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PYROLYSES OF THE ANION DIHYDRIDOTETRACARBONYLRHENATE. CRYSTAL AND MOLECULAR STRUCTURE OF BIS(TETRAETHYLAMMONIUM) μ-HYDRIDO-DODECACARBONYL-*triangulo*-TRIRHENATE(2—)

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Summary

The pyrolyses of $[NEt_4][H_2Re(CO)_4]$ in boiling n-heptane, n-octane and n-nonane are described. Mixtures of polynuclear carbonyl- and hydridocarbonylrhenium species are obtained, the principal products being $[Re_4(CO)_{16}]^{2-}$, $[H_2Re_3(CO)_{12}]^-$, $[H_3Re_3(CO)_{10}]^{2-}$, $[H_3Re_3O(CO)_9]^{2-}$ and $[H_6Re_4(CO)_{12}]^{2-}$. A red-orange crystalline species was isolated from the reaction in n-heptane and shown by X-ray diffraction to be $[NEt_4]_2[HRe_3(CO)_{12}]$. It gives orthorhombic crystals, space group *Pbca*, with cell constants *a* 16.07(1), *b* 23.39(2), *c* 19.49(1) Å. The structure was solved by Patterson and Fourier methods and refined by least-squares up to a final *R* value of 0.061, for 1303 independent counter data. The anion $[HRe_3(CO)_{12}]^{2-}$ contains an isosceles metal atom triangle, with two short edges of 3.014(3) and 3.018(3) Å and a long hydrogen-bridged edge of 3.125(3) Å.

Introduction

We recently described the isolation and structure of the hydridic compound $[NEt_4][H_2Re(CO)_4]$ (I) and its reactions with strong acids and with ethanol, at room temperature, to give $H_3Re_3(CO)_{12}$ and $[H_4Re_4(CO)_{15}]^{2-}$ [1]. Treatment of I with boiling ethanol also gave the previously known species $[H_3Re_3(CO)_{10}]^{2-}$ [2,3], $[H_3Re_3O(CO)_9]^{2-}$ [2,3] and $[H_4Re_4(CO)_{13}]^{2-}$ [3,4]. The monomer $[H_2Re(CO)_4]^-$ thus has a marked tendency to condense to give cluster compounds. We therefore decided to study the reactions of I in boiling long chain hydrocarbons, such as n-heptane, n-octane and n-nonane. The reactions give mixtures of cluster species, many of which have been identified. A product isolated from the reaction in n-heptane showed IR and NMR spectra different from those of all known rhenium cluster species, and X-ray analysis has revealed that it is $[NEt_4]_2[HRe_3(CO)_{12}]$. The cluster anion was previously obtained by a different route [5] but an analysis was not reported. Some structural data are quoted in ref. 6, but the structure has not been previously described in detail.

Experimental

IR spectra were recorded on a Beckman IR 33 spectrometer. NMR spectra were recorded on a Varian NV 14 instrument at 60 MHz s^{-1}, with saturated solutions in deuterioacetone containing TMS as internal standard. Magnetic susceptibilities were measured on a Gouy balance at room temperature. Elemental analyses were carried out at the Microanalysis Laboratory of the University of Milan.

The parent compound $[NEt_4][H_2Re(CO)_4]$ (I) was obtained as described in ref. 1. In many cases the product contained small amounts of $[NEt_4][(CO)_3Re(OMe)_3Re(CO)_3]$, because of the difficulty of separation, as previously stated [1].

Reaction in n-heptane

A suspension of 0.2 g of compound I, in 6 ml of boiling n-heptane (ca. 98°C), was refluxed for 3 h in an oil bath with stirring under N_2. The pale-yellow suspended material turned orange-red. After cooling, the precipitate was filtered off and washed with hexane. The NMR spectrum of the precipitate revealed that it was a mixture of various hydridic species. The principal hydridic signals were found at τ 17.6, 18.4, 21.1, 22.8, 26.7, 27.2, 27.3 and 27.7 ppm. The crude product was recrystallized from acetone/ethanol. A mixture of several types of crystals was obtained in this way, and these were separated under a microscope and submitted to IR, NMR and elemental analyses. The following species were recognized: the red $[NEt_4]_2[H_3Re_3(CO)_{10}]$, the colourless $[NEt_4]_2[H_3Re_3O(CO)_9]$, the yellow $[NEt_4][H_2Re_4(CO)_{12}]$, the dark-red $[NEt_4]_2[Re_4(CO)_{16}]$, the pale-yellow $[NEt_4]_2[H_6Re_3(CO)_{12}]$ and a red-orange species which was shown to be $[NEt_4]_2[HRe_3(CO)_{12}]$.

