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Preliminary communication

SYNTHESIS OF THE ANIONS $[Re_3H_3(\mu\text{-}X)(CO)_{10}]^-$ (X = Cl, Br, I) AND X-RAY CHARACTERIZATION OF $[Re_3H_3(\mu\text{-}Cl)(CO)_{10}](NEt_4)$

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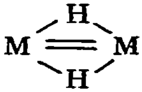
Summary

The novel anions $[Re_3H_3(\mu\text{-}X)(CO)_{10}]^-$ (X = Cl, Br, I), prepared by reaction of the unsaturated anion $[Re_3H_4(CO)_{10}]^-$ with the corresponding hydrogen halides HX, have been characterized by IR and NMR spectroscopy and by an X-ray diffraction study of the chloro derivative. The anion $[Re_3H_3(\mu\text{-}Cl)(CO)_{10}]^-$ contains an isosceles triangle of metal atoms, with two longer hydrogen-bridged Re—Re edges (mean 3.206 Å) and one shorter edge of 2.995(2) Å, doubly bridged by a hydride ligand and a chlorine atom (mean Re—Cl 2.497 Å).

We are currently studying the reactivity of the anion $[Re_3H_4(CO)_{10}]^-$ [1], which has a structure similar to that of $Os_3H_2(CO)_{10}$ [2]. Both compounds are unsaturated, possessing 46 valence electrons, instead of the usual 48 electrons for triangular clusters. They contain a  $M\overset{H}{\underset{H}{=}}M$ system, which can be described either as a doubly protonated double metal—metal bond [3] or as a four-center four-electron bond [2]. The same system is also present in the dianion $[Re_3H_3(CO)_{10}]^{2-}$ [4] and in the dimeric species $Re_2H_2(CO)_8$ [5], $Re_2H_2(CO)_6(dppm)$ [6] and $[W_2H_2(CO)_8]^{2-}$ [7]. The unsaturation of the Os_3 species has been considered to be responsible for its ready reactions with a variety of molecules, leading to saturated compounds [8]. For example, it undergoes facile addition reactions with CO or PR_3 [9]. Analogous additions have been recently found to occur also for $Re_2H_2(CO)_6(dppm)$ [6]. The anion

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$[Re_3H_4(CO)_{10}]^-$ does not behave in the same way as $Os_3H_2(CO)_{10}$ towards CO and PPh_3 [10]. It reacts in boiling alcohols ROH to give the saturated anions $[Re_3H_3(\mu_3\text{-}OR)(CO)_9]^-$ [11]. We report below its reactions with hydrogen halides HX (X = Cl, Br, I), which lead to the isolation of the novel anions $[Re_3H_3(\mu\text{-}X)(CO)_{10}]^-$.

A dilute acetone solution of the appropriate hydrogen halide is added to an acetone solution of the salt $[Re_3H_4(CO)_{10}](NEt_4)$ and the mixture is kept at room temperature for several hours. (The reaction rate increases with increasing molar ratio of HX to the carbonylrhenate and also in the order HI > HBr > HCl.) Removal of the solvent under reduced pressure leaves a solid (white with HCl and HBr, yellow with HI), which is washed with water, dried and crystallized from methylene chloride/diethyl ether. The reaction process is:

$$[Re_3H_4(CO)_{10}]^- + HX \rightarrow [Re_3H_3(\mu\text{-}X)(CO)_{10}]^- + H_2$$

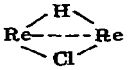
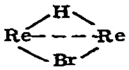
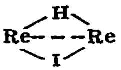
The hydrogen evolved has been identified by GLC. The iodo derivative $[Re_3H_3(\mu\text{-}I)(CO)_{10}]^-$ was previously obtained in two other ways: (i) by reaction of $[Re_3H_3(CO)_{10}]^{2-}$ or $[Re_3H_4(CO)_{10}]^-$ with I_2 [12] and (ii) as a component of the mixture formed by reaction of $[Re_4H_4I(CO)_{15}]^-$ with I_2 [13].

The IR and NMR data for the new compounds are listed in Table 1. The NMR spectra show the presence of two types of hydridic ligands, in accord with the structure of the anions (see below). While the IR spectra of the three products are almost identical, the NMR hydridic signals are shifted to higher field in the order I > Br > Cl.

