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Preliminary communication

SYNTHESIS OF THE NOVEL ANIONS $[Re_3H_3(\mu_3\text{-}OR)(CO)_9]^-$ (R = Et, i-Pr, t-Bu) AND X-RAY CHARACTERIZATION OF $[Re_3H_3(\mu_3\text{-}OEt)(CO)_9](NEt_4)$

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Summary

The novel anions $[Re_3H_3(\mu_3\text{-}OR)(CO)_9]^-$ (R = Et, i-Pr, t-Bu) have been obtained by reaction of the unsaturated anion $[Re_3H_4(CO)_{10}]^-$ with the corresponding alcohols. They have been characterized by IR and NMR spectra and by an X-ray diffraction study of the ethoxy species, which contains an equilateral metal atoms triangle (mean Re—Re 2.994 Å) with nine terminal CO groups, three for each metal, and a triply-bridging ethoxy ligand (mean Re—O 2.17 Å). The three hydride ligands are bridging on the edges of the Re_3 triangle.

We are currently studying the reactivities of the unsaturated anions $[Re_3H_3(CO)_{10}]^{2-}$ [1,2] and $[Re_3H_4(CO)_{10}]^-$ [3], and we already reported on their reactions with iodine in various solvents [4]. We describe here the reactions of $[Re_3H_4(CO)_{10}]^-$ with alcohols, which give the novel alkoxy anions $[Re_3H_3(\mu_3\text{-}OR)(CO)_9]^-$.

The compound $[Re_3H_4(CO)_{10}](NEt_4)$, prepared as described in ref. 4, was boiled with alcohols under nitrogen, for 6 h. GLC analysis of the evolved gas showed the presence of hydrogen and carbon monoxide. Removal of the solvent under reduced pressure gave a white solid which was recrystallized from ethanol and hexane to give colourless crystals of the saturated cluster compound $[Re_3H_3(\mu_3\text{-}OR)(CO)_9](NEt_4)$:

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

The IR spectra in acetone are consistent with the presence of $Re(CO)_3$ groups of C_{3v} local symmetry, showing two strong C—O bands (see Table 1).

TABLE 1

IR AND NMR DATA FOR COMPOUNDS $[Re_3H_3(\mu_3\text{-OR})(CO)_9](NEt_4)$

R	IR[a] ν(C—O) (cm^{-1})	NMR[b]			
		Proton resonance (τ)	Relative intensity	Fine structure	Assignment
Et	2007(s), 1917(vs)	5.5	2	quadruplet	$O—CH_2$
		6.5	8	quadruplet	$N—CH_2$
		8.6	3	triplet	$O—CH_2—CH_3$
		21.3	3	singlet	Re—*H*—Re
i-Pr	2005(s), 1916(vs)	6.1	1	multiplet	$O—CH—(CH_3)_2$
		6.5	8	quadruplet	$N—CH_2$
		8.5	6	doublet	$O—CH—(CH_3)_2$
		21.5	3	singlet	Re—*H*—Re
t-Bu	2005(s), 1915(vs)	6.5	8	quadruplet	$N—CH_2$
		8.5	9	singlet	$O—C—(CH_3)_3$
		21.7	3	singlet	Re—*H*—Re

[a] IR spectra were recorded on a Nicolet MX-1 spectrophotometer in acetone solution. [b] NMR spectra were recorded on a Varian XL-200 spectrophotometer in deuteroacetone solution.

The NMR spectra, listed in Table 1, exhibit only one high-field signal, due to the presence of three equivalent hydride ligands, at a τ value close to that observed for the species $[Re_3H_3(\mu_3\text{-O})(CO)_9]^{2-}$ [1,2].

The stereochemistry of the new anions was elucidated by a single-crystal X-ray investigation on the tetraethylammonium salt of the ethoxy derivative $[Re_3H_3(\mu_3\text{-OEt})(CO)_9]^-$*. The anion is illustrated in Fig. 1. It contains an equilateral triangle of rhenium atoms capped by a triple-bridging ethoxy ligand. Each metal atom bears three terminal carbonyl ligands. This stereochemistry resembles that of the dianion $[Re_3H_3(\mu_3\text{-O})(CO)_9]^{2-}$ [1,5]. The three hydride ligands have not been directly located, but the ligand geometry clearly indicates that they bridge at the three Re—Re edges, at the side of the Re_3 plane opposite to the μ_3-OEt ligand.

The Re—Re bond lengths are very similar, with a mean value of 2.994 Å, close to the corresponding value in $[Re_3H_3(\mu_3\text{-O})(CO)_9]^{2-}$ (2.968 Å) [5]. These bonds are not, as is usual, lengthened by the hydrides compared with an unbridged Re—Re single bond because of the simultaneous presence of the μ_3-OEt ligand (see ref. 5 and refs. therein).

