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ISOLATION, REACTIONS AND X-RAY STRUCTURE OF TETRAETHYLAMMONIUM DIHYDRIDOTETRACARBONYLRHENATE

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Summary

The isolation and characterization of the novel hydridic compound $[NEt_4][H_2Re(CO)_4]$, obtained from the reaction of $Re_2(CO)_{10}$ with methanolic KOH, are described. Its reactions with I_2, strong acids, and ethanol are reported. The salt gives triclinic crystals, investigated by X-ray analysis, with cell constants $a = 14.493(6)$, $b = 7.564(3)$, $c = 7.930(3)$ Å, $\alpha = 72.97(4)°$, $\beta = 81.73(4)°$, $\gamma = 96.63(4)°$; space group $P\bar{1}$. The structure was solved by conventional Patterson and Fourier methods and refined by least-squares up to a final R value of 0.071, for 1586 independent counter data. The anion exhibits a distorted octahedral geometry, with the two hydrido ligands in *cis* position between themselves. The mean values of the Re—C and C—O distances are 1.89 and 1.21 Å. The carbonyl groups are significantly bent towards the hydrido ligands.

Introduction

In a previous paper [1] on the reactions of $Re_2(CO)_{10}$ in methanolic KOH we described the products obtained upon refluxing the solution for few minutes, namely the methoxo compound $[NEt_4][(CO)_3Re(OMe)_3Re(CO)_3]$, which is precipitated upon addition of a tetraethylammonium halide, and a hydridic species, formulated as $[NEt_4]_3[H_4Re_4(OMe)(CO)_{16}]$, obtained by evaporation of the mother liquor. This formulation, however, was not wholly satisfactory because it is difficult to propose a reasonable structure for the anion. Moreover, when the progress of the reaction is monitored by the change in the IR spectrum, variations of the relative intensities of the carbonyl bands were apparent. We have therefore reinvestigated the overall reaction process, and have found that our formulation of the hydrido compound was erroneous, and arose from the misleading analysis given by a mixture of nearly constant composition. The

TABLE 1

ANALYTICAL AND IR DATA

Compound		Colour	Elemental analysis: found (calcd.) %			IR ν(CO) (cm^{-1})
			C	H	N	
I	$[NEt_4][H_2Re(CO)_4]$	colourless	33.33(33.48)	5.20(5.01)	3.15(3.26)	2020vw, 1995w, 1930vs, 1895s [a]
II	$[NEt_4][(CO)_3Re(OMe)_3Re(CO)_3]$	cream	26.58(26.70)	3.61(3.80)	1.97(1.83)	1990s, 1875vs [a]
III	$[NEt_4][ReI_2(CO)_4]$	pale-yellow	21.23(21.11)	2.98(2.93)	2.08(2.05)	2100w, 2000vs, 1980m, 1925s [b]
IV	$H_3Re_3(CO)_{12}$	colourless	16.73(16.00)	0.79(0.67)		2090m, 2030vs, 2010s, 1985s [c]
V	$[NEt_4]_2[H_4Re_4(CO)_{15}]$	yellow	26.40(26.40)	3.30(3.00)	2.00(1.93)	2050w, 2000vs, 1960vs, 1950(sh), 1920m, 1890m, 1880(sh) [b]

[a] In dichloromethane solution. [b] In acetone solution. [c] In cyclohexane solution.

hydridic component of this mixture has now been proved to be the new monomeric diamagnetic anion $[H_2Re(CO)_4]^-$.

In this paper the isolation of pure $[NEt_4][H_2Re(CO)_4]$, its characterization, and some its reactions are described. The complete results of a single-crystal X-ray analysis are also reported. This is the second example of a structural investigation of a mononuclear complex containing carbonyl and hydrido ligands only, the first involving $HMn(CO)_5$ [2].

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 deuteroacetone 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. Analytical and IR data are reported in Table 1.

Tetraethylammonium dihydridotetracarbonylrhenate (I)

1 g of decacarbonyldirhenium was treated with 10 ml of methanolic potassium hydroxide solution (3 *N*) and refluxed for a short time (8 min). On addition of 10 ml of water, white crystals of unchanged $Re_2(CO)_{10}$ (42%) separated; these were filtered-off and, on addition of an excess of tetraethylammonium bromide (1.4 g, molar ratio 1/4.5) to the filtrate, cream-white crystals of $[NEt_4][(CO)_3Re(OMe)_3Re(CO)_3]$ (II) separated (ca. 20%). These were filtered-off, and the pale yellow solution was concentrated until white microcrystals separated; these were shown to be $[NEt_4][H_2Re(CO)_4]$ (I) (ca. 10%). By further evaporation of the mother liquor, mixtures of compounds I and II are obtained, until the precipitate contains only compound II. The filtered solution was evaporated to dryness; the residue was shown to contain CO_3^{2-} and $HCOO^-$. Compound I is soluble in acetone, dichloromethane, methanol, and ethanol.