Reaction in n-octane

A similar procedure using boiling n-octane (ca. 125°C) gave a solid, the NMR spectrum of which showed principal hydridic signals at τ 22.8, 23.4, 26.7, 27.2 and 27.3 ppm. After recrystallization from acetone/ethanol the following species were isolated and identified: $[NEt_4]_2[H_3Re_3O(CO)_9]$, $[NEt_4][H_2Re_3(CO)_{12}]$, $[NEt_4]_2[H_6Re_4(CO)_{12}]$, $[NEt_4]_2[Re_4(CO)_{16}]$, and an orange-brown crystalline species which was shown to be $[NEt_4]_2[Re_4(CO)_{16}] \cdot \frac{1}{2}[NEt_4][H_2Re(CO)_4]$.

Reaction in n-nonane

A similar procedure using boiling n-nonane (ca. 150°C) gave a precipitate, the NMR spectrum of which shows hydridic signals at τ 16.3, 17.0, 18.5, 21.1, 21.3, 22.8, 23.4, 24.7, 25.6, 26.2, 26.7, 27.2, 27.3 and 30.0 ppm. After recrystallization from acetone/ethanol the only products isolated and recognized were $[NEt_4]_2[H_6Re_4(CO)_{12}]$, $[NEt_4][H_2Re_3(CO)_{12}]$ and $[NEt_4]_2[Re_4(CO)_{16}]$.

Single-crystal X-ray data for $[NEt_4]_2[HRe_3(CO)_{12}]$

$C_{28}H_{41}N_2O_{12}Re_3$, mol. wt. 1156.2, orange-red orthorhombic crystals, space group *Pbca* (No. 61) from systematic absences, with cell constants a 16.07(1), b 23.39(2), c 19.49(1) Å, U 7326 Å^3, D_m 2.15(3) (by flotation), D_c 2.10 g cm^{-3} for $Z = 8$, $F(000) = 4352$; Mo-K_α radiation (λ 0.7107 Å), μ(Mo-K_α) 105.3 cm^{-1}.

Intensity measurements

The crystal sample was a prism of dimensions 0.17 × 0.19 × 0.40 mm. The intensity data were measured on the BASIC diffractometer *, using graphite monochromatized Mo-K_α radiation, by the ω-scan method within the sphere $3.5° < \theta < 20°$. The total number of collected data was 3773. The crystal showed a total decay of ca. 15% at the end of the collection. The integrated intensities were corrected for Lorentz, polarization, decay and absorption effects. The transmission factors, computed by the Busing and Levy method [7], were found to be in the range 0.17—0.23. After rejection of all data having $\sigma(I)/I > 0.40$ a set of 1303 independent reflections was used in the solution and refinement of the structure.

Structure solution and refinement

The structure solution was based on a three-dimensional Patterson map which showed the position of the rhenium atoms. After a preliminary refinement of the metal atom parameters a successive difference-Fourier map revealed all the remaining non-hydrogen atoms. The refinement was carried out by full-matrix least-squares. The central NC_4 moieties of the cations were treated as rigid bodies (tetrahedral geometry, N—C 1.52 Å), with a single isotropic thermal factor for each group. Anisotropic thermal factors were assigned to the rhenium atoms only. Since, at this stage, the C—O distances were rather scattered we decided to assign them, in the last cycles, a fixed value of 1.24 Å, the average of all the interactions. The final values of the reliability indices R and R_w were 0.061 and 0.076, respectively. The observations were weighted according to the formula $w = 1/(A + BF_0 + CF_0^2)$ where, in the final cycles, A, B and C had values 530.2, —2.59 and 0.0057, respectively, and were chosen on the basis of an analysis of $\Sigma w\Delta^2$. Atomic scattering factors were taken from ref. 8 for all atoms, those for rhenium being corrected for the effects of the anomalous dispersion [9]. The final difference-Fourier synthesis showed residual peaks not exceeding 1.3 $e^-/\text{Å}^3$ near to the metal atoms.

