Journal of Organometallic Chemistry, 96 (1975) 259—264

A NEW CARBONYLHYDRIDORHENIUM CLUSTER

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(Received March 7th, 1975)

Summary

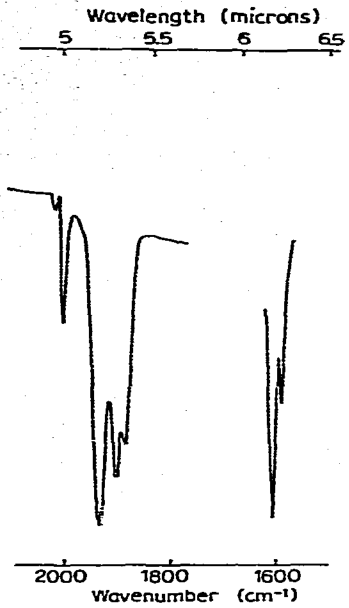
The preparation and properties of new polynuclear carbonylhydrido complexes $(NEt_4)_3[H_4Re_4(OCH_3)(CO)_{16}]$ (I) and $(NEt_4)_2[H_4Re_4(CO)_{15}]$ (II) are reported. Infrared and NMR spectra of these compounds are presented and discussed. The structure of compound II has been established by X-ray crystallographic analysis.

Introduction

The metal carbonyls are especially reactive towards methanolic potassium hydroxide, with which they give various compounds containing μ-alkoxo groups, hydridic hydrogen atoms, or cluster metal atoms [1]. We thought it likely that decacarbonyldirhenium might react with methanolic potassium hydroxide in a similar way, and indeed from the reaction mixture we have previously isolated some μ-alkoxo compounds [2]. However, we were more interested in obtaining cluster compounds, and we have now accomplished this as described below.

Results and discussion

The decacarbonyldirhenium is boiled for a short time with methanolic potassium hydroxide. Addition of a salt of bulky cation, such as $(NEt_4)I$, then gives an off-white, microcrystalline, diamagnetic compound, corresponding to $(NEt_4)_3$-$[H_4Re_4(OCH_3)(CO)_{16}]$ (I). This is an hydridocarbonyl electrolyte, which in the IR spectrum shows four bands in the C—O stretching region (Fig. 1, Table 1), and in the NMR spectrum (Table 2) gives a signal centered at τ 17.2 ppm, indicating the presence of hydridic hydrogen. In agreement with the proposed formula, the intensity ratio of the methoxyl, methylenic and hydridic hydrogens signals is 3/24/4. The compound I is very unstable in the solid state and in solu-



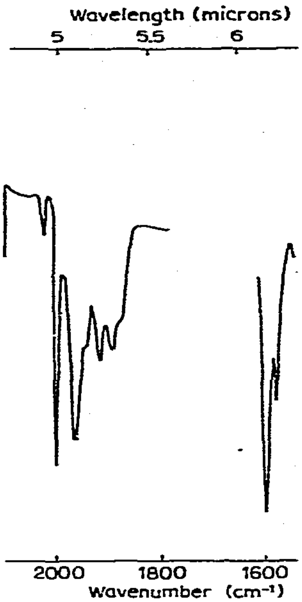


Fig. 1. IR spectrum of $[H_4Re_4(OCH_3)(CO)_{16}]^{3-}$ in acetone solution.

Fig. 2. IR spectrum of $[H_4Re_4(CO)_{15}]^{2-}$ in acetone solution.

TABLE 1

IR SPECTRA IN ACETONE

Compound	ν(C—O)
$(NEt_4)_3[H_4Re_4(OCH_3)(CO)_{16}]$ (I)	2000m, 1930s, 1900s, 1880m
$(NEt_4)_2[H_4Re_4(CO)_{15}]$ (II)	2050w, 2000vs, 1960s, 1920m, 1890m, 1880(sh)

TABLE 2

NMR SPECTRA IN DEUTEROACETONE AT 38°C

Compound	Proton resonance (τ ppm)	Relative intensity	Fine structure	Assignment
I	5.9	3	s	$-OCH_3$
	6.6	24	q	$-CH_2$
	17.2	4	s	Re—H
II	6.7	8	q	$-CH_2$
	20.57	1	(st)	Re—H
	26.93	1	s	Re—H—Re

