2v}$ symmetry. It is unsaturated (46 valence electrons, as in the parent species I) and, consequently, it requires the presence of a metal—metal double bond, which is localized on the Re(2)—Re(3) interaction.

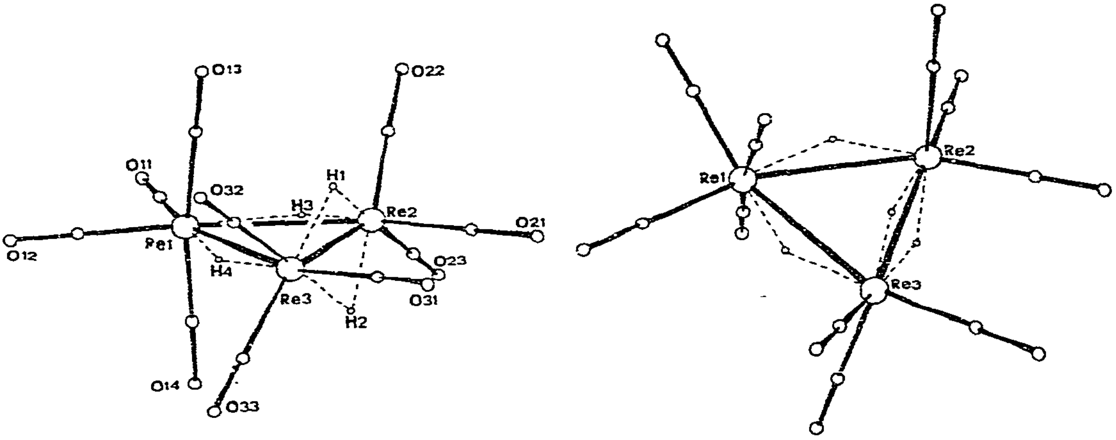


Fig. 1. Two views of the anion $[H_4Re_3(CO)_{10}]^-$ with postulated hydridic atoms locations.

The positions of the four hydrido ligands (not directly located) can be easily

TABLE 1

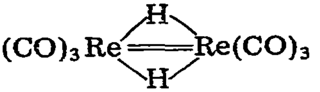
BOND DISTANCES (Å) AND ANGLES (deg.) WITHIN THE ANION $[H_4Re_3(CO)_{10}]^-$

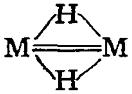
| | |
|---|---|
| Re(1)—Re(2) | 3.173(7) |
| Re(1)—Re(3) | 3.194(7) |
| Re(2)—Re(3) | 2.821(7) |
| Re(1)—C [a] | 1.94(4) |
| Re(2,3)—C [a] | 1.90(4) |
| | |
| Re(2)—Re(1)—Re(3) | 52.6(2) |
| Re(1)—Re(2)—Re(3) | 64.1(2) |
| Re(1)—Re(3)—Re(2) | 63.3(2) |
| Re(2)—Re(1)—C(11) | 108(1) |
| Re(2)—Re(1)—C(12) | 157(1) |
| Re(2)—Re(1)—C(13) | 82(1) |
| Re(2)—Re(1)—C(14) | 90(1) |
| Re(3)—Re(1)—C(11) | 160(1) |
| Re(3)—Re(1)—C(12) | 105(1) |
| Re(3)—Re(1)—C(13) | 85(1) |
| Re(3)—Re(1)—C(14) | 90(1) |
| C(11)—Re(1)—C(12) | 95(2) |
| C(11)—Re(1)—C(13) | 94(2) |
| C(11)—Re(1)—C(14) | 89(2) |
| C(12)—Re(1)—C(13) | 93(2) |
| C(12)—Re(1)—C(14) | 94(2) |
| C(13)—Re(1)—C(14) | 172(2) |
| Re(1)—Re(2)—C(21) | 160(2) |
| Re(1)—Re(2)—C(22) | 100(2) |
| Re(1)—Re(2)—C(23) | 106(2) |
| Re(3)—Re(2)—C(21) | 96(2) |
| Re(3)—Re(2)—C(22) | 132(2) |
| Re(3)—Re(2)—C(23) | 141(2) |
| C(21)—Re(2)—C(22) | 95(2) |
| C(21)—Re(2)—C(23) | 88(2) |
| C(22)—Re(2)—C(23) | 86(3) |
| Re(1)—Re(3)—C(31) | 160(1) |
| Re(1)—Re(3)—C(32) | 103(1) |
| Re(1)—Re(3)—C(33) | 103(2) |
| Re(2)—Re(3)—C(31) | 98(1) |
| Re(2)—Re(3)—C(32) | 135(1) |
| Re(2)—Re(3)—C(33) | 136(2) |
| C(31)—Re(3)—C(32) | 87(2) |
| C(31)—Re(3)—C(33) | 94(2) |
| C(32)—Re(3)—C(33) | 88(2) |

[a] Mean value.

derived from the cluster geometry and from the carbonyl arrangement. Two of them, H(1) and H(2), are bridging the rhenium—rhenium double bond, and the other two, H(3) and H(4), are bridging the two long triangular edges, whose lengths are comparable to those found in other hydrogen-bridged Re—Re single bonds [2].

Neglecting the intermetallic bonds, the coordination around each rhenium atom is approximately octahedral. The net anionic charge must be equally shared by the Re(2) and Re(3) atoms.

This structure is very similar in the  $(CO)_3\mathrm{Re}\overset{H}{\underset{H}{=\!=}}\mathrm{Re}(CO)_3$ fragment, to that of I (in which the remaining part of the dianion was somewhat obscured by disorder [1]). The corresponding Re—Re—C(*cis*), Re—Re—C and C—Re—C angles have mean values of 101°, 134° and 90° in I vs. 97°, 136° and 90° in the present case.

The bis($\mu$-H) rhenium—rhenium double bond (2.821(7) Å, very close to the value of 2.797(4) Å found in I) is ca. 0.2 Å shorter than an unbridged Re—Re single bond, e.g. 3.02 Å in $Re_2(CO)_{10}$ [3]. Similar  $\mathrm{M}\overset{H}{\underset{H}{=\!=}}\mathrm{M}$ bonds are present also in the species $H_2Re_2(CO)_8$ [4], $H_2Os_3(CO)_{10}$ [5] and $[H_2W_2(CO)_8]^{2-}$ [6]. The expected bond lengthening effect of the bridging hydrides cannot be demonstrated since there are no data on corresponding M=M unbridged double bonds in carbonylic species. Various trinuclear halide clusters of rhenium are known, with metal—metal distances of 2.43—2.51 Å, in which the bond order is believed to be 2 [7]; however, the different natures of halide and carbonyl ligands prevents any direct comparison.

The results confirm our suggestion about the location of the hydridic atoms in I, and the assignments of their NMR signals. The two equivalent hydrides bridging the metal—metal double bond give very similar signals in the two anions ($\tau$ 18.5 vs. 18.4 in I). The other two equivalent hydrides, H(3) and H(4), give a signal at somewhat higher field than that of the third hydride of I ($\tau$ 23.4 vs. 21.1). All these signals, as already pointed out [1], are at rather low values for bridging hydrides, because of unsaturation.

We thank the Italian C.N.R. for financial support.

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