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Preliminary communication

REACTION OF THE UNSATURATED ANION $[Re_3H_4(CO)_{10}]^-$ WITH MERCAPTANS. SYNTHESIS AND X-RAY CHARACTERIZATION OF THE ANION $[Re_3H_3(CO)_9(\mu_3\text{-}SBu^t)]^-$

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Summary

The novel anion $[Re_3H_3(CO)_9(\mu_3\text{-}SBu^t)]^-$, obtained by reaction of $[Re_3H_4(CO)_{10}]^-$ with t-butyl mercaptan, has been characterized by IR, NMR and X-ray diffraction studies. It contains an equilateral Re_3 triangle (mean Re—Re 3.091 Å), with nine terminal carbonyl groups, three for each metal atom, and a triply-bridging thiolate ligand (mean Re—S 2.393 Å). The three hydrides are bridging on the edges of the triangle of metal atoms.

In the course of our studies on the reactivity of the unsaturated anion $[Re_3H_4(CO)_{10}]^-$ (a triangular cluster with 46 valence electrons) [1] we previously described its reactions with hydrogen halides, leading to the anions $[Re_3H_3(\mu\text{-}X)(CO)_{10}]^-$ (X = Cl, Br, I) [2], and with alcohols, giving the anions $[Re_3H_3(CO)_9(\mu_3\text{-}OR)]^-$ (R = Et, Pr^i, Bu^t) [3]. These reactions show the tendency of the parent compound to give saturated products (with 48 valence electrons), with the insertion either of a double-bridging three-electron donor ligand (substituting a μ-H ligand) or of a triple-bridging five-electron donor ligand (substituting a μ-H and a CO group). Both halides and alkoxides are able to give double or triple bridges, and so these previously reported results were related to the reaction conditions as well as to the nature of the donor atom. We have now examined the reaction of $[Re_3H_4(CO)_{10}]^-$ with t-butylmercaptan in order to establish the preferred coordination mode and we describe below the characterization of the product $[Re_3H_3(CO)_9(\mu_3\text{-}SBu^t)]^-$.

The salt $[Re_3H_4(CO)_{10}](NEt_4)$, dissolved in a 50% solution of t-butyl mercaptan in acetone, is heated at 50°C under N_2 for 24 h. Upon addition of

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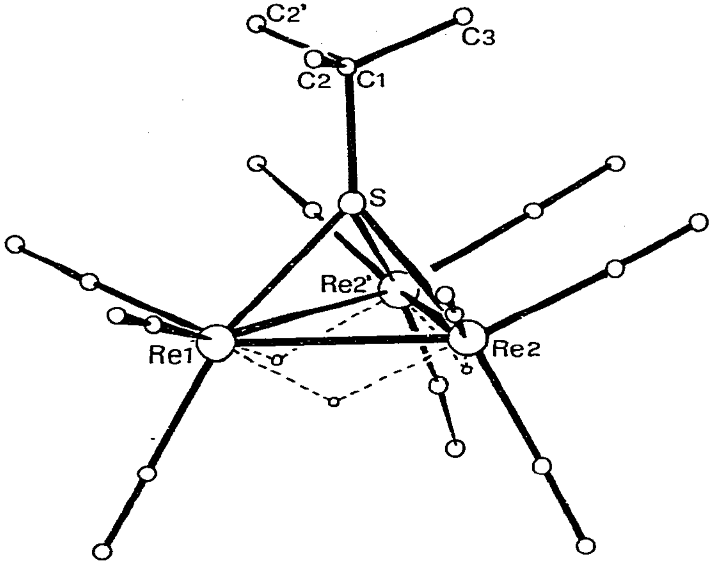

Fig. 1. A view of the novel anion $[Re_3H_3(CO)_9(\mu_3\text{-}SBu^t)]^-$. The Re—Re and Re—S bond distances are: Re(1)—Re(2) 3.092(1), Re(2)—Re(2') 3.090(1), Re(1)—S 2.390(3) and Re(2)—S 2.394(2) Å.

n-hexane, a white solid is obtained. Crystallization from acetone/ethanol/hexane gives colourless crystals of $[Re_3H_3(CO)_9(\mu_3\text{-}SBu^t)](NEt_4)$ as the main product, according to the following equation:

$$[Re_3H_4(CO)_{10}]^- + RSH \rightarrow [Re_3H_3(CO)_9(\mu_3\text{-}SR)]^- + H_2 + CO$$

The IR spectrum in acetone shows two strong bands in the ν(CO) region, at 2000 and 1922 cm^{-1}. The NMR spectrum in deuteroacetone exhibits one high-field signal at τ 26.95, attributable to the three equivalent hydrides, and a signal at τ 8.31, due to the thiolate methyl groups (shifted downfield of 0.26 ppm with respect to the free thiol). The integrations, using cationic methylene hydrogens as reference, are in agreement with the proposed stoicheiometry.

