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PRODUCTS OF THE REACTION OF $Re_2(CO)_{10}$ WITH METHANOLIC KOH. THE CRYSTAL AND MOLECULAR STRUCTURE OF THE TRIMETHYLBENZYLAMMONIUM SALT OF HEXA-μ_2-HYDRIDODECACARBONYL-*tetrahedro*-TETRARHENATE(2−)

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Summary

The compound $(Me_3BzN)_2[H_6Re_4(CO)_{12}]$ (Bz = benzyl) crystallizes in the monoclinic space group $P2_1/c$ with a 10.03(1), b 20.52(2), c 19.47(2) Å, β 96.30(8)°, Z = 4. Diffractometer data have been refined by least-squares methods to a final R of 5.1% for 1334 independent reflections. The anion contains a regular metal atom tetrahedron (mean Re—Re 3.157 Å); it is not disordered, in contrast with the situation in its $(AsPh_4)^+$ salt. The Re—C and C—O interactions have mean values of 1.81 and 1.21 Å. The M—M—C angles are significantly larger, and the C—M—C angles smaller, than in $Ir_4(CO)_{12}$, confirming the presence of the edge-bridging hydrido ligands on the six Re—Re bonds. The metal—metal interactions in the various known structures of polynuclear carbonylic species of rhenium are discussed.

Introduction

The reactions of decacarbonyldirhenium with alcoholic strong bases, previously studied by Hieber and coworkers [1], have recently been reinvestigated. Refluxing $Re_2(CO)_{10}$ in methanolic KOH solutions for short times gave products such as μ-alkoxo anions, formulated as $[(CO)_3Re(OMe)_3Re(CO)_3]^-$ [2], and polynuclear hydridocarbonyl compounds [3]. Prolonged heating gave, in addition to the μ-alkoxo prodcuts and other unidentified hydridic compounds, a tetrametal diamagnetic anionic species (isolated as the trimethylbenzylammonium salt) which showed IR and NMR spectra very similar to those of $[H_6Re_4(CO)_{12}]^{2-}$

TABLE 1

FINAL POSITIONAL AND THERMAL PARAMETERS [a/c]

A. Anisotropic atoms

Atom	x	y	z	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
Re(1)	1644(2)	3773(1)	2025(1)	75(3)	6(2)	8(2)	25(1)	−1(1)	22(1)
Re(2)	774(2)	2296(1)	1973(1)	50(2)	3(2)	−1(2)	26(1)	−10(1)	28(1)
Re(3)	3858(2)	2664(1)	2208(1)	60(2)	10(2)	8(2)	24(1)	−10(1)	29(1)
Re(4)	2005(2)	2932(1)	3381(1)	90(3)	3(2)	0(2)	24(1)	−1(1)	22(1)