Reactions of I

(a) With methanolic potassium hydroxide. 0.1 g of compound I were treated with 4 ml of methanolic potassium hydroxide (3 *N*). After stirring for 24 h, at room temperature, water (2 ml) was added to the solution in order to facilitate the precipitation. Cream-white crystals of $[NEt_4][(CO)_3Re(OMe)_3Re(CO)_3]$ (II) separated. The compound is soluble in acetone, dichloromethane, methanol, and ethanol.

(b) With iodine. 0.25 g of compound I were dissolved in ethanol (5 ml) and treated dropwise with an ethanolic solution of iodine (0.3 *M*) (molar ratio 1/1). The pale-yellow crystals which separated at room temperature after addition of hexane were shown to be $[Net_4][ReI_2(CO)_4]$ (III). The compound is soluble in acetone, ethanol and dichloromethane.

(c) With acids. 0.1 g of compound I were dissolved in ethanol (3 ml) and treated with an excess of ethanolic solution of $HClO_4$ (or HCl). On standing at room temperature, colourless crystals of $H_3Re_3(CO)_{12}$ (IV) were formed. The compound is sparingly soluble in cyclohexane, but insoluble in other common organic solvents.

TABLE 2

FINAL POSITIONAL AND THERMAL PARAMETERS [a,b]

A. ANISOTROPIC ATOMS

Atom	x	y	z	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
Re	2433(1)	1370(1)	426(1)	62(1)	20(2)	−62(2)	259(2)	−75(3)	137(2)
C(1)	1130(28)	1743(37)	638(31)	148(30)	−172(71)	−164(61)	267(62)	−86(86)	169(47)
O(1)	339(17)	1977(40)	683(31)	76(15)	149(60)	−138(47)	703(98)	−298(114)	324(56)
C(2)	2814(18)	2925(34)	−1960(31)	61(15)	−31(47)	−82(42)	258(55)	109(84)	163(48)
O(2)	3110(17)	3994(33)	−3485(28)	111(17)	67(53)	−59(44)	466(65)	−45(92)	252(47)
C(3)	2778(25)	3227(49)	1547(37)	111(24)	249(83)	−76(60)	416(91)	−63(116)	196(54)
O(3)	3089(19)	4373(34)	2183(33)	142(22)	−4(58)	−208(58)	445(66)	−499(114)	390(62)
C(4)	2230(28)	−813(76)	−111(43)	103(27)	545(135)	−127(68)	969(192)	−415(193)	266(68)
O(4)	2090(23)	−2409(38)	−326(42)	172(27)	183(72)	−182(75)	412(70)	−619(137)	566(91)

B. ISOTROPIC ATOMS

Atom	x	y	z	B (Å^2)	Atom	x	y	z	B (Å^2)
N(1)	5000	0	5000	3.6(4)	N(2)	0	5000	5000	3.8(4)
CT11	4647(39)	1227(74)	5999(71)	5.6(10)	CT21	674(43)	4153(82)	4302(81)	6.5(12)
CT12	4171(32)	−862(61)	4355(59)	4.5(8)	CT22	−46(45)	6930(86)	3668(84)	7.0(13)
CT13	5409(35)	−1547(65)	6327(65)	4.9(9)	CT23	−1061(38)	3707(72)	5530(71)	5.6(10)
CT14	5809(32)	942(61)	3458(60)	4.5(8)	CT24	80(44)	5212(82)	6779(81)	6.7(12)
CT15	4562(23)	−2264(44)	3288(44)	7.3(7)	CT25	−1202(26)	3445(49)	3555(49)	8.3(8)
CT16	5420(25)	2642(48)	2021(47)	8.0(8)	CT26	789(23)	2070(43)	5608(43)	7.1(7)

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

(d) With ethanol. To 0.5 g of compound I in 10 ml of ethanol at room temperature 1 ml of water (or hexane) was added. The yellow crystals which slowly separated on standing were shown to be $[NEt_4]_2[H_4Re_4(CO)_{15}]$ (V). The compound is soluble in acetone but insoluble in other common organic solvents.