The Re—C and C—O bonds within the carboxyl ligands have mean values of 1.86 and 1.19 Å, respectively. The Re—O(ethoxy) mean bond length, 2.17 Å, is somewhat longer than the corresponding mean Re—O bond in $[Re_3H_3(\mu_3\text{-O})(CO)_9]$ (2.12 Å), and also than the mean Re—O(alkoxy) bond in the anions $[Re_2(\mu\text{-OR})_3(CO)_6]^-$ (2.08 Å) [6]. Other relevant bond parameters within the ethoxy ligand are: O—C 1.48(2) Å, C—C 1.54(4) Å and O—C—C 109(2)°.

The solid state structure of the ethoxy species is consistent with the IR and NMR spectra in solution. The other alkoxy species must have analogous structures, as indicated by the similarity of the spectroscopic data (see Table 1).

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*Crystal data. $C_{19}H_{28}NO_{10}Re_3$, M = 989.0. Monoclinic, space group $P2_1/n$ (No. 14), with a 15.147(3), b 12.562(2), c 15.587(4) Å, β 111.38(2)°, Z = 4. The structure has been solved by conventional Patterson and Fourier methods and refined by least-squares, on the basis of 2817 significant counter data, up to a current R value of 5.0%.

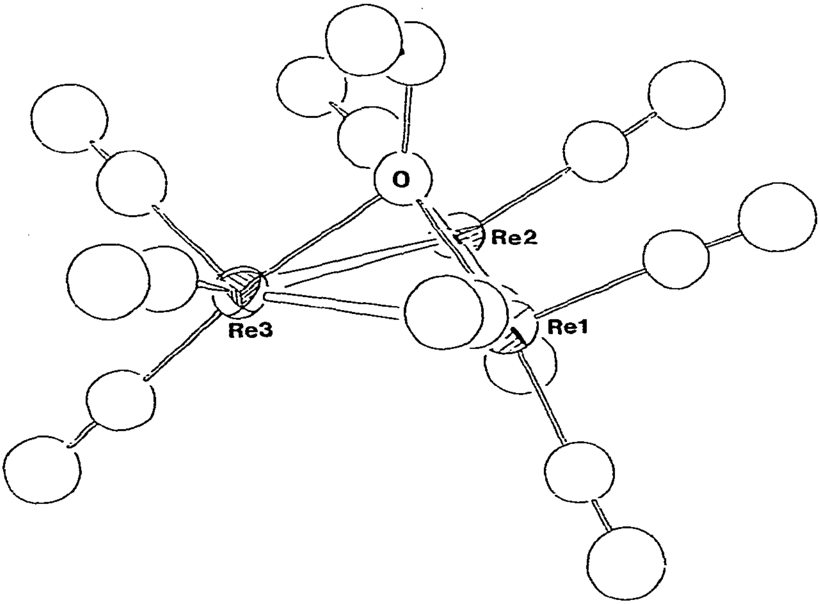

Fig. 1. A view of the anion $[Re_3H_3(\mu_3\text{-OEt})(CO)_9]^-$. The metal—metal distances are: Re(1)—Re(2) 2.998(1), Re(1)—Re(3) 2.998(1) and Re(2)—Re(3) 2.985(1) Å. The Re—O(ethoxy) distances are: Re(1)—O 2.18(1), Re(2)—O 2.15(1) and Re(3)—O 2.17(1) Å.

For the reaction sequence leading to these new anions we suggest a two-step sequence, with an intermediate species containing a double-bridged alkoxy ligand:

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

Osmium compounds similar to the intermediate species are known, with formula $Os_3H(\mu\text{-OR})(CO)_{10}$ [7], and an X-ray determination of the structure of the methoxy derivative has been carried out [8]. However, we have not yet been able to stop the process after the first step. Further investigations are in progress.

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References

1 A. Bertolucci, M. Freni, P. Romiti, G. Ciani, A. Sironi and V.G. Albano, J. Organometal. Chem., 113 (1976) C61.
2 M. Freni, P. Romiti and G. D'Alfonso, J. Organometal. Chem., 140 (1977) 195.
3 G. Ciani, G. D'Alfonso, M. Freni, P. Romiti and A. Sironi, J. Organometal. Chem., 136 (1977) C49.
4 G. Ciani, G. D'Alfonso, M. Freni, P. Romiti and A. Sironi, J. Organometal. Chem., 186 (1980) 353.
5 G. Ciani, A. Sironi and V.G. Albano, J. Chem. Soc. Dalton, (1977) 1667.
6 G. Ciani, A. Sironi and A. Albinati, Gaz. Chim. Ital., 109 (1979) 615.
7 K.A. Azam, A.J. Deeming, R.E. Kimber and P.R. Shukla, J. Chem. Soc. Dalton, (1976) 1853, and refs. therein.
8 R. Mason, Pure Appl. Chem., 33 (1973) 513; R. Mason and D.M.P. Mingos, J. Organometal. Chem., 50 (1973) 53.