B. Isotropic atoms

Atom	x	y	z	B (Å^2)	Atom	x	y	z	B (Å^2)
C(11)	1352(74)	4054(30)	1088(32)	8.0(17)	N(1)	3484(43)	4856(18)	6297(18)	4.2(9)
O(11)	1081(48)	4259(21)	548(21)	8.4(11)	CT11	3603(70)	4182(30)	6009(30)	7.3(16)
C(12)	2510(58)	4504(24)	2166(26)	5.0(13)	CT12	2061(72)	5137(30)	6018(31)	7.6(17)
O(12)	3070(42)	5043(17)	2288(18)	6.5(9)	CT13	3376(68)	4797(29)	7061(30)	7.2(16)
C(13)	60(64)	4116(27)	2224(28)	6.1(14)	CT14	4729(56)	5221(23)	6214(24)	4.4(11)
O(13)	−978(45)	4309(19)	2435(19)	7.5(10)	C(1)	2191(43)	5316(18)	5191(13)	7.2(16)
C(21)	653(53)	1987(22)	1001(22)	4.0(11)	C(2)	1649(46)	4904(15)	4663(18)	6.5(15)
O(21)	579(50)	1813(21)	443(21)	8.8(12)	C(3)	1609(38)	5102(16)	3978(15)	3.6(10)
C(22)	607(83)	1521(35)	2296(36)	9.5(20)	C(4)	2109(43)	5709(18)	3818(13)	3.9(11)
O(22)	473(45)	939(19)	2531(20)	7.8(11)	C(5)	2652(46)	6120(15)	4345(18)	7.9(17)
C(23)	−867(71)	2377(31)	1882(32)	8.1(17)	C(6)	2693(38)	5923(16)	5032(15)	6.8(15)
O(23)	−2070(43)	2442(18)	1869(19)	7.5(10)					
C(31)	4532(60)	2568(25)	1296(26)	5.6(13)	N(2)	2278(47)	−3307(20)	698(20)	13.5(12)
O(31)	4778(44)	2512(18)	766(19)	7.5(10)	CT21	1252(64)	−3176(39)	79(27)	13.5(12)
C(32)	4742(65)	2011(27)	2397(27)	6.3(14)	CT22	1611(70)	−3242(27)	1358(26)	13.5(12)
O(32)	5356(40)	1474(17)	2619(18)	6.5(9)	CT23	3416(68)	−2817(33)	705(33)	13.5(12)
C(33)	5201(67)	3110(28)	2539(29)	6.6(15)	CT24	2831(83)	−3993(23)	646(32)	13.5(12)
O(33)	6202(43)	3436(18)	2847(19)	7.2(10)	C(7)	3173(88)	−4232(40)	−15(32)	16.8(16)
C(41)	1862(70)	2203(31)	3856(31)	7.9(17)	C(8)	2568(68)	−4627(38)	−541(49)	16.8(16)
O(41)	2053(49)	1743(21)	4273(21)	8.8(12)	C(9)	3271(87)	−4803(30)	−1090(37)	16.8(16)
C(42)	3158(75)	3318(32)	4072(32)	8.2(18)	C(10)	4580(88)	−4585(40)	−1113(32)	16.8(16)
O(42)	3990(41)	3541(17)	4463(18)	6.7(9)	C(11)	5185(68)	−4191(38)	−586(49)	16.8(16)
C(43)	363(87)	3217(35)	3714(37)	10.3(22)	C(12)	4481(87)	−4014(30)	−37(37)	16.8(16)
O(43)	−332(40)	3509(17)	3982(18)	7.2(9)					

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[a] The estimated standard deviation in the last significant figure is given in parentheses. [b] All the parameters $\times 10^4$, except for the isotropic B factors. [c] The anisotropic temperature factors are given by $\exp -(h^2b_{11} + k^2b_{22} + l^2b_{33} + hkb_{12} + hlb_{13} + klb_{23})$.

[4], previously obtained by a different route and characterized as its tetraphenylarsonium salt [5].

We are currently studying the structures of all these products for which crystals are obtainable, and decided to carry out an X-ray structural analysis of the compound in order to confirm the formulation and, possibly, to obtain more structural information on the anion, since in the structure of the $(AsPh_4)^+$ salt it was affected by disorder [5]. We report below the complete results for the structure of $(Me_3BzN)_2[H_6Re_4(CO)_{12}]$. We have found an ordered metal atom cluster and we have unambiguously confirmed the edge-bridging locations of the hydrido ligands on the basis of the observed carbonyl stereochemistry. A comparative discussion on the known structures of the polynuclear hydridocarbonylrhenium compounds is also presented.

Experimental

Crystal data. $C_{32}H_{38}N_2O_{12}Re_4$, mol. wt. 1387.4, monoclinic, a 10.03(1), b 20.52(2), c 19.47(2) Å, β 96.30(8)°, U 3983 Å^3, D_m 2.29(2) (by flotation), $Z = 4$, D_c 2.31 g cm^{-3}, $F(000) = 2560$. Space group $P2_1/c$ (No. 14) Mo-K_α radiation, λ 0.7107 Å, $\mu(\text{Mo-}K_\alpha) = 128.8$ cm^{-1}.

