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Preliminary communication

SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF THE ANION TRI-μ-HYDRIDOIODOUNDECACARBONYL-*triangulo*-TRIRHENATE(1–)

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Summary

The novel anion $[Re_3H_3I(CO)_{11}]^-$ has been obtained by reaction of ethanolic I_2 solutions with either $[Re_4H_4I(CO)_{15}]^-$ or $[Re_4H_4(CO)_{15}]^{2-}$. It has been characterized by IR, NMR and single-crystal X-ray analysis. The anion contains an equilateral metal atoms triangle (mean Re—Re 3.265 Å) bearing six equatorial and five axial CO groups. The iodide ligand is terminally bound in axial position (Re—I 2.839(4) Å). The hydride ligands are bridging on the Re_3 triangular edges.

We previously reported the reaction of the anion $[Re_4H_4(CO)_{15}]^{2-}$ (I) with ethanolic I_2 solution, in equimolar amounts, to give the iodo derivative $[Re_4H_4I(CO)_{15}]^-$ (II), which contains an open tetrametal array, as in the parent species I, with the iodine atom terminally bound to the apical rhenium atom (see Fig. 1) [1]. We have now found that compound II further reacts with iodine with fragmentation of the metal cluster.

The white salt $(NEt_4)[Re_4H_4I(CO)_{15}]$, suspended in ethanol, was treated dropwise with ethanolic I_2 at room temperature (molar ratio of the reagents 1/1); the colour became yellow, and II disappeared. By addition of n-hexane we isolated white crystals of the known monomeric species $(NEt_4)[ReI_2(CO)_4]$ (III) [2], yellow crystals of the species $(NEt_4)[Re_3H_3I(CO)_{10}]$ (IV) (previously obtained by reaction of the unsaturated clusters $[Re_3H_3(CO)_{10}]^{2-}$ and $[Re_3H_4(CO)_{10}]^-$ with I_2 [3]) and, in lower yields, yellow crystals of the new species $(NEt_4)[Re_3H_3I(CO)_{11}]$ (V). The same products were also obtained by treating $(NEt_4)_2[Re_4H_4(CO)_{15}]$ directly with two molar proportions of I_2 in ethanol.

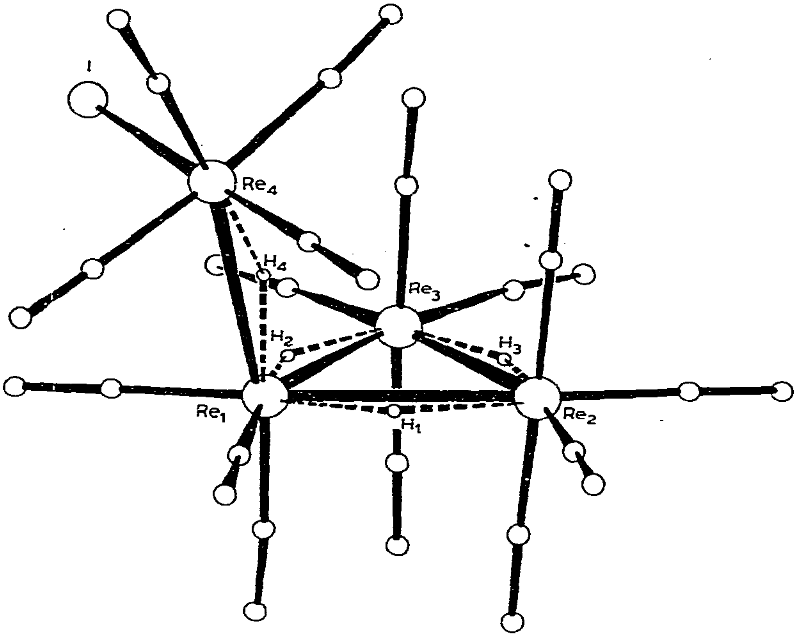

Fig. 1. A schematic view of the parent anion $[Re_4H_4I(CO)_{15}]^-$ (II).

The IR spectrum of the novel anion V in acetone, shows the following bands due to terminal CO groups: 2075m, 2010vs, 1995s, 1950ms, 1920m and 1880m cm^{-1}. The NMR spectrum, in deuteroacetone solution, exhibits two high field singlets at τ 24.8 and 27.2 (ratio 2/1), whose integration with respect to the cationic methylene hydrogens is in good agreement with the proposed stoichiometry.