The results of the refinements are reported in Table 1. A list of observed and computed structure factors moduli can be obtained on application to the authors. All computations were performed on a UNIVAC 1108 computer using local programmes.

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* BASIC stands for 'Basic Siemens Controlled' diffractometer. It has been assembled by Prof. P.L. Bellon with a Siemens—Hoppe four circle goniometer and a 8K Hewlett & Packard computer, programmed in the BASIC language.

TABLE 1

FINAL POSITIONAL AND THERMAL PARAMETERS IN $[NEt_4]_2[HRe_3(CO)_{12}]$ [a,b]

Anisotropic atoms

Atom	x	y	z	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
Re(1)	2591(2)	757(1)	1154(1)	57(1)	8(1)	4(2)	16(1)	4(1)	40(1)
Re(2)	1412(1)	1736(1)	898(1)	43(1)	10(2)	7(2)	19(1)	−3(1)	40(1)
Re(3)	2911(1)	1501(1)	−83(1)	51(1)	9(1)	13(2)	19(1)	2(1)	40(1)

Isotropic atoms

Atom	x	y	z	$B(Å^2)$	Atom	x	y	z	$B(Å^2)$
C(11)	3332(36)	209(26)	895(37)	8.2(19)	O(33)	3950(68)	2353(46)	668(64)	9.6(14)
O(11)	3913(51)	−140(38)	880(62)	10.5(14)	C(34)	2291(35)	897(23)	−531(30)	7.0(17)
C(12)	2358(37)	520(23)	1927(26)	6.1(15)	O(34)	1812(64)	556(35)	−817(50)	9.7(13)
O(12)	2143(63)	296(38)	2475(35)	9.7(13)	N(1)	8(33)	3818(21)	2657(26)	16.4(16)
C(13)	1782(36)	357(25)	669(34)	7.5(18)	CT11	−660(47)	3904(36)	2114(39)	16.4(16)
O(13)	1255(59)	8(37)	466(55)	9.7(13)	CT12	44(56)	4341(28)	3119(39)	16.4(16)
C(14)	3304(38)	1240(27)	1686(35)	7.8(18)	CT13	846(40)	3734(36)	2309(44)	16.4(16)
O(14)	3918(57)	1525(45)	1861(62)	14.0(19)	CT14	−199(55)	3293(27)	3084(40)	16.4(16)
C(21)	893(39)	1512(26)	1634(29)	7.7(17)	CT15	1415(65)	3778(38)	1854(48)	18.7(29)
O(21)	521(61)	1287(41)	2121(44)	8.0(12)	CT16	−245(46)	2742(27)	2435(40)	8.7(19)
C(22)	798(48)	2385(31)	732(48)	11.9(26)	CT17	233(45)	4982(31)	2779(35)	9.1(20)
O(22)	294(71)	2783(43)	667(76)	9.6(13)	CT18	−1567(65)	3934(40)	2727(49)	19.4(32)
C(23)	2168(36)	2158(24)	1481(28)	6.6(15)	N(2)	2037(23)	1263(15)	4264(17)	10.8(10)
O(23)	2560(58)	2478(45)	1872(44)	10.2(13)	CT21	1307(31)	895(27)	4491(25)	10.8(10)
C(24)	724(37)	1340(26)	295(30)	7.4(17)	CT22	1790(36)	1605(19)	3634(22)	10.8(10)
O(24)	239(67)	1058(40)	−67(48)	9.8(13)	CT23	2773(33)	881(27)	4093(31)	10.8(10)
C(31)	3856(41)	1120(30)	−329(40)	10.0(22)	CT24	2273(42)	1669(19)	4841(21)	10.8(10)
O(31)	4482(55)	811(46)	−338(67)	11.6(16)	CT25	3504(56)	1075(37)	3796(44)	15.9(26)
C(32)	3013(51)	1885(30)	−848(31)	10.2(21)	CT26	2682(43)	1394(30)	5468(34)	8.6(19)
O(32)	3047(83)	2157(46)	−1394(41)	9.8(13)	CT27	1135(58)	2027(39)	3722(51)	13.8(30)
C(33)	3481(46)	1975(29)	445(39)	10.6(23)	CT28	825(54)	554(38)	3939(44)	12.6(27)

[a] All parameters X 10^4, *except for the isotropic B factors.* [b] The b_{ij} values are the coefficients of $\exp - (h^2b_{11} + k^2b_{22} + l^2b_{33} + hkb_{12} + hlb_{13} + klb_{23})$.