Single-crystal X-ray data

$C_{12}H_{22}NO_4Re$, mol. wt. 430.5, colourless triclinic crystals, space group $P\bar{1}$ (No. 2), with cell constants a = 14.493(6), b = 7.564(3), c = 7.930(3) Å, α = 72.97(4)°, β = 81.73(4)°, γ = 96.63(4)°; U = 811.1 Å^3; D_m = 1.81(2) (by flotation), D_c = 1.76 g cm^{-3} for Z = 2, $F(000)$ = 416. Mo-K_α radiation, λ = 0.7107 Å, μ(Mo-K_α) = 79.2 cm^{-1}.

Intensity measurements

The intensity data were obtained from a very small crystal, mounted on a four-circle automatic diffractometer, by the $\theta - 2\theta$ method, with graphite monochromatized Mo-K_α radiation, in the interval $3° < 2\theta < 45°$. The total number of measured reflections was 2143. Two standard reflections, measured at regular intervals, showed a strong decay of the sample upon X-ray exposure (ca. 50% at the end of the collection). The integrated intensities were corrected for Lorentz, polarization and decay effects. After rejection of all data having $\sigma(I)/I > 0.30$, a set of 1586 independent reflections was used in the solution and refinement of the structure.

Determination of the structure

The structure solution was based on a three-dimensional Patterson map which showed the Re atom location. After a preliminary refinement of the rhenium parameters a successive difference-Fourier map revealed the positions of all the remaining non-hydrogen atoms. The $[NEt_4]^+$ cations were found to lie on inversion centres, and were thus disordered, with the four carbon atoms bound to the nitrogen atom doubled to give an approximate cube of half atoms, while the four external carbon atoms appear as two pairs correctly related by the inversion centre.

The refinement was carried out by full-matrix least-squares with all the anionic atoms treated anisotropically and the cationic atoms isotropically. The final values of the conventional R and R_w indices were 0.071 and 0.093, respectively. The observations were weighted according to the formula $w = 1/(A + BF_0 + CF_0^2)$, where A, B and C, in the final cycles of the refinement, had values 11.9, —0.46 and 0.011, chosen on the basis of an analysis of $\Sigma w\Delta^2$. The atomic scattering factors were taken from ref. 3; the rhenium factor was corrected both for the real and imaginary part of the anomalous dispersion [4].

The final difference-Fourier map revealed residual peaks, not exceeding 1.5 e^-/Å^3, close to the metal atom. In this map a peak was found, *trans* to CO(2), suitable for one of the hydridic hydrogens (Re—H ca. 1.8 Å), but in the position expected for the second one, *trans* to CO(1), only a rather broad residual peak was observed. Attempts to locate the hydridic atoms by the method of La Placa and Ibers [5] were unsatisfactory. We have therefore performed an indirect location through potential energy calculations, as previously described in the case of $ReH_2(NO)(PPh_3)_3$ [6]. The Re—H distance was assigned a value of 1.75

TABLE 3

INTERATOMIC DISTANCES AND ANGLES WITHIN THE ANION $[H_2Re(CO)_4]^-$

Distances (Å)					
Re—C(1)	1.93(4)	C(2)—O(2)	1.20(3)	C(1)···C(4)	2.78(6)
Re—C(2)	1.87(3)	C(3)—O(3)	1.20(5)	C(2)···C(3)	2.85(4)
Re—C(3)	1.93(4)	C(4)—O(4)	1.26(7)	C(2)···C(4)	2.74(5)
Re—C(4)	1.83(6)	C(1)···C(2)	2.82(4)		
C(1)—O(1)	1.18(5)	C(1)···C(3)	2.80(5)	H···C(*cis*) [a]	2.47
Angles (*deg.*)					
C(1)—Re—C(2)	96(1)	O(2)···Re···O(3)	96.2(6)	H(1)—Re—C(1)	179
C(1)—Re—C(3)	93(1)	O(2)···Re···O(4)	97.6(7)	H(1)—Re—C(2)	85
C(1)—Re—C(4)	96(2)	O(3)···Re···O(4)	160.8(8)	H(1)—Re—C(3)	86
C(2)—Re—C(3)	97(1)	Re—C(1)—O(1)	177(2)	H(1)—Re—C(4)	85
C(2)—Re—C(4)	96(1)	Re—C(2)—O(2)	176(2)	H(2)—Re—C(1)	91
C(3)—Re—C(4)	164(1)	Re—C(3)—O(3)	173(3)	H(2)—Re—C(2)	174
O(1)···Re···O(2)	96.2(6)	Re—C(4)—O(4)	174(3)	H(2)—Re—C(3)	82
O(1)···Re···O(3)	96.3(8)	H(1)—Re—H(2)	88	H(2)—Re—C(4)	84
O(1)···Re···O(4)	95.4(9)				

[a] Mean value.