Intensity measurements. A very small crystal of the compound was mounted on a Pailred linear equi-inclination diffractometer and graphite monochromatized Mo-K_α radiation was used. Data were measured corresponding to the levels $0kl$—$6kl$, within the limit $2\theta < 50°$, by the ω-scan method. The total number of collected reflections was 3503. Some standard reflections, sampled after completion of each layer, revealed a marked decay of the crystal (ca. 40% at the end of the collection). The integrated intensities were corrected for Lorentz, polarization and decay effects. All intensities having $\sigma(I)/I > 0.25$ were discarded and a set of 1334 reflections was used for the structure resolution and refinement.

Determination and refinement of the structure. The metal atom positions were obtained from a three-dimensional Patterson map. After a preliminary refinement of the rhenium parameters a successive difference-Fourier synthesis revealed most of the non-hydrogen atoms. The structure was refined by the least-squares method in the block-diagnoal approximation. Anisotropic temperature factors were assigned to the rhenium atoms only. One of the cations (containing N(2)) was found to be disordered, showing for various atoms double images very close together in the Fourier maps. Attempts to refine two half cations were tried unsuccessfully. It was therefore refined using a rigid-body model for the phenyl group (D_{6h} symmetry, C—C 1.39 Å) and another one for the NC_4 moiety (tetrahedral geometry, N—C 1.52 Å) and assigning an average isotropic thermal factor to each of the two groups. In the other cation only the phenyl group was refined rigidly.

The final values of the reliability indices R and R', $\{R' = [\Sigma w(F_o - K|F_c|)^2/\Sigma wF_o^2]^{1/2}\}$, were 0.051 and 0.061. The observations were weighted according to the formula $w = 1/(A + BF_o + CF_o^2)$; in the final cycles A, B and C had values 282.9, −1.48 and 0.0037, and were chosen on the basis of an analysis of $\Sigma w\Delta^2$. The atomic scattering factors were taken from ref. 6; the rhenium factor was corrected both for the real and imaginary part of the anomalous dispersion [7]. The final difference-Fourier map did not show peaks exceeding ca. 1.5 $e/Å^3$ in the vicinity of the metal atoms. The results of the refinements are reported in Table 1. A list of observed and computed structure factors can be obtained on application to the authors.

We have also performed a constrained refinement of the anion. The carbonyl groups were assigned a linear geometry and unique values for all the R—C as well as for all the C—O distances were refined. The corresponding R and R' values were 0.052 and 0.063. No significant change was observed in the cluster geometry, and the other bond parameters are illustrated in the discussion. All the computations were performed on a UNIVAC 1106 computer using local programs.

Discussion

Description of the structure. The crystal packing consists of discrete $[H_6Re_4(CO)_{12}]^{2-}$ anions and $(Me_3BzN)^+$ cations in the ratio 1/2. One of the cations