Results and discussion

Pyrolysis reactions

The pyrolyses of compound I in boiling long chain hydrocarbons give mixtures containing several cluster species.

The crude product obtained from the reaction in n-heptane shows a complex high-field NMR spectrum. Hydridic signals are present which can be assigned to known species: τ 18.4 and 21.1 ppm to $[H_3Re_3(CO)_{10}]^{2-}$ [2], τ 22.8 ppm to $[H_3Re_3O(CO)_9]^{2-}$ [2], τ 26.7 and 27.3 ppm to $[H_4Re_4(CO)_{13}]^{2-}$ [4] and a very strong signal at τ 27.2 ppm due to $[H_2Re_3(CO)_{12}]^-$ [10]; in addition, two new signals (τ 17.6 and 27.7 ppm) were found. After recrystallization of the mixture we isolated and characterized the tetraethylammonium salts of the known anions $[Re_4(CO)_{16}]^{2-}$ [11], $[H_2Re_3(CO)_{12}]^-$, $[H_3Re_3(CO)_{10}]^{2-}$, $[H_3Re_3O(CO)_9]^{2-}$ and $[H_6Re_4(CO)_{12}]^{2-}$ [12], the last two in small amounts. We also isolated a red-orange crystalline species (in poor yield) whose NMR spectrum showed a signal at τ 27.7 ppm. The IR spectrum in acetone exhibits the following CO bands: 1992s, 1970(sh), 1948vs and 1865s(br) cm^{-1}. The X-ray analysis of this species (see below) has shown it to be $[NEt_4]_2[HRe_3(CO)_{12}]$.

The reaction in n-octane gave a mixture whose NMR spectrum revealed the presence of the known anions $[H_3Re_3O(CO)_9]^{2-}$, $[H_4Re_4(CO)_{13}]^{2-}$, $[H_2Re_3(CO)_{12}]^-$ and $[H_6Re_4(CO)_{12}]^{2-}$; in addition a new signal at τ 23.4 ppm was found. Upon recrystallization, the following compounds were isolated: $[NEt_4]_2[Re_4(CO)_{16}]$, $[NEt_4][H_2Re_3(CO)_{12}]$, $[NEt_4]_2[H_3Re_3O(CO)_9]$ and $[NEt_4]_2[H_6Re_4(CO)_{12}]$, the last two in very small amounts. A few crystals of an orange-brown tetragonal species (II) were also isolated. Its IR spectrum in acetone, in the CO stretching region, shows a pattern essentially similar to that of $[Re_4(CO)_{16}]^{2-}$. However, the molecular weight of compound II (obtained from density) was found higher than that of $[NEt_4]_2[Re_4(CO)_{16}]$. Moreover, this latter species gives dark-red elongated crystals of different symmetry (monoclinic, $P2_1/c$, with a 8.80(1), b 20.10(2), c 11.29(1) Å, β 99.90(8)°). Thus we decided to perform a complete X-ray analysis on II, and the results are described below.

The mixtures obtained from the n-nonane solutions showed some variations on repeating the reaction. In one case the NMR spectrum exhibited up to fourteen hydridic signals, seven of which are novel. However after recrystallization we have been able to identify only the known species $[NEt_4]_2[Re_4(CO)_{16}]$, $[NEt_4][H_2Re_3(CO)_{12}]$ and $[NEt_4]_2[H_6Re_4(CO)_{12}]$. Further studies of this reaction are in progress.

