SYNTHESIS AND CHARACTERIZATION OF THREE HYDRIDOCARBONYLRHENIUM CLUSTERS

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Summary

We describe three new hydridocarbonylrhenium cluster anions, isolated as tetraethylammonium salts, viz. the triangular $[H_3Re_3(CO)_{10}]^{2-}$, the tetrahedral $[H_4Re_4(CO)_{13}]^{2-}$ and the triangular $[H_3Re_3(\mu_3\text{-}O)(CO)_9]^{2-}$. These are obtained by decomposition of the hydride $[H_4Re_4(CO)_{15}][NEt_4]_2$ in boiling ethanol under different conditions. The reactions also yield the known species $[H_2Re_3(CO)_{12}]^-$ and $[H_6Re_4(CO)_{12}]^{2-}$ as tetraethylammonium salts.

Introduction

The reaction of metal carbonyls with bases is a well known route to hydrido-metal clusters [1]. Although the first hydridorhenium clusters were synthesized in a different way [1], we have shown [2,3,4] that many hydridocarbonylrhenium clusters can be obtained from the reaction of decacarbonyldirhenium with potassium hydroxide in methanol.

The reaction of $Re_2(CO)_{10}$ with KOH in boiling methanol for 15 min gives a hydridic product (NMR τ 17), which was isolated as the tetraethylammonium salt, and suggested in a previous paper [2] to have the formula $[H_4Re_4\text{-}(OCH_3)(CO)_{16}][NEt_4]_3$. We have now found that it is a mixture A of two carbonyl compounds, which however we have so far been unable to separate, containing a new hydridocarbonyl species (τ 17), which is at present under investigation [5]. The solution of A in ethanol is not stable, and on standing gives yellow crystals of the known compound [2,6] $[H_4Re_4(CO)_{15}][NEt_4]_2$ (I). Reaction of $Re_2(CO)_{10}$ with KOH in boiling methanol for 6 h on the other hand, gives $[H_6Re_4(CO)_{12}]^{2-}$ [7], the structure of which has been previously determined [8].

The unusual structural features of compound I induced us to study its reactions with solvents and acids. We describe here its decomposition in boiling

ethanol to give three new carbonylhydridorhenium compounds. A preliminary account has already appeared [3,4].

Results and discussion

The decomposition of tetrahydridopentadecacarbonyltetrarhenate dianion, in boiling ethanol under various conditions give the results summarized in Scheme 1. Refluxing of $2 \times 10^{-2} M$ solutions of I in ethanol under nitrogen

SCHEME 1

i In ethanol, about 2×10^{-2} M under nitrogen atmosphere
ii In dilute ethanol solution under nitrogen atmosphere
iii In dilute ethanol solution in air
iv In aceton solution under oxygen atmosphere
(a) the compound separates from hot solution
(b) the compound separates after cooling under nitrogen atmosphere
(c) compounds present in the mother liquor
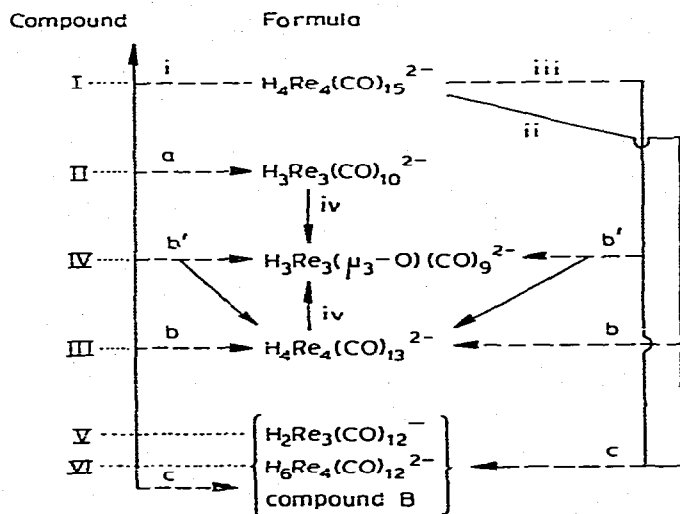
leads to separation of red crystals of $[H_3Re_3(CO)_{10}][NEt_4]_2$ (II). After cooling, the mother liquor gives an orange precipitate of $[H_4Re_4(CO)_{13}][NEt_4]_2$ (III). Both compounds II and III are obtained in very poor yields. However under different conditions the compound II is not obtained.