tion, and we have been unable to determine its structure. We think that it is not a cluster compound, because there is no evidence of carbonyl or hydrogen bridging, and the large total number of electrons in the molecule is not consistent with a tetrahedral disposition of the rhenium atoms. Ethanol solutions of compound I gave on standing yellow crystals, corresponding to $(NEt_4)_2$-$[H_4Re_4(CO)_{15}]$ (II). This is also a hydridocarbonyl electrolyte, which in the IR spectrum shows several bands in the C—O stretching region (Fig. 2), and in the NMR spectrum shows two signals, one broad centered at τ 20.57, and one sharp centered at τ 26.93 ppm, indicating the presence of hydridic hydrogen atoms. The intensity ratio of the methylenic and hydridic hydrogen atoms is 8/1/1. It is clear that the four hydridic hydrogen atoms are not equivalent but that there were two groups of two equivalent atoms, respectively terminal (τ 20.57) and bridging (τ 26.93).

X-ray crystallographic analysis (which will be described in detail later) shows that compound II has two equivalent bridging hydrogen atoms in the plane of three rhenium atoms, which give rise to the signal at τ 26.93 ppm, with the other non-equivalent. They behave as equivalent nuclei in the NMR spectrum at τ 20.57 ppm probably because of rapid intramolecular exchange in solution. This exchange occurs at the relatively high temperature at which the spectrum is recorded, but it seemed likely that at lower temperatures it would be possible to detect by NMR the presence of two types of hydrogen as revealed by the X-ray structure. This was, indeed, the case; the broad signal at τ 20.57 ppm is split into two signals at —39°C, one at lower field (τ 15.04) characteristic of a terminal hydrogen, and one at higher field (τ 25.95 ppm) characteristic of a bridging hydrogen [3]. We decomposed compound II in boiling solvents which gave several other hydridocarbonyl cluster compounds which will be reported later.

Description of the structure

The structure of the anion $[H_4Re_4(CO)_{15}]^{2-}$ is shown in Fig. 3. The more

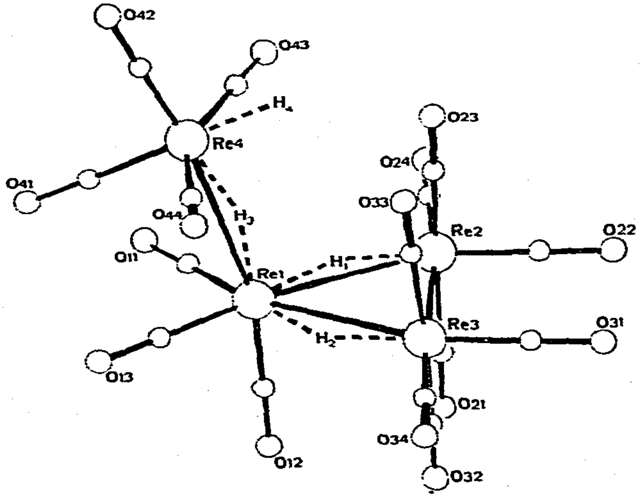


Fig. 3.

important bonding parameters are reported in Table 3. The metal-atom cluster is a novel arrangement consisting of an isosceles triangle of rhenium atoms, Re(1) Re(2) Re(3), with the fourth metal atom apically bound to Re(1) and lying in the plane perpendicular to the basal triangle and bisecting the Re(2)—Re(3) edge. This plane is approximately a symmetry plane for the whole anion, so that we can assign to it an idealized C_s symmetry. All fifteen carbonyl groups are terminally bound, four to each of the Re(2), Re(3) and Re(4) atoms and three to Re(1).

The hydridic hydrogen atoms were not directly located. Their positions can, however, be deduced from the values of the Re—Re distances and from the coordination geometries of the carbonyl groups. In the metal-atom triangle the Re(2)—Re(3) distance, 3.032(8) Å, has a value typical for a normal Re—Re single bond, very similar to the values found in $Re_2(CO)_{10}$ (3.02 Å) [4] and in $[Re_4(CO)_{16}]^{2-}$ (2.96-3.02 Å) [5]. The other two distances, Re(1)—Re(2) and Re(1)—Re(3) are markedly larger (3.192(8) and 3.211(8) Å respectively). This effect has been attributed to the presence of bridging hydrogen atoms on the two longer edges of the triangle. Comparable bond lengths have been found in