X-ray analysis of the tetragonal species II

The crystal structure of II * contains $[Re_4(CO)_{16}]^{2-}$ anions lying on mmm (D_{2h}) special positions (c in Wyckoff notation) and disordered $[NEt_4]^+$ cations on $2/m$ (C_{2h}) special positions (f in Wyckoff notation), in the ratio 1/2 in

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* Crystal data: Tetragonal, a 15.282(2), c 21.435(5) Å, U = 5005.9 Å^3. Space group $I4/mmm$ (No. 139). D_m 2.22(3) g cm^{-3} (by flotation). The intensity data were collected on an automatic diffractometer, within $2\theta \leq 42°$, with graphite monochromatized Mo-K_α radiation. The structure was solved by conventional Patterson and Fourier methods; the refinements were carried out by block-matrix least-squares, based on 520 independent reflections with $\sigma(I)/I < 0.30$, up to a final R value of 0.052.

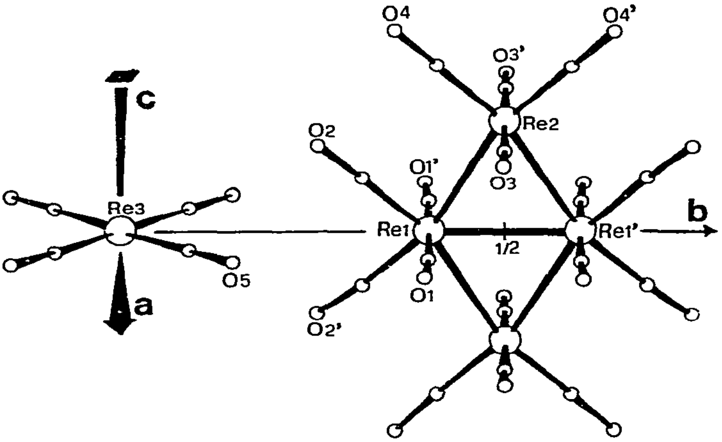

Fig. 1. A view of the two anions in the tetragonal species II.

agreement with a formulation $[NEt_4]_2[Re_4(CO)_{16}]$. However, in addition, on the $4/mmm$ (D_{4h}) special positions (*a* in Wyckoff notation) monomeric species were found showing a $Re(CO)_4$ planar array; above and below this plane (in the direction of the four-fold axis) no residual peak, in the difference-Fourier maps, was found at a bond distance from the metal atom. Residual peaks were observed around the special positions $4/mmm$ (*b* in Wyckoff notation) which may be due to the presence of disordered $[NEt_4]^+$ cations, which we were unable to refine. A reasonable interpretation is that the monomers are parent $[H_2Re(CO)_4]^-$ anions with a *trans* configuration of the hydridic ligands, in contrast with the *cis* geometry of this anion both in solution and in the salt $[NEt_4][H_2Re(CO)_4]$ [1]. Packing factors may be responsible for this situation; unfortunately we have no further evidence to support our suggestion. The probable formulation of the compound is, therefore, that of a mixed salt $[NEt_4]_2[Re_4(CO)_{16}] \cdot \frac{1}{2}[NEt_4][H_2Re(CO)_4]$.

A view of the two anions, with their respective positions in the cell, is shown in Fig. 1. Interatomic distances and angles are reported in Table 2. The Re—C and C—O bond lengths in the monomer, 1.88(4) and 1.23(6) Å, are comparable with the corresponding mean values in *cis*-$[H_2Re(CO)_4]^-$ (1.89, 1.21 Å) [1]. The bond parameters in the anion $[Re_4(CO)_{16}]^{2-}$ are similar to those previously reported for this anion in its tetra-n-butylammonium salt [11]; a comparison is given in Table 2. The anion here possesses a rigorous, crystallographically imposed D_{2h} symmetry, while, in the previous case it showed a skewed conformation of the carbonyls relative to the Re_4 plane, which was attributed to intramolecular O···O repulsions [11]. We have found comparable oxygen—oxygen contacts; thus the distortion noted previously was probably also due to different intermolecular packing interactions.

Description of the structure of $[NEt_4]_2[HRe_3(CO)_{12}]$

The crystal packing consists of discrete $[HRe_3(CO)_{12}]^{2-}$ anions and $[NEt_4]^+$ cations in the ratio 1/2, as illustrated in Fig. 2.