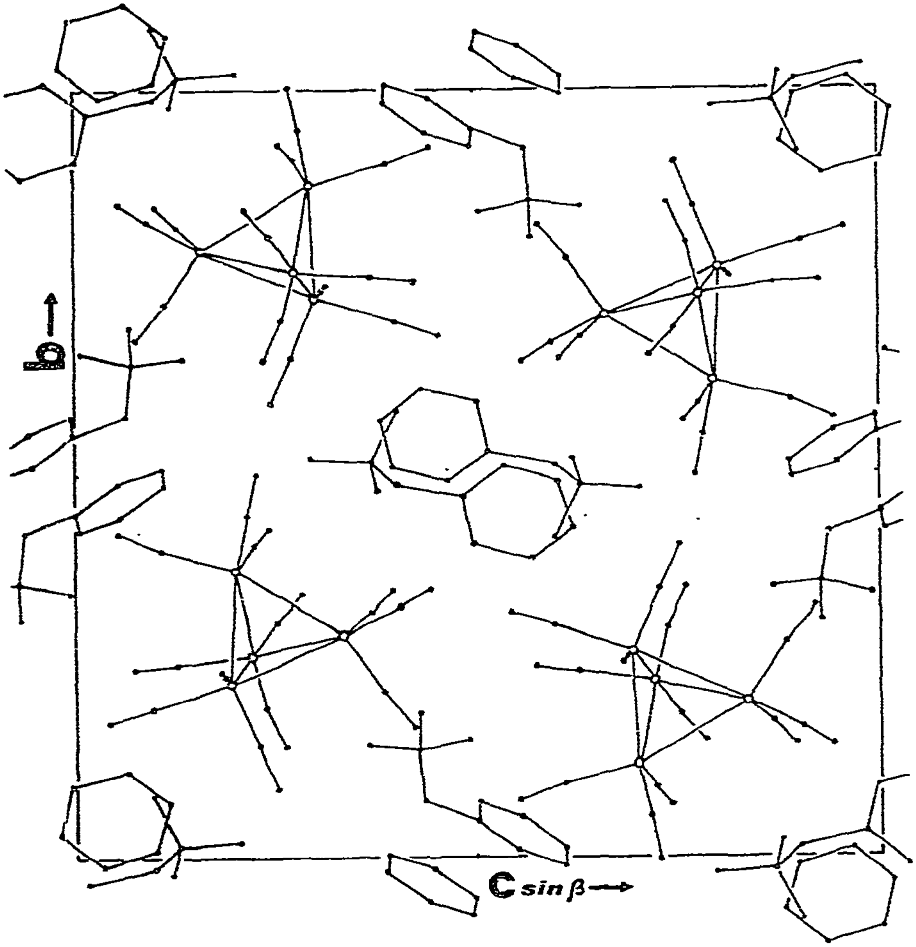


Fig. 1. Projection of the structure down the a axis.

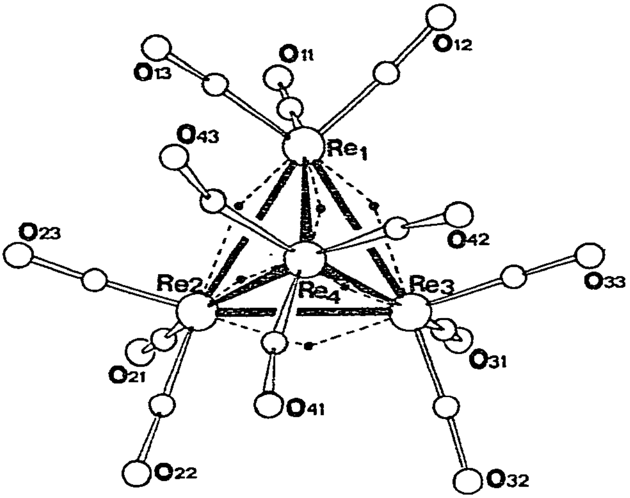


Fig. 2. A view of the anion $[H_6Re_4(CO)_{12}]^{2-}$ with the postulated hydridic atoms locations.

shows some disorder (see the Experimental part). A view of the structure down the a axis is illustrated in Fig. 1.

The anion $[H_6Re_4(CO)_{12}]^{2-}$ contains a regular metal atoms tetrahedron, the six edges being in the range 3.142—3.172(3) Å and the Re—Re—Re angles in the range 59.6—60.6(1)°. The mean Re—Re distance, 3.157 Å, is nearly coincident with the corresponding mean value found in the previous structural determination of $(AsPh_4)_2[H_6Re_4(CO)_{12}]$ (3.160 Å) [5].and shows that these bonds are lengthened by the presence of the six edge-bridging hydrido ligands, lying nearly *trans* to the carbonyl groups, as illustrated in Fig. 2. The bond distances within the anion are listed in Table 2. The Re—C and C—O bong lengths are rather scattered; their mean values, 1.81 and 1.21 Å, are comparable with similar interactions in many carbonylrhenium compounds. The idealized anion symmetry is T_d, but distorsions are present due to packing effects; the oxygen atoms define