The salt $(NEt_4)[Re_3H_3I(CO)_{11}]$ has been investigated by single-crystal X-ray analysis*. The novel anion, of idealized C_s symmetry, is illustrated in Fig. 2. It contains an almost equilateral metal atom triangle bearing eleven CO groups and one iodide ligand, all terminally bound to the rhenium atoms. The three hydride ligands, not directly located, are assumed to be bridging on the three triangular edges. The structure can be derived from that of the parent anion II (see Fig. 1) by replacing the apical $ReHI(CO)_4$ moiety with the iodide ligand, axially bound to the triangle. It can also be related to the structure supposed for the neutral species $Re_3H_3(CO)_{12}$ (see ref. 4), by replacement of an axial CO by an iodide ligand.

The Re—Re bond lengths are very similar, with a mean value of 3.265 Å, showing the usual lengthening of the metal—metal bonds due to the presence of bridging hydride ligands. The Re—I bond length, of 2.839(4) Å, is very similar to the Re—I interaction (2.813(2) Å) in the parent anion II. The Re(1)—C,

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*Crystal Data. $C_{19}H_{23}INO_{11}Re_3$, M = 1126.9, Monoclinic, space group $P2_1/c$ (No. 14), with a 11.923(3), b 14.172(4), c 17.548(5) Å, β 94.11(3)° and Z = 4. The structure was solved by conventional Patterson and Fourier methods, and refined by least-squares methods, on the basis of 2575 significant independent counter data, up to a current R value of 0.098.

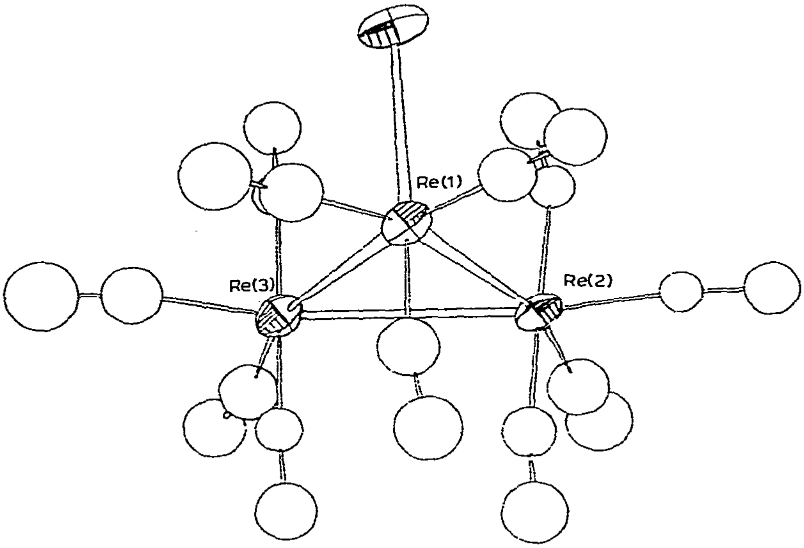

Fig. 2. A view of the novel anion $[Re_3H_3I(CO)_{11}]^-$ (V). The Re—Re bond distances are: Re(1)—Re(2) 3.267(2), Re(1)—Re(3) 3.255(2) and Re(2)—Re(3) 3.273(2) Å.

Re(2,3)—C and C—O mean bond distances are 1.86, 1.92 and 1.18 Å, respectively. The geometry of the equatorial carbonyl ligands confirms the presence of the hydride ligands in bridging positions on the Re—Re triangular edges, almost coplanar with the metal atoms.

The products isolated suggest the reaction path as shown in Scheme 1. The

$$\begin{tikzcd}
{[Re_4H_4(CO)_{15}]^{2-}} \arrow[r, "I_2"] & {[Re_4H_4I(CO)_{15}]^- + I^-} \\
(I) & (II) \arrow[d, "I_2"'] \\
 & {[Re_3H_3I(CO)_{11}]^- + [ReI_2(CO)_4]^- + H^+} \\
 & (V) \qquad\qquad (III) \arrow[d] \\
 & {[Re_3H_3(\mu\text{-}I)(CO)_{10}]^- + CO} \\
 & (IV)
\end{tikzcd}$$

SCHEME 1

initially instantaneous electrophilic addition of I^+ to compound I, which gives the stable species II, is followed, upon further addition of I_2, by the cleavage of the apical $ReI(CO)_4$ moiety, with separation of a mononuclear (III) and a triangular species (V). Compound V readily loses CO to give species IV, which was previously obtained in a different way and for which a structure containing an edge-bridging iodide ligand was suggested [3].

The reaction was monitored by NMR analysis in deuterotetrahydrofuran solution. This analysis confirms the intermediate character of species V, which is present at low concentrations throughout the process but ultimately disappears as the concentration of IV increases. However, other unidentified species appear to be present in the reaction mixture, and further investigation is in progress.

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