The anion is depicted in Fig. 3. It contains an isosceles metal atom triangle

TABLE 2

INTERATOMIC DISTANCES AND ANGLES IN COMPOUND II

Distances (Å)		Angles (degree)	
Re(1)—Re(2)	3.010(2) [3.003] ^{a}	Re(2)—Re(1)—Re(1')	60.2(1) [60.5]
Re(1)—Re(1')	2.994(2) [2.956]	Re(1)—Re(2)—Re(1')	59.7(1) [59.0]
Re(1)—C ^{b}	1.92 [1.93]	Re(2)—Re(1)—C(1)	90(1) [89]
Re(2)—C ^{b}	1.87 [1.89]	Re(2)—Re(1)—C(2)	75(1) [73]
C—O ^{b}	1.15 [1.19]	Re(1')—Re(1)—C(1)	90(1) [89]
O···O(ax) ^{b}	3.11 [3.12]	Re(1')-Re(1)—C(2)	135(1) [133]
O(2)···O(4)	3.18(3) [3.13]	C(1)—Re(1)—C(2)	90(1) [91]
Re(3)—C(5)	1.88(4)	C(2)—Re(1)—C(2')	90(1) [94]
C(5)—O(5)	1.23(6)	C(1)—Re(1)—C(1')	179(2) [177]
		Re(1)—Re(2)—C(3)	89(1) [88]
		Re(1)—Re(2)—C(4)	104(1) [105]
		C(3)—Re(2)—C(4)	91(1) [92]
		C(4)—Re(2)—C(4')	92(1) [91]
		C(3)—Re(2)—C(3')	178(2) [175]

^{a} In square brackets are reported the corresponding mean values found in [$N(C_4H_9)_4]_2[Re_4(CO)_{16}$] (ref. 11). ^{b} Mean values.

with one edge longer than the other two; each metal atom bears four terminal CO ligands. The idealized anion symmetry is C_{2v}. Interatomic distances and angles are reported in Table 3. The two short Re—Re edges (mean 3.016 Å) are

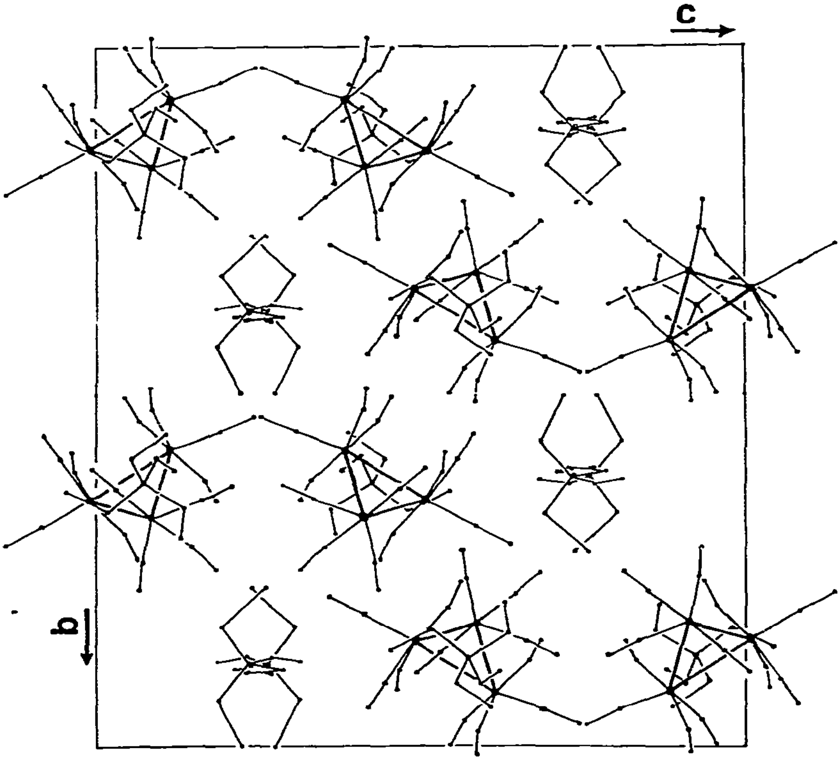

Fig. 2. Projection of the cell content down the *a* axis in the salt [$NEt_4]_2[HRe_3(CO)_{12}$].