When cooling is carried out in the air, after several hours, a mixture was formed of compound III and of colourless crystals of $[H_3Re_3(\mu_3\text{-}O)(CO)_9]$-$[NEt_4]_2$ (IV). From the mother liquor, we have in both cases isolated successively, as tetraethylammonium salts, two known hydridocarbonyl cluster anions, $[H_2Re_3(CO)_{12}]^-$ (V) [9] and $[H_6Re_4(CO)_{12}]^{2-}$ (VI) [7], and a unknown species (B) which shows a signal at τ 21 in the NMR spectrum, and which is under investigation.

Much better yields of compound III are obtained when I is boiled in ethanol. In presence of air we also obtained compound IV.

Acetone solutions of compounds II and III in air slowly give the compound IV: these reactions are speeded up if the solutions are refluxed in an oxygen atmosphere.

In view of the easy transformation of the mixture A into compound I in cold ethanol and the subsequent conversion of I into II on boiling, we tried the direct reaction of A with boiling ethanol. Using a concentrated solution, under nitrogen we obtained the compound II in very good yield, probably because it is produced without the intermediate formation of compound I. In contrast the same reaction in dilute solution, gives only compound III in very poor yield; in the presence of oxygen, compound IV is also formed.

Compound III gives two crystalline forms having identical IR and NMR spectra and analytical data: the first, yellow-orange, is monoclinic and its structure has been determined by X-ray diffraction methods; the second, which is orange, is cubic and disordered, so that X-ray determination of the structure is impossible.

Properties

All these compounds are readily soluble in acetone and in nitrobenzene, and little or not at all (as in the case of compound II) soluble in ethanol, and insoluble in water or non-polar organic solvents. They can be easily recrystallized from acetone and ethanol. They are diamagnetic; their melting points and their molar conductibilities are listed in Table 1. The latter are consistent with the anionic charges.

Compound IV appears to be indefinitely stable in air as the solid, while compounds II and III undergo slow decomposition.

Structures

The structure of these compounds have been determined by X-ray diffraction methods and reported previously [3,4,6]. The anions are illustrated in Fig. 1. The positions of the hydrogen atoms were based on the positions of the other ligands and the NMR spectra (as discussed later). The anion II is an example of an electron deficient triangular cluster compound (46 valency electrons) comparable to the isoelectronic species $H_2Os_3(CO)_{10}$ [10], and requires the presence of a metal—metal double bond, which can be localized between the two rhenium atoms bearing three CO ligands, which show a Re—Re distance of only 2.797 Å.
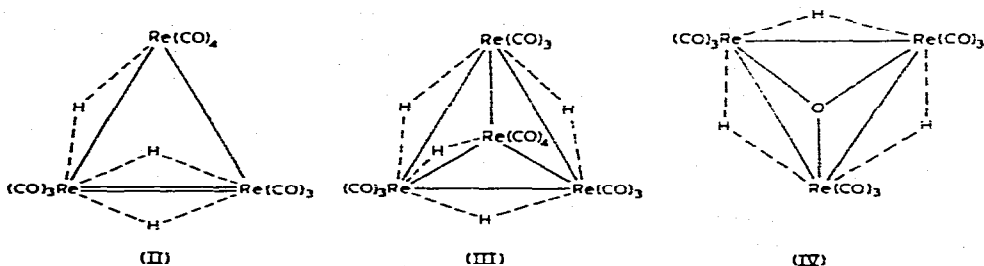

Fig. 1. The structure of the three hydridocarbonylrhenium clusters.

