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Preliminary communication

REACTIONS OF THE UNSATURATED ANION $[Re_3H_4(CO)_{10}]^-$ WITH CARBOXYLIC ACIDS AND X-RAY CHARACTERIZATION OF THE ANIONS $[Re_3H_3(CO)_{10}(\mu\text{-}O_2CR)]^-$ (R = H, CF_3)

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Summary

The novel anions $[Re_3H_3(CO)_{10}(\mu\text{-}O_2CR)]^-$ (R = H, CH_3, CF_3), obtained by reaction of $[Re_3H_4(CO)_{10}]^-$ with the corresponding carboxylic acids, have been characterized by IR and NMR spectra and by X-ray analysis of the formate and trifluoroacetate derivatives. They contain a triangle of rhenium atoms, with the carboxylate group diaxially bridging on the shorter Re—Re edge.

Continuing our investigation on the reactivity of the unsaturated anion $[Re_3H_4(CO)_{10}]^-$, we describe below its reactions with carboxylic acids. The previously studied derivatives showed that the insertion of the entering ligand can occur either in a double-bridging, as in $[Re_3H_3(\mu\text{-}X)(CO)_{10}]^-$ (X = Cl, Br, I) [1], or a triple-bridging location, as in $[Re_3H_3(CO)_9(\mu_3\text{-}OR)]^-$ (R = Et, Pr^i, Bu^t) [2] and $[Re_3H_3(CO)_9(\mu_3\text{-}SBu^t)]^-$ [3]. We have, therefore, attempted the reactions with organic acids RCO_2H in order to establish the preferred way of coordination of the carboxylate groups to the metallic triangle, since these groups are known to show various types of bonding to transition metals [4]. We report below the synthesis and characterization of the novel anions $[Re_3H_3(CO)_{10}(\mu\text{-}O_2CR)]^-$ (R = H, CH_3, CF_3), which have been shown to contain symmetrical diaxially bridging RCO_2^- groups.

The parent compound is dissolved in a mixture of acetone containing a large excess of the appropriate carboxylic acid, and the solution is stirred under N_2 for a time ranging from 24 h (in the case of trifluoroacetic acid) to about one week (in the case of acetic acid). The following reaction occurs:

$$[Re_3H_4(CO)_{10}]^- + RCO_2H \rightarrow [Re_3H_3(CO)_{10}(\mu\text{-}O_2CR)]^- + H_2$$

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The progress of the reaction is monitored by GLC determination of the H_2 evolved. At the end water is added, causing the precipitation of a white solid, which is washed, dried, and crystallized from methylene chloride/diethyl ether.

The IR and NMR data of the new compounds are reported in Table 1. The NMR spectra show the presence of two types of hydrides (ratio 1/2) in agreement with the solid state structures.

Single crystal X-ray analyses have been performed on the tetraethylammonium salts of the formate and trifluoroacetate species*.

The structure of the anion $[Re_3H_3(CO)_{10}(\mu\text{-}O_2CH)]^-$ (I) is illustrated in Fig. 1 and that of the anion $[Re_3H_3(CO)_{10}(\mu\text{-}O_2CCF_3)]^-$ (II) in Fig. 2. They show very similar bonding parameters, reported in Table 2.

The anions contain an almost isosceles Re_3 triangle, with one shorter (3.181 Å in I and II) and two longer Re—Re edges (3.246 Å in I and 3.239 Å in II), bearing ten terminally bonded carbonyl groups and a diaxially bridging carboxylate group on the shorter Re—Re triangular edge. On the basis of the metal—metal bond lengths and of the stereochemistry of the other ligands, it can be concluded that the three hydride ligands are located in bridging positions, on the three Re—Re edges.