TABLE 3

INTERATOMIC DISTANCES AND ANGLES IN THE ANION $[HRe_3(CO)_{12}]^{2-}$

Distances (Å)	
Re(1)—Re(2)	3.014(3)
Re(1)—Re(3)	3.018(3)
Re(2)—Re(3)	3.125(3)
Re(1)—C(11)	1.82(6)
Re(1)—C(12)	1.65(5)
Re(1)—C(13)	1.86(6)
Re(1)—C(14)	1.91(6)
Re(2)—C(21)	1.74(6)
Re(2)—C(22)	1.84(7)
Re(2)—C(23)	1.94(6)
Re(2)—C(24)	1.86(6)
Re(3)—C(31)	1.82(7)
Re(3)—C(32)	1.75(6)
Re(3)—C(33)	1.77(7)
Re(3)—C(34)	1.94(6)
C—O	1.24
O···O(ax) [a]	3.11

Angles (degree)	
Re(2)—Re(1)—Re(3)	62.4(1)
Re(1)—Re(2)—Re(3)	58.9(1)
Re(1)—Re(3)—Re(2)	58.7(1)
Re(2)—Re(1)—C(11)	154(2)
Re(2)—Re(1)—C(12)	105(2)
Re(2)—Re(1)—C(13)	82(2)
Re(2)—Re(1)—C(14)	91(2)
Re(3)—Re(1)—C(11)	94(2)
Re(3)—Re(1)—C(12)	164(2)
Re(3)—Re(1)—C(13)	90(2)
Re(3)—Re(1)—C(14)	89(2)

Angles (degree)	
Re(1)—Re(2)—C(21)	86(2)
Re(1)—Re(2)—C(22)	173(2)
Re(1)—Re(2)—C(23)	84(2)
Re(1)—Re(2)—C(24)	96(2)
Re(3)—Re(2)—C(21)	145(2)
Re(3)—Re(2)—C(22)	117(2)
Re(3)—Re(2)—C(23)	88(2)
Re(3)—Re(2)—C(24)	89(2)
Re(1)—Re(3)—C(31)	94(2)
Re(1)—Re(3)—C(32)	174(2)
Re(1)—Re(3)—C(33)	89(2)
Re(1)—Re(3)—C(34)	82(2)
Re(2)—Re(3)—C(31)	153(2)
Re(2)—Re(3)—C(32)	120(2)
Re(2)—Re(3)—C(33)	86(2)
Re(2)—Re(3)—C(34)	90(2)
C(11)—Re(1)—C(12)	99(3)
C(11)—Re(1)—C(13)	88(3)
C(11)—Re(1)—C(14)	100(3)
C(12)—Re(1)—C(13)	98(3)
C(12)—Re(1)—C(14)	81(3)
C(13)—Re(1)—C(14)	172(3)
C(21)—Re(2)—C(22)	98(3)
C(21)—Re(2)—C(23)	88(3)
C(21)—Re(2)—C(24)	95(3)
C(22)—Re(2)—C(23)	91(3)
C(22)—Re(2)—C(24)	89(3)
C(23)—Re(2)—C(24)	177(3)
C(31)—Re(3)—C(32)	87(3)
C(31)—Re(3)—C(33)	92(3)
C(31)—Re(3)—C(34)	87(3)
C(32)—Re(3)—C(33)	97(3)
C(32)—Re(3)—C(34)	92(3)
C(33)—Re(3)—C(34)	170(3)
Re(1)—C(11)—O(11)	164(8)
Re(1)—C(12)—O(12)	173(6)
Re(1)—C(13)—O(13)	166(7)
Re(1)—C(14)—O(14)	161(7)
Re(2)—C(21)—O(21)	172(6)
Re(2)—C(22)—O(22)	171(8)
Re(2)—C(23)—O(23)	171(6)
Re(2)—C(24)—O(24)	175(6)
Re(3)—C(31)—O(31)	165(8)
Re(3)—C(32)—O(32)	177(8)
Re(3)—C(33)—O(33)	165(8)
Re(3)—C(34)—O(34)	172(6)