TABLE 1

ANALYTICAL DATA

No.	Compound	Colour	M.p. (°C)	Λ_M (ohm^{-1} cm^2 mol^{-1})	Analysis found (calcd.) (%)			
					C	H	N	O
II	$[H_3Re_3(CO)_{10}][NEt_4]_2$	Red	183	196	27.59 (28.33)	3.46 (3.90)	2.38 (2.54)	14.56 (14.35)
III	$[H_4Re_4(CO)_{13}][NEt_4]_2$	Orange	274	—	24.96 (25.00)	3.13 (3.15)	2.15 (2.09)	
IV	$[H_3Re_3(\mu_3\text{-}O)(CO)_9][NEt_4]_2$	Colourless	214	178	27.43 (27.92)	3.81 (4.00)	2.43 (2.51)	

The anion III is electron complete (60 valencey electrons) and contains a tetrahedral rhenium atoms cluster. The carbonyl groups are all terminally bonded (differently from the related species $H_2Ru_4(CO)_{13}$ [11]). The six Re—Re distances are rather scattered and do not fall into two classes which might indicate the positions of bridging hydrogen atoms. The locations depicted in Fig. 1 are deduced from steric considerations and agree with the NMR spectrum (see later).

The anion IV is also electron complete (48 valency electrons) and possesses an overal idealized C_{3v} symmetry. The disposition of the carbonyl groups implies that the hydrido ligands are on the opposite side of the Re_3 plane from the μ_3-ligand. The Re—Re bonds are normal single bonds, not lengthened by the bridging hydrogen ligands. Similar behaviour is found in other molecules with μ_2 or μ_3 bridging ligands on the same metal—metal bond [12,13], probably because any lengthening would lead to too weak metal—ligand bonds.

IR spectra

Spectra data for the region 1700—2200 cm^{-1} (in acetone) are shown in Table 2. No bands due to bridging carbonyl groups are observed.

The complex nature of the spectrum of compound II in the carbonyl stretching mode region, indicates that the compound has a low symmetry, as in the structure depicted in Fig. 1. The spectrum shows some resemblance to that of the isoelectronic species $H_2Os_3(CO)_{10}$ [14], whose bands, however, appear at higher wave numbers, as expected for a neutral compound.

The relative simplicity of the spectrum of the compound III, might indicate an higher symmetry in solution, than that shown in solid state by the X-ray analysis, and the presence of undedected very weak or superposed bands must be assumed.

The simplicity of the spectrum of the compound IV in the region of carbonyl stretching modes indicates a structure of C_{3v} symmetry, like that shown by the X-ray investigation. In order to find bands due to Re—O stretching modes, we scanned the sample, in nujol mull, in the region below 1200 cm^{-1}. No band is present in the usual Re—O stretching region. However the oxygen atom in the compound IV is triply-bridging to the rhenium atoms, so that the Re—O bonds are weaker than in compounds in which an oxygen atom is bonded to only one rhenium atom (Re—O in the range 912—985 cm^{-1} [15]) and they are even weaker than in complexes with a doubly-bridging oxygen atom. For these Re—O—Re species the ν_{as} band can be as low as 720 cm^{-1}, while the ν_s band is localized at about 200 cm^{-1} [15].

The $Re_3(\mu_3\text{-O})$ groups in compound IV have C_{3v} symmetry, so that we ex-

TABLE 2

IR SPECTRA IN ACETONE

Compound	ν(C—O)
II	1990m, 1955m, 1920s, 1880m, 1860(sh)
III	2000s, 1980s, 1910s(br)
IV	1980s, 1800s.

pect two absorption bands at very low frequencies. Tentatively we can attribute to the ν_{as} and ν_s, respectively, the two bands at 715m cm^{-1} and 680s cm^{-1} or, alternatively, we can attribute to the ν_{as} one of these bands and to ν_s one of the eight bands in the region 650—440 cm^{-1} (which are due mainly to the ν(Re—C) and to the δ(Re—C—O).

NMR spectra

The NMR peaks are listed in Table 3, with the relative intensities and the main assignements.

The high field spectrum of compound II exhibits two single sharp resonances; from the intensity ratio we deduce that there are three hydridic hydrogens, two of which are equivalent, in accordance with the structure shown in Fig. 1. The intensity ratio is also in agreement with structures in which only one hydrogen atom bridges the Re—Re double bond, while the other two bridge the normal Re—Re bonds. However the type of disorder observed in X-ray analysis, together with steric considerations, seem to exclude this possibility

The low τ value of these bridging hydrides is caused by the unsaturation of the compound. Similar low values are found in $H_2Re_2(CO)_8$ [16] (τ 19.04 in CDCl$_3$) and in $H_2Os_3(CO)_{10}$ [8] (τ 20.9 in CDCl$_3$).