TABLE 3

BOND DISTANCES (Å) AND ANGLES (°) IN THE ANION $[H_4Re_4(CO)_{15}]^{2-}$

Bond distances	
Re(1)—Re(2)	3.192(8)
Re(1)—Re(3)	3.211(8)
Re(1)—Re(4)	3.288(9)
Re(2)—Re(3)	3.032(8)
Bond angles	
Re(2)—Re(1)—Re(3)	56.5(2)
Re(1)—Re(2)—Re(3)	62.0(2)
Re(1)—Re(3)—Re(2)	61.4(2)
Re(2)—Re(1)—Re(4)	103.6(2)
Re(3)—Re(1)—Re(4)	103.5(3)
Re(2)—Re(1)—C(11)	103(3)
Re(2)—Re(1)—C(12)	90(2)
Re(2)—Re(1)—C(13)	171(2)
Re(3)—Re(1)—C(11)	159(3)
Re(3)—Re(1)—C(12)	88(2)
Re(3)—Re(1)—C(13)	116(2)
Re(4)—Re(1)—C(11)	80(3)
Re(4)—Re(1)—C(12)	166(2)
Re(4)—Re(1)—C(13)	81(2)
C(11)—Re(1)—C(12)	92(4)
C(11)—Re(1)—C(13)	86(3)
C(12)—Re(1)—C(13)	86(3)
Re(1)—Re(2)—C(21)	89(2)
Re(1)—Re(2)—C(22)	158(2)
Re(1)—Re(2)—C(23)	91(2)
Re(1)—Re(2)—C(24)	111(1)
Re(3)—Re(2)—C(21)	91(2)
Re(3)—Re(2)—C(22)	96(2)
Re(3)—Re(2)—C(23)	86(2)
Re(3)—Re(2)—C(24)	173(1)
C(21)—Re(2)—C(22)	87(3)
C(21)—Re(2)—C(23)	177(3)
C(21)—Re(2)—C(24)	91(2)
C(22)—Re(2)—C(23)	92(3)
C(22)—Re(2)—C(24)	91(3)
C(23)—Re(2)—C(24)	92(2)
Re(1)—Re(3)—C(31)	149(2)
Re(1)—Re(3)—C(32)	88(2)
Re(1)—Re(3)—C(33)	92(3)
Re(1)—Re(3)—C(34)	122(2)
Re(2)—Re(3)—C(31)	87(2)
Re(2)—Re(3)—C(32)	86(2)
Re(2)—Re(3)—C(33)	97(2)
Re(2)—Re(3)—C(34)	174(2)
C(31)—Re(3)—C(32)	85(3)
C(31)—Re(3)—C(33)	97(4)
C(31)—Re(3)—C(34)	89(3)
C(32)—Re(3)—C(33)	177(3)
C(32)—Re(3)—C(34)	90(3)
C(33)—Re(3)—C(34)	88(3)
Re(1)—Re(4)—C(41)	82(3)
Re(1)—Re(4)—C(42)	173(2)
Re(1)—Re(4)—C(43)	87(2)
Re(1)—Re(4)—C(44)	92(2)
C(41)—Re(4)—C(42)	91(4)
C(41)—Re(4)—C(43)	105(3)
C(41)—Re(4)—C(44)	101(3)
C(42)—Re(4)—C(43)	95(3)
C(42)—Re(4)—C(44)	90(3)
C(43)—Re(4)—C(44)	154(3)

other hydridocarbonyl clusters in which edge-bridging hydrogens have been postulated, e.g. in $[H_6Re_4(CO)_{12}]^{2-}$ (3.160 Å, average of six values) [6], in $[H_2Re_3(CO)_{12}]^-$ (3.177 Å, average on two values) [7] and in $[HRe_3(CO)_{12}]^{2-}$ (3.144 Å) [8]. The bridging geometry for hydrogen ligands has been experimentally demonstrated in the X-ray structure of $H_3Mn_3(CO)_{12}$ [9].

The anion $[H_4Re_4(CO)_{15}]^{2-}$ can be formally derived from the anion $[H_2Re_3(CO)_{12}]^-$ by replacement of an axial CO ligand bound to Re(1) by a $[H_2Re(CO)_4]^-$ group. The geometries of the two metal triangles are strictly comparable and the dispositions of the carbonyl groups are also very similar, and show similar enlargement of the Re—Re—C_{eq} angles when the long hydrogen-bridged edges are involved, due to steric repulsions between H and CO ligands. Two hydridic hydrogen atoms must, therefore, be placed on the basal triangle plane, nearly *trans* to equatorial carbonyls (see Fig. 3), as also indicated by the structure of $H_3Mn_3(CO)_{12}$.