The shortening of one Re—Re hydrogen-bridged edge is due to the simultaneous presence on it of the bridging carboxylate ligand, as already observed [5]. This shortening effect on $Re(\mu\text{-}H)(\mu\text{-}X)Re$ edges, however, is much more significant when the bridging group X is bound through one atom to the two metals,

TABLE 1

IR AND NMR DATA FOR COMPOUNDS $[Re_3H_3(CO)_{10}(\mu\text{-}O_2CR)]^-$

	IR (cm^{-1})		NMR^c	
R	$\nu(CO)^a$	$\nu(COO)^b$	τ	assignment
H	2095w, 2030m, 2010vs, 1995s, 1945m, 1915s, 1898ms	1569 antisym 1351 sym	2.31 (1) 19.00 (1) 22.91 (2)	μ-OOCH Re—H—Re Re—H—Re
CH_3	2095w, 2030m, 2010vs, 1995s, 1945m, 1915s, 1898ms	1558 antisym 1427 sym	8.27 (3) 18.93 (1) 22.89 (2)	μ-$OOCCH_3$ Re—H—Re Re—H—Re
CF_3	2095w, 2030m, 2012vs, 1998s, 1953m, 1925s, 1908 ms	1657 antisym	18.85 (1) 22.77 (2)	Re—H—Re Re—H—Re

^{a}In acetone. ^{b}CsI pellet; Na^+ salt for R = H and CH_3, NEt_4^+ salt for R = CF_3. ^{c}In deuteroacetone; relative intensities in parentheses; all signals are singlets.

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*Crystal data. $C_{19}H_{24}NO_{12}Re_3$, Compound I, M = 1017.0, monoclinic, space group $P2_1/c$ (No. 14), cell constants a 13.979 (2), b 12.821 (2), c 16.519 (3) Å, β 110.01 (1)°, Z = 4. $C_{20}H_{23}F_3NO_{12}Re_3$, Compound II, M = 1085.0, monoclinic, space group $P2_1/a$ [non-standard setting of $P2_1/c$ (No. 14)], cell constants a 17.325 (4), b 13.267 (4), c 25.704 (4) Å, β 92.79 (2)°, Z = 8. The intensity data were collected on an Enraf-Nonius CAD4 automated diffractometer using graphite monochromatized Mo-K_α radiation (λ = 0.71073 Å) within the ranges $3° < \vartheta < 25°$ (I) and $3° < \vartheta < 23.5°$ (II). The structures were solved by conventional Patterson and Fourier methods, and refined by least-squares, on the basis of 3198 (I) and 3186 (II) significant reflections, up to current R values of 0.030 (I) and 0.056 (II), respectively. The structure of II shows the presence of two independent anions and cations in the asymmetric unit.

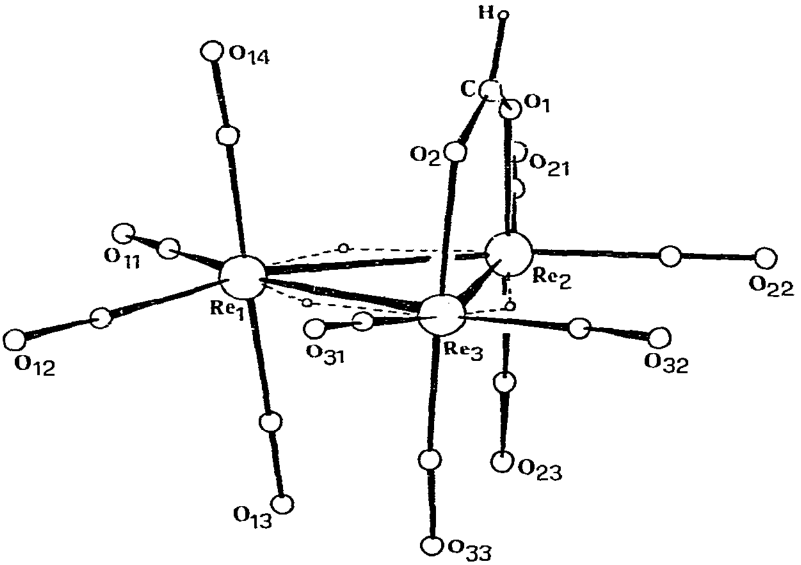

Fig. 1. A view of the anion $[Re_3H_3(CO)_{10}(\mu\text{-}O_2CH)]^-$ with the postulated hydridic atoms positions.