The intensity ratio of the two sharp singlets at high field in the NMR spectrum of compound III agrees with the structure depicted in Fig. 1. However the integrations of these signals are not in very good agreement with these calculated probably because of the difficulty of obtaining a large quantity of pure compound III.

The NMR spectrum of compound IV exhibits at high field, only one, rather broad, signal, whose integration with respect to the cationic methylene hydrogens agrees with the stoichiometry. The NMR signal for these hydrides is the lowest ever found for such bridging ligands on a Re—Re single bond. In some hydridocarbonyls of ruthenium ($H_2Ru_4(CO)_{13}$ and $H_4Ru_4(CO)_{12}$) the bridging hydrogen atoms give signal at even lower values (τ 19.1 and τ 18.6 respectively, in CDCl$_3$), confirming that the correlation between chemical shift and position of hydrogen atoms (terminal or bridging) must be regarded with caution [17].

We have thought that this broad hydridic signal at an unusual position might arise in solution from a rapid interchange of the hydrogen atoms between ter-

TABLE 3

NMR SPECTRA IN DEUTEROACETONE

Compound	Proton resonance (τ. ppm)	Relative intensity	Fine structure	Assignment
II	6.7	16	q	—CH$_2$
	18.4	2	s	Re—H—Re
	21.1	1	s	Re—H—Re
III	6.7	16	q	—CH$_2$
	26.7	3	s	Re—H—Re
	27.3	1	s	Re—H—Re
IV	6.7	16	q	—CH$_2$
	22.8	2.3	s(br)	Re—H—Re

minal and bridging locations. If this was the case, a NMR spectrum at lower temperature would give a sharp signal at another chemical shift value, corresponding either to a terminal or to a bridging hydride. However, at low temperature ($-90°C$) we do observe a sharper signal, but in the same position, while at higher temperature (in $C_6D_5NO_2$) the signal becomes broader, up to 140°C, at which the compound decomposes.

Experimental

IR spectra were recorded with a Beckman IR 33 spectrometer in acetone and in Nujol mulls in the region 4000—600 cm^{-1}, and with a Perkin—Elmer mod. 621 in the range 600—250 cm^{-1}. NMR spectra were recorded at 38°C on a Varian NV 14 instrument at 60 MHz, with saturated solutions in deuteroacetone containing TMS as internal standard.

Tetraethylammonium trihydridodecacarbonyltrirhenate (II)

(a) Compound I (0.5 g) in 15 ml of ethanol is refluxed for 3 h under N_2. A red precipitate of compound II (about 5 mg) is formed in the hot solution. The mother liquors are decanted, and the precipitate is washed with boiling ethanol and then with hexane, and finally dried in vacuo.

(b) Much improved yields are obtained starting from the mixture A obtained as described in ref. [2]. 0.5 g of this mixture in 8 ml of ethanol are refluxed for 3 h under N_2. A red precipitate of compound II separates from the hot solution. The mother liquors are separated, concentrated to about 5—6 ml and refluxed over night under N_2. A further precipitate of compound II is isolated (120 mg), and the combined samples are washed with boiling ethanol and then with hexane, and dried in vacuo.

Tetraethylammonium tetrahydridotridecacarbonyltetrarhenate (III)

(a) Compound I (0.5 g) in 30 ml of ethanol is refluxed for 3 h under N_2. The solution turns orange, and on cooling still under N_2, gives an orange precipitate of compound III (about 5 mg). The mother liquors are decanted and the compound is washed with ethanol and then with hexane, and dried in vacuo.

(b) Compound III can also be obtained, in similarly very low yields, starting from mixture A (0.5 g in 25 ml of ethanol): the procedure is the same.

Tetraethylammonium trihydrido-μ_3-oxoenneacarbonyltrirhenate (IV)

(a) Compound I (0.5 g) in 30 ml of ethanol is refluxed for 3 h in air. Slow cooling precipitates a mixture of compounds III and IV, which is washed with ethanol and hexane and dried in vacuo. The components are then separated by hand. The yields of compound IV are small.

(b) Compound IV can also be obtained starting from mixture A (0.5 g in 25 ml of ethanol): the procedure and the yields are the same.

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