Å; however, small variations of the distance have minor effects on the values of the derived bond angles (reported in Table 3).

The results of the refinements are reported in Table 2. 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.

Results and discussion

Isolation and characterization of $[NEt_4][H_2Re(CO)_4]$

When $Re_2(CO)_{10}$ is refluxed for a few minutes in methanolic KOH in the air it reacts as follows:

$$2\,Re_2(CO)_{10} + 3\,MeOH + 11\,OH^- \rightarrow [(CO)_3Re(OMe)_3Re(CO)_3]^- + 2[H_2Re(CO)_4]^- + 2\,CO_3^{2-} + 4\,HCOO^- + 3\,H_2O \qquad (1)$$

Reaction 1 is fast, and gives a mixture of the new hydridic species $[H_2Re(CO)_4]^-$ with the known μ-methoxo anion [7]. Upon addition of water the non-reacted $Re_2(CO)_{10}$ is precipitated, and can be filtered-off. The addition to the solution of a large excess of $[NEt_4]Br$ then causes precipitation of $[NEt_4][(CO)_3Re(OMe)_3Re(CO)_3]$ (II). At this stage concentration of the remaining solution gives a precipitate of $[NEt_4][H_2Re(CO)_4]$ (I). The first precipitate of I is pure, showing in the CO stretching region the IR spectrum depicted in Fig. 1A. Subsequent samples, obtained by further evaporation of the solution, show IR spectra which derive from the overlap of those in Fig. 1A and B, with increasing B character. The last precipitates exhibit pure B type spectra. These results imply a transformation of compound I. We have now found that I reacts in methanolic KOH at

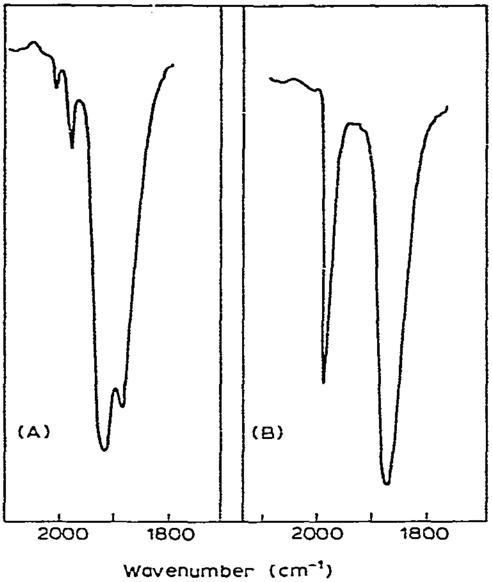

Fig. 1. IR spectra in CH_2Cl_2 of compounds I (A) and II (B).

room temperature to give compound II. The reaction is very probably the following:

$$2\ [H_2Re(CO)_4]^- + 4\ MeOH \xrightarrow{OH^-} [(CO)_3Re(OMe)_3Re(CO)_3]^- + 4\ H_2 + 2\ CO + MeO^- \quad (2)$$

Without heating the reaction is slow. The gaseous products have been recognized by GLC. The amount of H_2 evolved is in good agreement with the stoicheiometry, while that of CO is lower, possibly because it is partly transformed into CO_2 or, more likely, because it reacts in the strongly basic solution to give $HCOO^-$.

The isolation of pure compound I is, therefore, rather difficult both because it is produced in mixture and, because once formed it reacts as shown in eq. 2. Care must be taken to not heat the solution too long, otherwise the only product obtained is the μ-methoxo species.

The NMR spectrum of I in CD_3COCD_3 shows a singlet at τ 17.0, which remains unchanged upon variation of the temperature from −75°C to 40°C. The integration of this hydridic peak with respect to the cationic methylene hydrogen gave a ratio of 1/4.4, in agreement with the stoichiometry of the compound.