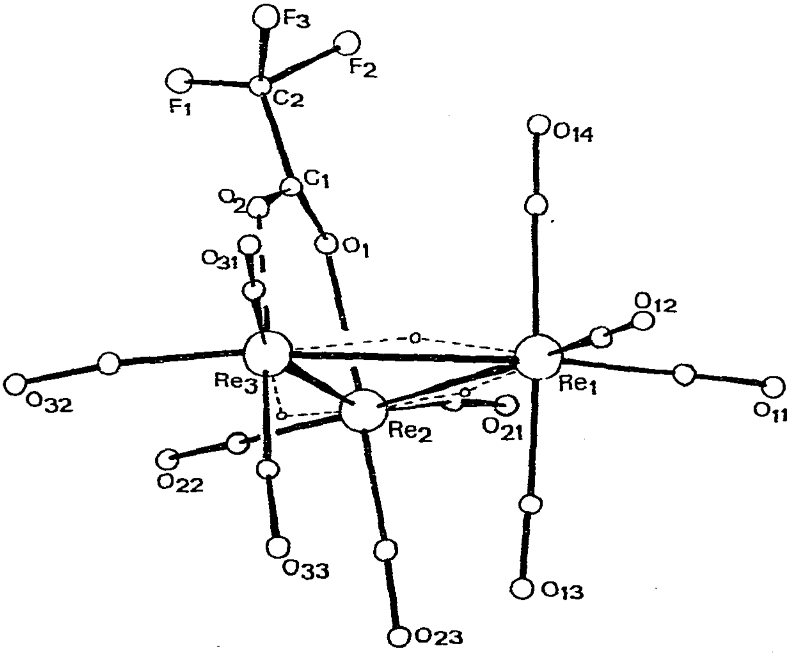

Fig. 2. A view of the anion $[Re_3H_3(CO)_{10}(\mu\text{-}O_2CCF_3)]^-$ with the postulated hydridic atoms positions.

TABLE 2[a,b]

SELECTED MEAN BOND PARAMETERS IN THE ANIONS $[Re_3H_3(CO)_{10}(\mu\text{-}O_2CR)]^-$

Formate		Trifluoroacetate (average on two anions)	
Re(1)—Re(2)	3.264(1)	Re(1)—Re(2,3)	3.239
Re(1)—Re(3)	3.229(1)		
Re(2)—Re(3)	3.181(1)	Re(2)—Re(3)	3.181
Re(1)—C_{eq}	1.93	Re(1)—C_{eq}	1.89
Re(1)—C_{ax}	1.99	Re(1)—C_{ax}	1.96
Re(2,3)—C_{eq}	1.91	Re(2,3)—C_{eq}	1.87
Re(2,3)—C_{ax}	1.89	Re(2,3)—C_{ax}	1.81
C—O (carbonyl)	1.15	C—O (carbonyl)	1.18
Re(2,3)—O(1,2)	2.170	Re(2,3)—O(1,2)	2.18
C—O(1,2)	1.25	C(1)—O(1,2)	1.25
C—H	0.99(10)	C(1)—C(2)	1.53
Re(2,3)—Re(1)—C_{eq} (*cis*)	105.2	Re(2,3)—Re(1)—C_{eq} (*cis*)	105
Re(2,3)—Re(1)—C_{eq} (*trans*)	162.8	Re(2,3)—Re(1)—C_{eq} (*trans*)	163
C—Re(1)—C(*cis*)	91.2	C—Re(1)—C(*cis*)	91
C(13)—Re(1)—C(14)	174.7(5)	C(13)—Re(1)—C(14)	177
Re(1)—Re(2,3)—C_{eq} (*cis*)	104.7	Re(1)—Re(2,3)—C_{eq} (*cis*)	103
Re(1)—Re(2,3)—C_{eq} (*trans*)	165.7	Re(1)—Re(2,3)—C_{eq} (*trans*)	168
Re(1)—Re(2,3)—C_{ax}	92.3	Re(1)—Re(2,3)—C_{ax}	93
Re(1)—Re(2,3)—O(1,2)	87.6	Re(1)—Re(2,3)—O(1,2)	88
C_{eq}—Re(2,3)—C_{eq}	89.4	C_{eq}—Re(2,3)—C_{eq}	90
O(1,2)—Re(2,3)—C (*trans*)	178.9	O(1,2)—Re(2,3)—C (*trans*)	178
O(1,2)—Re(2,3)—C (*cis*)	91.2	O(1,2)—Re(2,3)—C (*cis*)	91
Re(2,3)—O(1,2)—C	127.3	Re(2,3)—O(1,2)—C(1)	128
O(1)—C—O(2)	130(1)	O(1)—C(1)—O(2)	128