The structure of $[Re_3H_3(\mu\text{-}Cl)(CO)_{10}](NEt_4)$ has been determined by X-ray

TABLE 1

IR AND NMR DATA FOR THE COMPOUNDS $[Re_3H_3(\mu\text{-}X)(CO)_{10}](NEt_4)$

Compound	IR[a] ν(C—O) (cm^{-1})	NMR[b] Proton resonance (τ)	Relative intensity	Fine structure	Assignment
X = Cl	2080w, 2025m, 2005(sh), 2000vs, 1945m, 1928(sh), 1905s	6.5	8	quadruplet	N—CH_2—
		20.60	1	singlet	 $Re\overset{H}{\underset{Cl}{----}}Re$
		22.15	2	singlet	Re— —H— —Re
X = Br	2080w, 2025m, 2005(sh), 2000vs, 1945m, 1928m, 1905s	6.5	8	quadruplet	N—CH_2—
		21.15	1	singlet	 $Re\overset{H}{\underset{Br}{----}}Re$
		24.80	2	singlet	Re— —H— —Re
X = I	2085w, 2025m, 2005(sh), 2000vs, 1945m, 1930m, 1905s	6.5	8	quadruplet	N—CH_2—
		22.15	1	singlet	 $Re\overset{H}{\underset{I}{----}}Re$
		25.75	2	singlet	Re— —H— —Re

[a] IR spectra were recorded on a Perkin—Elmer 297 in acetone solution. [b] NMR spectra were recorded on a Bruker-80 in deuteroacetone solution.

diffraction*. The anion, of idealized C_S symmetry, is illustrated in Fig. 1. It contains an isosceles Re_3 triangle, bearing ten terminal CO ligands and one edge-bridging chlorine atom. The three hydride ligands, not directly located, are assumed to bridge the three Re—Re edges (see Fig. 1). Neglecting the metal—metal interactions, each rhenium atom exhibits an approximate octahedral coordination: Re(1) with four CO and two hydride ligands, Re(2) and Re(3) both with three CO, two hydrides and the chlorine atom. Bond distances and angles are listed in Table 2.

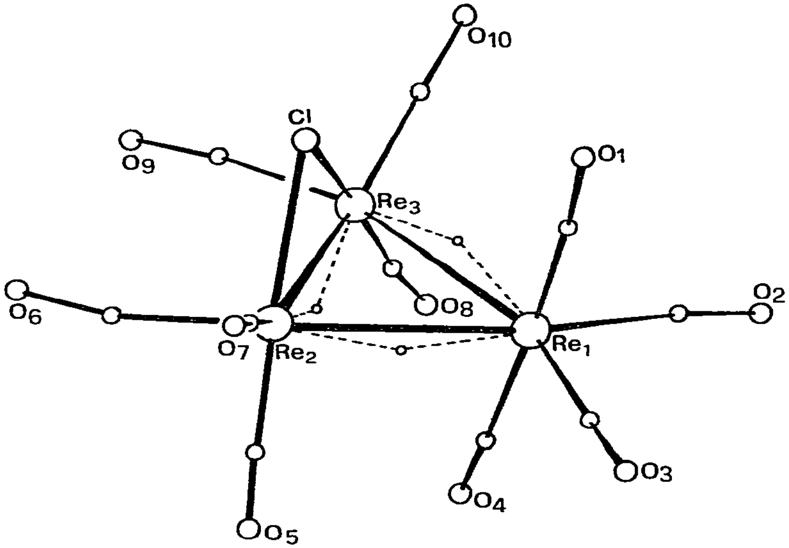


Fig. 1. A view of the anion $[Re_3H_3(\mu\text{-}Cl)(CO)_{10}]^-$ with the postulated hydridic atoms positions.

The anion geometry is derived from that of the parent anion $[Re_3H_4(CO)_{10}]^-$, by replacement of one of the two bridging hydrides on the Re—Re short bond by a bridging chlorine atom. The main effects of this substitution are: (i) a lengthening of ca. 0.17 Å of the Re(μ-H)(μ-Cl)Re edge with respect to the Re(μ-H)$_2$Re one (2.995(2) vs. 2.821(7) Å), and (ii) a rotation of the CO groups bound to Re(2) (CO(5) and CO(7)) and to Re(3) (CO(8) and CO(10)), approximately lying in the plane Re(2),Re(3),Cl, away from the halogen atom (Re—Re—C 146° vs. 119°). The observed differences compared to $[Re_3H_4(CO)_{10}]$ are easily rationalised: the first effect is due to the fact that Cl acts as a three-electron donor, leading to saturation of the cluster, and the second effect is related to the higher steric hindrance of a chlorine than of a hydrogen atom.

The structural relationship between $[Re_3H_4(CO)_{10}]^-$ and $[Re_3H_3(\mu\text{-}X)(CO)_{10}]^-$ corresponds to that between $Os_3H_2(CO)_{10}$ and $Os_3H(\mu\text{-}X)(CO)_{10}$ (X = Cl [14] and Br [15]). Significant structural differences, however, can be observed between the corresponding rhenium and osmium species, arising from the presence in the former species of the two additional hydrides.

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*Crystal data. $C_{18}H_{23}ClNO_{10}Re_3$, M = 1056.9, orthorhombic, space group *Pbcn* (No. 60), with *a* 12.767(3), *b* 11.984(3), *c* 35.119(7) Å, Z = 8. It is isomorphous with the parent compound. The structure was solved by conventional Patterson and Fourier methods and refined by least-squares, on the basis of 1800 significant counter data, up to a current R value of 6.0%.