The IR spectrum in solution in the CO stretching region indicates a *cis* stereochemistry of the anion. Such a species, of C_{2v} symmetry, should give rise to four CO bands ($2A_1 + B_1 + B_2$) and two Re—H bands ($A_1 + B_1$). Four bands are observed (see Fig. 1A and Table 1), which are all very probably due to carbonyl modes. The isoelectronic species *cis*-$H_2M(CO)_4$, with M = Fe [8], Ru [9] and Os [10], show four principal CO bands and, in addition, one weak band at lower frequency, assigned to ν(M—H). In the present case we cannot assign Re—H bands; probably either they are too weak to be observed or they overlap with the other bands.

Some reactions of I have been carried out, in order also to confirm its formulation. It reacts with I_2, strong acids and ethanol according to the following equations:

$$[H_2Re(CO)_4]^- + I_2 \rightarrow [ReI_2(CO)_4]^- + H_2 \quad (3)$$

$$3\,[H_2Re(CO)_4]^- + 3\,H^+ \rightarrow H_3Re_3(CO)_{12} + 3\,H_2 \quad (4)$$

$$4\,[H_2Re(CO)_4]^- + 2\,EtOH \rightarrow [H_4Re_4(CO)_{15}]^{2-} + 3\,H_2 + CO + 2\,EtO^- \quad (5)$$

The products of these reactions were already known [11,12,1]; the gases evolved have been recognized by GLC. Reactions 4 and 5 show that $[H_2Re(CO)_4]^-$ has a

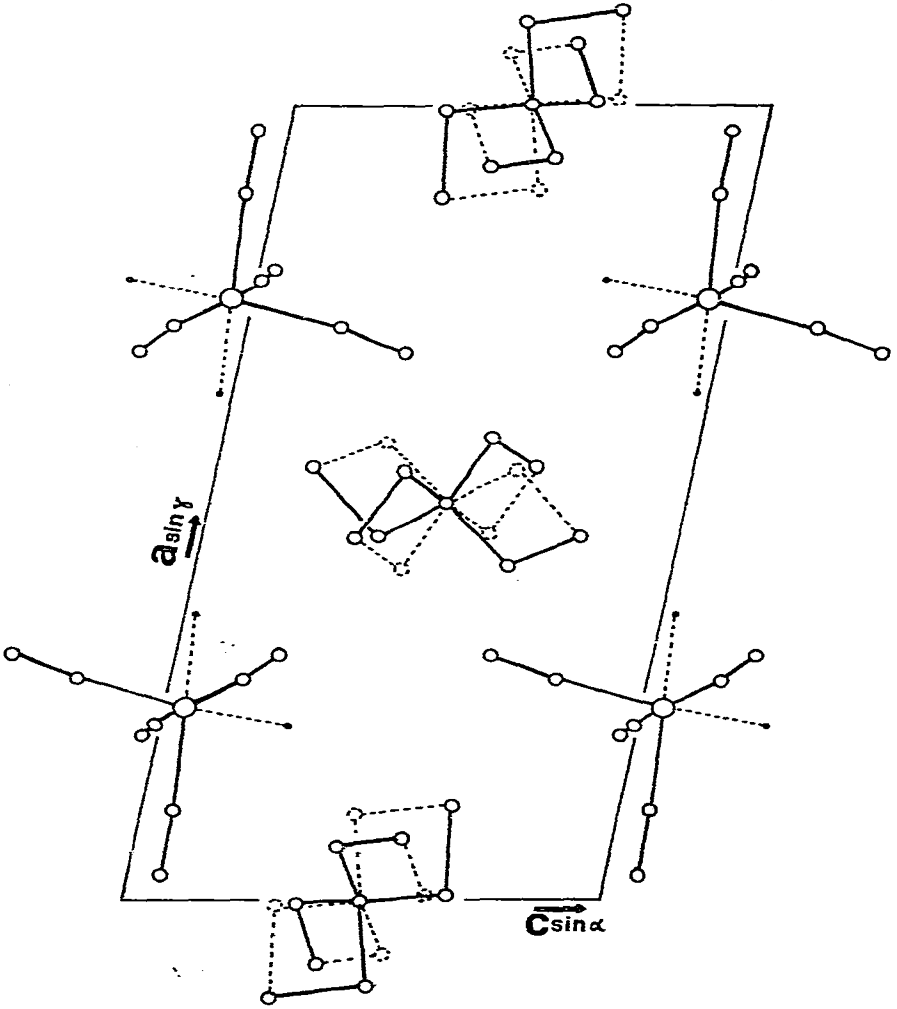

Fig. 2. Projection of the structure down the *b* axis.