[a] Mean value.

normal unbridged single bonds, while the third edge, 3.125(3) Å, shows a lengthening due to the presence of the bridging hydrido ligand. These values are close to those previously found for the same anion, 3.004 and 3.144 Å [6]. The Re—C distances are rather scattered and subject to large uncertainties; their mean value is 1.83 Å. However, the equatorial carbonyl ligands exhibit markedly shorter Re—C bonds (mean 1.77 Å) than the axial ones (mean 1.88 Å); this is reasonable

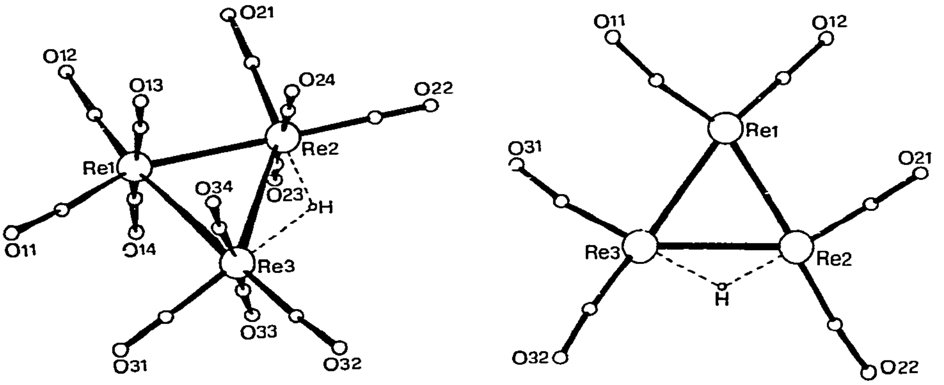

Fig. 3. A view of the anion $[HRe_3(CO)_{12}]^{2-}$ (on the left) and of its equatorial plane (on the right).

since the latter ones are competitive among themselves for the back-donated metal-to-ligand electrons. Analogous differences were found, for instance, in $H_3Mn_3(CO)_{12}$ (1.79 vs. 1.85 Å) [13] and in $[H_4Re_4(CO)_{15}]^{2-}$ (1.88 vs. 1.93 Å) [14].

The carbonyl ligands show some distortions with respect to the idealized C_{2v} symmetry. The axial CO groups deviate from perpendicularity to the Re_3 plane, the $Re—Re—C_{ax}$ angles ranging from 82 to 96° (mean 88°). The mean values of the $C_{ax}—Re—C_{ax}$ and $C_{ax}—Re—C_{eq}$ angles are 173 and 91°, respectively

The dispositions of the equatorial carbonyls (see Fig. 3) clearly indicate the location of the bridging hydrogen atom (not directly located). The coordination around Re(1) strictly resembles that found for each metal atom in the species $Os_3(CO)_{12}$ [15] and $Ru_3(CO)_{12}$ [16], of idealized D_{3h} symmetry. The equatorial Re—Re(1)—C(*cis*) (mean 100°) and C—Re(1)—C (99°) angles are comparable with the corresponding mean values in the two above species, e.g. in $Ru_3(CO)_{12}$ [Ru—Ru—C(*cis*) 99°, C—Ru—C 103°]. On the other hand, the equatorial carbonyl groups bound to Re(2) and Re(3) are rotated in such a way to make a place for the bridging H atom; thus the Re—Re(2,3)—C(*cis*) angles involving the hydrogen-bridged metal—metal bond are distinctly larger than the other Re—Re(2,3)—C(*cis*) angles (mean values: 119 vs. 90°). A similar situation was found in $[H_2Re_3(CO)_{12}]^-$ for two of the metal atoms [Re—Re—C(*cis*) mean values: 115 vs. 92°] [10].

Assuming average C_{2v} parameters and locating the hydrido ligand exactly *trans* to CO(21) and CO(31), the estimated Re—H and Re—H—Re values are ca. 1.83 Å and 118°. These values are reasonable compared with the corresponding values, directly determined, in $H_3Mn_3(CO)_{12}$ (1.72(3) Å, 131(7)°) [13], taking into account the different covalent radii of the metal atoms.

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