TABLE 2

BOND DISTANCES (Å) IN THE ANION $[H_6Re_4(CO)_{12}]^{2-}$

Re(1)—Re(2)	3.151(3)	Re (4)—C(41)	1.77(6)
Re(1)—Re(3)	3.172(3)	Re (4)—C(42)	1.85(6)
Re(1)—Re(4)	3.142(3)	Re (4)—C(43)	1.93(9)
Re(2)—Re(3)	3.168(3)	C (11)—O(11)	1.14(7)
Re(2)—Re(4)	3.163(3)	C (12)—O(12)	1.25(6)
Re(3)—Re(4)	3.148(3)	C (13)—O(13)	1.23(8)
Re(1)—C (11)	1.90 (6)	C (21)—O(21)	1.14(6)
Re(1)—C (12)	1.74 (5)	C (22)—O(22)	1.29(8)
Re(1)—C (13)	1.82 (6)	C (23)—O(23)	1.21(8)
Re(2)—C (21)	1.99 (4)	C (31)—O(31)	1.09(7)
Re(2)—C (22)	1.73 (7)	C (32)—O(32)	1.31(7)
Re(2)—C (23)	1.65 (7)	C (33)—O(33)	1.30(7)
Re(3)—C (31)	1.98 (6)	C (41)—O(41)	1.25(8)
Re(3)—C (32)	1.63 (6)	C (42)—O(42)	1.16(7)
Re(3)—C (33)	1.70 (6)	C (43)—O(43)	1.10(9)