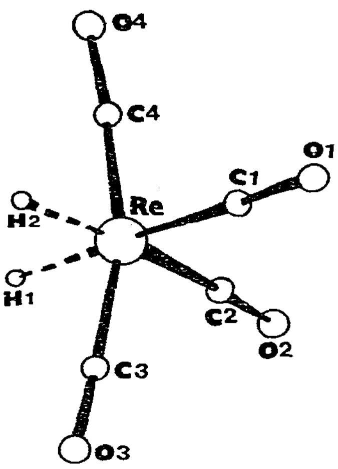

Fig. 3. A view of the anion $[H_2Re(CO)_4]^-$.

marked tendency to form metal atom cluster species. The anion reacts also in boiling ethanol, under N_2 atmosphere, to give the unsaturated species $[H_3Re_3(CO)_{10}]^{2-}$ [13] (yield of ca. 20%).

The crude product I, recrystallized from CH_2Cl_2/hexane upon cooling at ca. −20°C, gives colourless crystals (m.p. 73°C) suitable for X-ray analysis.

Description of the structure

The crystal structure of compound I consists of the packing of discrete cations and anions, as illustrated in Fig. 2. The cations are disordered, lying on inversion centres (see the Experimental part).

The anion $[H_2Re(CO)_4]^-$ is shown in Fig. 3. Interatomic distances and angles are reported in Table 3. The rhenium atom exhibits a distorted octahedral coordination, with the two hydrido ligands (themselves *cis*) and two carbonyl ligands lying in an equatorial plane, the other two CO groups being axial, and significantly bent towards the hydrido atoms. The idealized anion symmetry is C_{2v}.

The Re—C and C—O bond lengths have mean values, 1.89 and 1.21 Å, which are comparable with the corresponding interactions in other mononuclear carbonylrhenium complexes, e.g. 1.91, 1.14 Å in $Re(CO)_2(PPh_3)_2(S_2CH)$ [14], 1.85, 1.17 Å in $Re(CO)_2(PPh_3)_2(O_2CCH_3)$ [15], and 1.89, 1.16 Å in $[Re(CO)_3(B_9C_2H_{11})]^-$ [16]. The Re—C(equatorial) distances (mean 1.90 Å) do not differ significantly from the Re—C(axial) ones (mean 1.88 Å). The hydrido ligands (indirectly located, as described in the Experimental part) lie fairly well in the equatorial plane, containing Re, CO(1) and CO(2), nearly *trans* to the carbonyl groups (mean H—Re—C 176°), with a H—Re—H angle of 88°.

The carbonyl ligands are bent towards the hydrogen atoms, which have a low steric requirement, in order to reduce the non-bonded C···C interactions (mean C···C 2.80 Å). The mean values of the C—Re—C(*cis*) and H—Re—C(*cis*) angles are 96° and 85°, respectively. The largest deviation from the ideal octahedral geometry is shown by the C—Re—C axial angle, 164(1)° (O···Re···O 160.8(8)°). Similar distortions are usual in hydridic complexes; in $HMn(CO)_5$ the mean values of the C_{ax}—Mn—C_{eq} and C_{eq}—Mn—C_{eq}(*trans*) angles are 97° and 166°

[2]. In octahedral *cis*-dihydrido complexes a regular increase of the distortions is observed with increasing bulkiness of the other ligands [6]; thus in *cis*-$H_2Ru(PPh_3)_4$ the disposition of the four bulky phosphine ligands is close to a tetrahedral geometry [17].

Various polynuclear compounds, e.g. $H_2Re_2(CO)_8$, $[H_{3-x}Re_3(CO)_{12}]^{x-}$ (x = 0, 1, 2) and $[Re_4(CO)_{16}]^{2-}$, contain $Re(CO)_4$ units connected by metal—metal bonds. Structural data for these species indicate that the (OC)—Re—(CO) angles are generally close to the regular octahedral values; distortions are prevented by intramolecular contacts, mainly involving the CO groups bound to adjacent metal atoms. The anion $[H_4Re_4(CO)_{15}]^{2-}$ [1,18] formally derives from $[H_2Re_3(CO)_{12}]^-$ by substitution of an axial CO group with a monomeric $[H_2Re(CO)_4]^-$ anion. This apical $H_2Re(CO)_4$ moiety has C—Re—C bond angles quite similar to those of the free anion. The mean values of the C—Re—C(*cis*) and C—Re—C(*trans*) angles (in forms I and II) are 95° and 165°, respectively [18].

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