TABLE 2

BOND DISTANCES AND ANGLES WITHIN THE ANION $[Re_3H_3(\mu\text{-}Cl)(CO)_{10}]^-$

Distances (Å)

Re(1)—Re(2)	3.194(2)	Re(2)—C(5)	1.75(4)	C(3)—O(3)	1.11(3)
Re(1)—Re(3)	3.219(2)	Re(2)—C(6)	1.90(4)	C(4)—O(4)	1.08(4)
Re(2)—Re(3)	2.995(2)	Re(2)—C(7)	1.92(4)	C(5)—O(5)	1.04(5)
Re(2)—Cl	2.493(8)	Re(3)—C(8)	1.80(3)	C(6)—O(6)	1.16(4)
Re(3)—Cl	2.502(7)	Re(3)—C(9)	1.89(3)	C(7)—O(7)	1.23(5)
Re(1)—C(1)	1.92(3)	Re(3)—C(10)	1.75(4)	C(8)—O(8)	1.24(3)
Re(1)—C(2)	1.97(2)	C(1)—O(1)	1.18(3)	C(9)—O(9)	1.16(3)
Re(1)—C(3)	1.88(3)	C(2)—O(2)	1.13(3)	C(10)—O(10)	1.20(4)
Re(1)—C(4)	1.92(4)				

Angles (deg.)

Re(1)—Re(2)—Cl	82.8(2)	Re(2)—Re(3)—C(9)	101(1)
Re(1)—Re(3)—Cl	82.1(2)	Re(2)—Re(3)—C(10)	147(1)
Re(2)—Cl—Re(3)	73.7(2)	C(1)—Re(1)—C(2)	92(1)
Re(2)—Re(1)—C(1)	95(1)	C(1)—Re(1)—C(3)	87(1)
Re(2)—Re(1)—C(2)	161(1)	C(1)—Re(1)—C(4)	175(1)
Re(2)—Re(1)—C(3)	104(1)	C(2)—Re(1)—C(3)	94(1)
Re(2)—Re(1)—C(4)	82(1)	C(2)—Re(1)—C(4)	93(1)
Re(3)—Re(1)—C(1)	98(1)	C(3)—Re(1)—C(4)	91(1)
Re(3)—Re(1)—C(2)	106(1)	Cl—Re(2)—C(5)	173(1)
Re(3)—Re(1)—C(3)	160(1)	Cl—Re(2)—C(6)	96(1)
Re(3)—Re(1)—C(4)	83(1)	Cl—Re(2)—C(7)	93(1)
Re(1)—Re(2)—C(5)	94(1)	C(5)—Re(2)—C(6)	86(2)
Re(1)—Re(2)—C(6)	165(1)	C(5)—Re(2)—C(7)	94(2)
Re(1)—Re(2)—C(7)	108(1)	C(6)—Re(2)—C(7)	87(2)
Re(3)—Re(2)—C(5)	119(1)	Cl—Re(3)—C(8)	172(1)
Re(3)—Re(2)—C(6)	105(1)	Cl—Re(3)—C(9)	90(1)
Re(3)—Re(2)—C(7)	145(1)	Cl—Re(3)—C(10)	96(1)
Re(1)—Re(3)—C(8)	92(1)	C(8)—Re(3)—C(9)	94(1)
Re(1)—Re(3)—C(9)	162(1)	C(8)—Re(3)—C(10)	92(2)
Re(1)—Re(3)—C(10)	108(1)	C(9)—Re(3)—C(10)	89(2)
Re(2)—Re(3)—C(8)	119(1)	Re—C—O	167(4)—177(3)

The triangular edges Re(1)—Re(2) and Re(1)—Re(3) have bond lengths typical of Re—H—Re hydrogen-bridged bonds (mean 3.206 Å). These two bridging hydrides can be considered almost coplanar with the Re_3 plane. The Cl atom forms a symmetric bridge, with a mean Re—Cl bond length of 2.497 Å, somewhat longer than the corresponding interaction in $[Re_3Cl_{12}]^{3-}$ (mean Re—Cl 2.39(2) Å) [16]. The dihedral angle between the planes Re(1),Re(2), Re(3) and Re(2),Re(3),Cl is 102.1° (the corresponding angle in $Os_3H(\mu\text{-}Cl)(CO$ is 108.6°).

A variety of $Os_3H(\mu\text{-}X)(CO)_{10}$ compounds (mentioned, for instance, in ref. 17) have been characterized in addition to the above mentioned chloro and bromo species. They contain an X bridging group acting as a three-electron donor (as OR, SR, NRR′ etc.). The similarities here described, in the case of the halogeno-bridged compounds, suggest that an analogous series of $[Re_3H_3(\mu\text{-}X)(CO)_{10}]^-$ anions could also be obtained. Further work along this line is in progress.

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