TABLE 3

BOND ANGLES IN THE ANION $[H_6Re_4(CO)_{12}]^{2-}$

Angle (deg.)	Refinement I	Refinement II [a]
Re (2)—Re (1)—C(11)	104(2)	105(1)
Re (3)—Re (1)—C(11)	111(2)	113(1)
Re (4)—Re (1)—C(11)	164(2)	165(1)
Re (2)—Re (1)—C(12)	165(2)	165(1)
Re (3)—Re (1)—C(12)	106(2)	106(1)
Re (4)—Re (1)—C(12)	109(2)	109(1)
Re (2)—Re (1)—C(13)	98(2)	97(1)
Re (3)—Re (1)—C(13)	151(2)	148(1)
Re (4)—Re (1)—C(13)	93(2)	91(1)
Re (1)—Re (2)—C(21)	109(1)	109(1)
Re (3)—Re (2)—C(21)	100(2)	100(1)
Re (4)—Re (2)—C(21)	159(2)	159(1)
Re (1)—Re (2)—C(22)	156(2)	156(1)
Re (3)—Re (2)—C(22)	107(3)	107(1)
Re (4)—Re (2)—C(22)	96(2)	96(1)
Re (1)—Re (2)—C(23)	100(2)	100(1)
Re (3)—Re (2)—C(23)	160(2)	160(1)
Re (4)—Re (2)—C(23)	110(2)	109(1)
Re (1)—Re (3)—C(31)	106(2)	105(1)
Re (2)—Re (3)—C(31)	106(2)	104(1)
Re (4)—Re (3)—C(31)	163(2)	161(1)
Re (1)—Re (3)—C(32)	167(2)	164(1)
Re (2)—Re (3)—C(32)	110(2)	108(1)
Re (4)—Re (3)—C(32)	109(2)	106(1)
Re (1)—Re (3)—C(33)	100(2)	100(1)
Re (2)—Re (3)—C(33)	155(2)	154(1)
Re (4)—Re (3)—C(33)	98(2)	96(1)
Re (1)—Re (4)—C(41)	153(2)	157(1)
Re (2)—Re (4)—C(41)	93(2)	97(1)
Re (3)—Re (4)—C(41)	109(2)	108(1)
Re (1)—Re (4)—C(42)	112(2)	112(1)
Re (2)—Re (4)—C(42)	163(2)	161(1)
Re (3)—Re (4)—C(42)	103(2)	101(1)
Re (1)—Re (4)—C(43)	95(2)	95(1)
Re (2)—Re (4)—C(43)	99(2)	104(1)
Re (3)—Re (4)—C(43)	153(2)	155(1)
C (11)—Re (1)—C(12)	85(3)	85(1)
C (11)—Re (1)—C(13)	92(3)	93(1)
C (12)—Re (1)—C(13)	94(3)	93(1)
C (21)—Re (2)—C(22)	93(3)	93(1)
C (21)—Re (2)—C(23)	89(3)	90(1)
C (22)—Re (2)—C(23)	90(4)	89(1)
C (31)—Re (3)—C(32)	84(3)	88(1)
C (31)—Re (3)—C(33)	93(3)	97(1)
C (32)—Re (3)—C(33)	88(3)	88(1)
C (41)—Re (4)—C(42)	93(3)	89(1)
C (41)—Re (4)—C(43)	88(3)	93(1)
C (42)—Re (4)—C(43)	97(3)	93(1)
Re (1)—C (11)—O(11)	173(6)	180
Re (1)—C (12)—O(12)	176(5)	
Re (1)—C (13)—O(13)	172(5)	
Re (2)—C (21)—O(21)	180(5)	
Re (2)—C (22)—O(22)	179(6)	
Re (2)—C (23)—O(23)	175(6)	
Re (3)—C (31)—O(31)	173(5)	
Re (3)—C (32)—O(32)	172(5)	
Re (3)—C (33)—O(33)	175(5)	
Re (4)—C (41)—O(41)	165(6)	
Re (4)—C (42)—O(42)	173(6)	
Re (4)—C (43)—O(43)	160(6)	

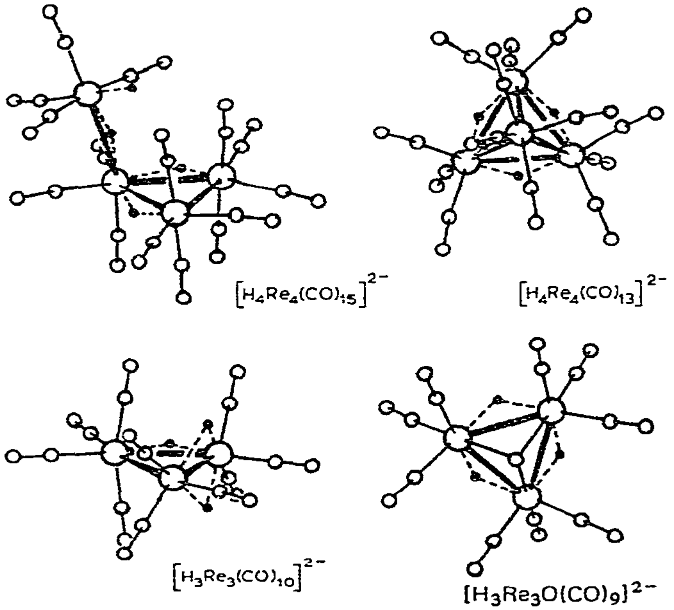
[a] *Constrained refinement (see text).*

a distorted cube-octahedron, the O···O contacts for the carbonyl groups bound to the same metal atom ranging in the interval 4.07—4.58 Å (av. 4.28 Å).

In order to get more information on the bond angles in the anion we have also performed a constrained refinement, imposing linear Re—C—O interactions and unique Re—C and C—O distances for all the carbonyl groups (see the Experimental part). The resulting bond lengths are 1.83(2) and 1.18(4) Å, respectively, and the bond angles are listed in Table 3. The individual angles in the two refinements differ up to a maximum of 5° but the average values of the Re—Re—C_{cis} (103°), Re—Re—C_{trans} (159°) and C—Re—C (91°) angles are coincident.