The Re(1)—Re(4) bond distance, 3.288(9) Å, is even longer than the two hydrogen-bridged triangular edges, but is shorter than the Re—Re distance in $HRe_2Mn(CO)_{14}$ (3.39 Å) for which a linear Re—H—Re bridge was suggested [10]. Another bridging hydrogen, associated with the Re(1)—Re(4) bond, is thus involved. The coordination geometry around the Re(4) atom clearly indicates the presence and location of the fourth hydridic hydrogen, terminally bound to the metal. Since hydrido ligands occupy definite coordination sites, their positions, when not directly known, have been assigned in many structures, e.g. in $[HW(OH)(CO)_3]_4$ [11], by inspection of bond angles among the other ligands. In the present case the disposition of the equatorial carbonyl groups CO(41), CO(43) and CO(44) shows that the hydrogen atom very probably lies *trans* to the CO(41) group, the C(43)—Re(4)—C(44) angle being much larger, 154(3)°, than the other two, 105(3)°, 101(3)°.

Because of the poor quality of the intensity data (see Experimental), the Re—C distances are too scattered (average 1.84 Å) and subject to too great uncertainties to be discussed in detail.

Experimental

IR spectra were recorded on a Beckman IR 33 spectrometer with Nujol mulls and acetone solutions (Table 1). NMR spectra were recorded on a Varian NV 14 instrument at 60 Mc/s, by using saturated solutions in deuterioacetone, with TMS as internal standard, at 38°C. The data and conditions of measurements are given in Table 2.

Tetraethylammonium tetrahydridoesadecacarbonyl-μ-methoxotetrarhenate (I)

1 g of decacarbonyldirhenium was treated with 10 ml of methanolic potassium hydroxide solution (3*N*), and refluxed for a short time (15 min). On addition of 5 ml of water, white crystals of unchanged $Re_2(CO)_{10}$ (42%) separated, these were filtered off, and 5 ml of methanolic tetraethylammonium iodide (400 mg in 5 ml of methanol), was added to the filtrate and the yellow solution was concentrated, until white crystals of $(NEt_4)[(CO)_3Re(OCH_3)_3Re(CO)_3]$ [2] separated (yield 36%). These were filtered off, and from the filtrate off-white microcrystals of $(NEt_4)_3[H_4Re_4(OCH_3)(CO)_{16}]$ (yield 14%) were obtained.

TABLE 4

ANALYTICAL DATA

Compound	Colour	M.p. (°C)	Analysis found (calcd.) (%)		
			C	H	N
I	Cream	62	30.4 (30.4)	4.40 (4.15)	2.78 (2.60)
II	Yellow	100 (dec.)	26.4 (26.4)	3.30 (3.00)	2.00 (1.93)

Tetraethylammonium tetrahydridopentadecacarbonyltetrarhenate (II)

To 0.5 g of compound I in 10 ml of ethanol at room temperature was added 1 ml of water. On standing, yellow crystals slowly separated, and were shown to be $(NEt_4)_2[H_4Re_4(CO)_{15}]$ (II) (40%). The compound is soluble in acetone but insoluble in other common organic solvents.

X-ray analysis

The compound $(NEt_4)_2[H_4Re_4(CO)_{15}]$, $M = 1430.8$, gives yellow monoclinic crystals. The crystal data are: $a = 11.60(1)$, $b = 20.68(2)$, $c = 17.97(2)$ Å, $\beta = 95°54'(6')$, $U = 4287.9$ Å^3, $Dm = 2.20(2)$, $Dc = 2.22$ g/cm^3, $Z = 4$, Mo-K_α radiation $\lambda = 0.7107$ Å, μ(Mo-K_α) = 119.9 cm^{-1}. Space group $P2_1/c$ (No. 14) from systematic absences.

The intensity data were collected on a Pailred linear equi-inclination diffractometer by the ω-scan technique at a rate of 2.5° min^{-1} (scan ranges 2.8-3.4°) with background counts of 24 sec on each side of the scan range. Measurements were made in the reciprocal lattice levels $0kl$—$7kl$ within the limit $2\vartheta \leqslant 46°$, giving a total of 4402 collected reflections. Three standard reflections were measured at the end of each layer collection and showed a strong decay of the crystal upon X-ray irradiation (more than 60% during the whole data collection). The integrated intensities were corrected for Lorentz, polarization, absorption and decay effects. A final set of 777 independent reflections, all having $\sigma(I)/I \leqslant 0.30$, was used in the solution and refinement of the structure. The structure solution was based on Patterson and Fourier methods. The refinements were carried out by the least-squares method with the carbonyl groups constrained in a linear Re—C—O geometry, with a fixed C—O distance of 1.16 Å. Anisotropic thermal factors were assigned to the rhenium atoms. The value of the conventional R factor is 0.087.

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