The tetraethylammonium salt of the novel anion has been investigated by X-ray diffraction*. The structure of the novel anion $[Re_3H_3(CO)_9(\mu_3\text{-}SBu^t)]^-$ is illustrated in Fig. 1. A crystallographic mirror plane passes through atoms Re(1) and S and the middle point of the Re(2)—Re(2') edge. The overall idealized symmetry of the anion is C_{3v}. It contains an equilateral triangle of Re atoms capped by the sulphur atom of the μ_3-SBu^t ligand. Each metal atom bears three terminal CO ligands. This ligand stereochemistry is similar to those found in the anions $[Re_3H_3(\mu_3\text{-}O)(CO)_9]^{2-}$ [4] and $[Re_3H_3(CO)_9(\mu_3\text{-}OEt)]^-$ [3]. The three hydride ligands, not directly located, are assumed to bridge the triangular edges, on the side of the Re_3 plane opposite to the triply-bridging

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*Crystal data. $C_{21}H_{32}NO_9Re_3S$, M = 1033.2, Monoclinic, Space Group $P2_1/m$ (No. 11), with a 8.690(1), b 20.431(5), c 8.707(1) Å, β 107.40(1)°, Z = 2. The structure was solved by Patterson and Fourier methods and refined by least-squares, on the basis of 2189 significant counter data, up to a current conventional R value of 4.2%. The anion was found to lie in special position, on a crystallographic mirror plane. The cation lies on an inversion centre, resulting disordered, so that the C atoms bound to N are doubled, forming an approximate cube of half-carbon atoms.

ligand. The Re—Re bond lengths have a mean value of 3.091 Å, larger than the corresponding mean values in $[Re_3H_3(\mu_3\text{-}O)(CO)_9]^{2-}$ (2.968 Å) [4] and in $[Re_3H_3(CO)_9(\mu_3\text{-}OEt)]^-$ (2.994 Å) [3]. This is due to the different nature of the capping atoms, S vs. O; the sulphur atom, with its larger covalent radius, permits the lengthening of the Re—Re bonds caused by the simultaneous presence of the μ-H ligands, which was prevented by the μ_3-O and μ_3-OEt ligands. These Re—Re bonds, however, are shorter than the usual Re—H—Re bond lengths (range ca. 3.13—3.40 Å). The Re—C and C—O bonds within the carbonyl ligands have mean values of 1.89 and 1.17 Å, respectively.

The Re—S mean bond length is 2.393 Å, very similar, for instance, to the corresponding interactions within the μ_3-S ligands in the octahedral species $Na_4Re_6S_{10}(S_2)$ (2.40(1) Å) [5]. Other relevant bond parameters within the thiolate ligand are: S—C(1) 1.88(1) Å, C(1)—C(2,3) mean 1.53 Å, Re—S—Re mean 80.5°, Re—S—C(1) mean 131.8° and S—C(1)—C mean 106.1°.

In contrast to the reaction with alcohols, which gave pure $[Re_3H_3(CO)_9(\mu_3\text{-}OR)]^-$ species [3], in the present case we obtained, together with a predominant amount of $[Re_3H_3(CO)_9(\mu_3\text{-}SBu^t)]^-$, small amounts of unidentified products, one of which might be the double bridged species $[Re_3H_3(CO)_{10}(\mu\text{-}SBu^t)]^-$. In order to force the SR group to act as a doubly-bridging three-electron donor, the reaction was also attempted under CO atmosphere at room temperature or with heating. In the former case no reaction occurred (even after many days), while in the latter the main product is again the triply-bridged species.

Analogous thiolate derivatives of triosmium clusters are known, namely $Os_3H(CO)_9(\mu_3\text{-}SR)$ (R = Me or Et) [6], and they undergo easy addition of two-electron donor ligands L (L = C_2H_4, CO, PR_3 and MeCN) to give $Os_3H(CO)_9(\mu\text{-}SR)L$ species. We suspect that similar reactions will also occur in the case of rhenium, and further work along these lines is in progress.

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