The carbonyl disposition gives a clear indication of the positions of the hydrido ligands. It is of particular interest to compare the anion with a very similar, but non-hydridic, structure, as that of $Ir_4(CO)_{12}$ [8]. The hydrogen atoms on the M—M bonds make larger the M—M—C angles (mean values: *cis* 103° vs. 95°; *trans* 159° vs. 151°) and smaller the C—M—C angles (mean 91° vs. 102°). Angles similar to those of $Ir_4(CO)_{12}$ are found in other non-hydridic tetrahedral cluster compounds containing $M(CO)_3$ units, as in the apical moiety of $Co_4(CO)_{12}$, recently re-refined by Cotton et al. (M—M—C_{cis} 97°, M—M—C_{trans} 151° and C—M—C 101°) [9]. Thus hydridic ligands show their presence by significantly influencing the disposition of the surrounding ligands. In the recently reported structure of $H_4Re_4(CO)_{12}$ the presence of face-bridging H atoms is clearly indicated by the disposition of the CO groups which are eclipsed with respect to the Re—Re bonds [10], in contrast with the staggered disposition in $[H_6Re_4(CO)_{12}]^{2-}$.

Considerations on the structural features of polynuclear hydridocarbonyls of rhenium. From the basic hydrolysis of $Re_2(CO)_{10}$ some new polynuclear species were obtained, i.e. $[H_4Re_4(CO)_{15}]^{2-}$ [3,11], $[H_4Re_4(CO)_{13}]^{2-}$ [12], $[H_3Re_3(CO)_{10}]^{2-}$



$[H_4Re_4(CO)_{15}]^{2-}$

$[H_4Re_4(CO)_{13}]^{2-}$

$[H_3Re_3(CO)_{10}]^{2-}$

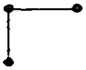
$[H_3Re_3O(CO)_9]^{2-}$

Fig. 3. New hydridocarbonyl clusters obtained starting from the reaction of $Re_2(CO)_{10}$ with methanolic KOH.

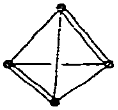
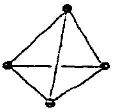
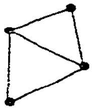
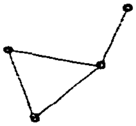
[13] and $[H_3Re_3O(CO)_9]^{2-}$ [13,14], whose structures are illustrated in Fig. 3. These species give further information which can be compared with the previously known data on this family of compounds. General features are: (i) the absence of bridging carbonyl ligands due to the long Re—Re interaction and (ii) the fact that all species obey the EAN formalism (see ref. 15 and refs. therein), as shown by Scheme 1.

SCHEME 1

Trimetal compounds

	Number of valence electrons 46	Number of electrons 48	Number of valence electrons 50
Metal atoms geometry			
Species	$[H_3Re_3(CO)_{10}]^{2-}$	$H_3Re_3(CO)_{12}$ $[H_2Re_3(CO)_{12}]^-$ $[HRe_3(CO)_{12}]^{2-}$ $[H_3Re_3O(CO)_9]^{2-}$	$HRe_3(CO)_{14}$

Tetrametal compounds

	Number of valence electrons	Number of electrons	Number of valence electrons	
	56	60	62	64
Metal atoms geometry				
Species	$H_4Re_4(CO)_{12}$*	$[H_6Re_4(CO)_{12}]^{2-}$ $[H_4Re_4(CO)_{13}]^{2-}$	$[Re_4(CO)_{16}]^{2-}$	$[H_4Re_4(CO)_{15}]^{2-}$

* Resonance of the double bonds.