[a] Eq = equatorial, ax = axial. [b] Typical esd's in the formate for the Re—C, Re—O and C—O bond lengths are of 0.01 Å; in the trifluoroacetate esd's for the Re—Re bond lengths are 0.002 Å, and for the others 0.02—0.04 Å.

as in $[Re_3H_3(\mu\text{-}Cl)(CO)_{10}]^-$ [Re(μ-H)(μ-Cl)Re 2.995 Å vs. Re(μ-H)Re 3.206 Å] [1].

The stereochemistry of the ligands in the anions $[Re_3H_3(CO)_{10}(\mu\text{-}O_2CR)]^-$ differs from that present in the parent anion $[Re_3H_4(CO)_{10}]^-$ and in the species $[Re_3H_3(\mu\text{-}X)(CO)_{10}]^-$ (X = Cl,Br,I), and is better regarded to be derived from that of $Re_3H_3(CO)_{12}$ and of $[Re_3H_3I(CO)_{11}]^-$ [6], with two adjacent axial ligands replaced by the carboxylate group. A similar ligand stereochemistry is present in $Os_3H(CO)_{10}(\mu\text{-}O_2CH)$ [7].

The carboxylate ligands show a *syn-syn* coordination, occupying two axial coordination sites, with some outward folding of the group around the Re(2)—Re(3) axis, the dihedral angles between the Re(1),Re(2),Re(3) plane and the "best" plane of the ligand being 98° in I and 97° in II. The lengths of the Re—O bonds, mean 2.17 in I and 2.18 Å in II, are strictly comparable with those of the corresponding bonds in $[Re_3H_3(CO)_9(\mu_3\text{-}OEt)]^-$ (mean 2.17 Å) [2]. The bond parameters within the organic ligands are normal; in both cases there is moderate asymmetry in the C—O interactions, one being shorter (mean 1.22 Å) than the other (mean 1.28 Å).

The analysis of the IR spectra in the ν(COO) region was carried out with the sodium salts of the novel anions, obtained by elimination of NEt_4^+ with $Na(BF_4)$ [8]. The separation between the antisymmetric and symmetric modes proved to be greater in the formate than in the acetate derivative (Δ 218 vs. 129 cm^{-1}), in the same sense as was observed for the sodium salts of the corresponding carboxylate anions (Δ 200 vs. 164 cm^{-1}) [9]. The assignment of the symmetric mode for the trifluoroacetate derivative was doubtful in the NEt_4^+ salt and attempts to obtain the sodium salt led to modification of the anion, probably with substitution of the carboxylate ligand. Trifluoroacetate is known to be a good leaving group, and it may be possible to utilize this property in order to obtain from $[Re_3H_3(CO)_{10}(\mu\text{-}O_2CCF_3)]^-$ compounds containing other type of bridging ligands.

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