Some comments on the Re—Re interactions (see Table 4) are as follows: an unbridged normal single bond has values in the range 2.96—3.04 Å. The presence of a bridging hydrido ligand causes a lengthening of the bond, the values ranging from 3.14 to 3.39 Å. The nature of a M—H—M bond has been widely discussed (see, for instance, refs. 24, 25, 26 and refs therein), the lenghtening being ascribed to the "protonation" of the M—M bond, which gives rise to a three-center two-electron bond. Longer bonds are associated with larger M—H—M angles. Moreover, the extent of the lengthening is related to intramolecular steric factors, as shown by Dahl et al. in comparing the $(CO)_5Re—H—Re(CO)_4$ fragments of VIII (Re—Re 3.39 Å, eclipsed disposition of the equatorial carbonyls) and

TABLE 4

Re—Re INTERACTIONS IN POLYNUCLEAR CARBONYL COMPOUNDS

Compound	Re—Re distances (Å)	Type of bonds [a]	Reference
I $Re_2(CO)_{10}$	3.02	Single, unbridged	16
II $Re_2(Ph_2Si)H_2(CO)_8$	3.121(2)	Single, ($SiPh_2$) bridged	17
III $H_2Re_2(CO)_8$	2.896(3)	Double, bis(μ_2-H)	18
IV $[H_2Re_3(CO)_{12}]^-$	3.173, 3.181(7)	Single, μ_2-H	19
	3.035(7)	Single, unbridged	
V $[HRe_3(CO)_{12}]^{2-}$	3.144	Single, μ_2-H	20
	3.004	Single, unbridged	
VI $[H_3Re_3O(CO)_9]^{2-}$	2.963, 2.973(1)	Single, μ_2-H, μ_3-O	13,14
VII $[H_3Re_3(CO)_{10}]^{2-}$	3.031(5)	Single, one μ_2-H, disordered on two bonds	13
	2.797(4)	Double, bis (μ_2-H)	
VIII $HRe_2Mn(CO)_{14}$	3.39	Single, μ_2-H, nearly linear Re—H—Re	21
IX $HRe_3(CO)_{14}$	3.295(2)	Single, μ_2-H	22
X $[H_6Re_4(CO)_{12}]^{2-}$	a 3.145—3.173(7)	Single, μ_2-H	5
	b 3.142—3.172(3)	Single, μ_2-H	this work
XI $H_4Re_4(CO)_{12}$	2.896—2.945(3)	Partially double, four μ_3-H	10
XII $[H_4Re_4(CO)_{13}]^{2-}$	3.026(5)—3.161(4) (av. 3.09)	Single, four μ_2-H, unclear assignment based on distances	12
XIII $[H_4Re_4(CO)_{15}]^{2-}$ (three crystal forms)	3.026 (av. on 3 values)	Single, unbridged	3,11
	3.195 (av. on 6 values)	Single, μ_2-H	
	3.287 (av. on 3 values)	Single, μ_2-H	
XIV $[Re_4(CO)_{16}]^{2-}$	2.956—3.024(7)	Single, unbridged	23

[a] Bond orders estimated by the EAN formalism.

of IX (Re—Re 3.295(2) Å, staggered disposition) [24]. Bond legnthening is, in the absence of direct evidence, a good source of information on location of the bridging hydridic atom. However, caution must be exercised. In compound II a rather long Re—Re distance was observed, which was not due to the presence of bridging hydrides but to intramolecular repulsions of the equatorial CO ligands which are eclipsed because of the Si-bridging [17]. Furthermore unsaturation causes shortening of the bonds, despite the presence of bridging H atoms, as in III, VII and XI. Finally the presence of other bridging ligands on the same metal—metal bond, as in compound VI, prevents the lengthening and sometimes makes it even shorter than a single unbridged bond, as recently illustrated by Churchill et al. by comparing several such structures [26]. A more certain indirect guide is, therefore, the analysis of the holes in the disposition of the ligands around the metal atom cluster.

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