REACTIONS OF THE UNSATURATED ANIONS [H$_3$Re$_3$(CO)$_{10}$]$^{2-}$ AND [H$_4$Re$_3$(CO)$_{10}$]$^-$ WITH IODINE IN VARIOUS SOLVENTS. X-RAY CHARACTERIZATION OF THE DERIVATIVE H$_3$Re$_3$(CO)$_{10}$(py)$_2$

G. CIANI, G. D'ALFONSO, M. FRENI, P. ROMITI and A. SIRONI

Centro di Studio per la Sintesi e la Struttura dei Composti dei Metalli di Transizione nei Bassi Stati di Ossidazione del C.N.R., Istituto di Chimica Generale ed Inorganica, Via G. Venezian 21, 20133 Milano (Italy)

Summary

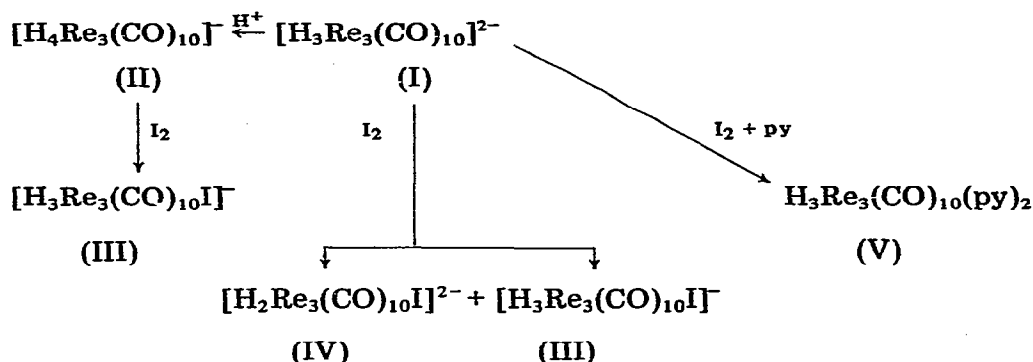Treatment of [H$_3$Re$_3$(CO)$_{10}$](NEt$_4$)$_2$ (I) with acids gives [H$_4$Re$_3$(CO)$_{10}$](NEt$_4$) (II) which is unsaturated, like the parent compound I. Both I and II react with iodine in ethanol; I gives a mixture of two saturated species [H$_3$Re$_3$(CO)$_{10}$I]-(NEt$_4$) (III) and [H$_2$Re$_3$(CO)$_{10}$I](NEt$_4$)$_2$ (IV), while II gives only compound III. If the same reactions are carried out with iodine in pyridine, crystals of the saturated non-electrolyte compound H$_3$Re$_3$(CO)$_{10}$(py)$_2$ (V) are obtained. The results of an X-ray analysis show that the latter species contains an equilateral metal atom triangle with long hydrogen-bridged Re—Re bonds of mean length 3.292 Å.

Introduction

We recently reported the synthesis and structure of two unsaturated anions, the red [H$_3$Re$_3$(CO)$_{10}$]$^{2-}$ (I) [1,2] and the yellow [H$_4$Re$_3$(CO)$_{10}$]$^-$ (II) [3], as tetraethylammonium salts. The latter is obtained by treating compound 1 with strong acids, and the reaction is not reversed on treatment of II with a strong base [3]. Both anions I and II are examples of electron deficient triangular cluster compounds (46 valency electrons), comparable to the isoelectronic species H$_2$Os$_3$(CO)$_{10}$ [4], and show the presence of a metal—metal double bond, which is located between the two rhenium atoms bearing three carbonyl ligands. For this reason both of these species might be more reactive toward nucleophiles than most hydrido-carbonyl clusters. However they do not seem to react easily with ligands such as CO and triphenylphosphine, but react readily with iodine in many solvents (benzene, hexane, ethanol) at room temperature to give iodide complexes. The nature of these reactions and of the products is discussed below.

Results and discussion

The reactions to be described below are represented by the following scheme:

$$[H_4Re_3(CO)_{10}]^- \overset{H^+}{\rightleftharpoons} [H_3Re_3(CO)_{10}]^{2-}$$

$$(II) \qquad\qquad (I)$$

$$\downarrow I_2 \qquad\qquad I_2 \qquad\qquad I_2 + py$$

$$[H_3Re_3(CO)_{10}I]^- \qquad\qquad\qquad\qquad H_3Re_3(CO)_{10}(py)_2$$

$$(III) \qquad\qquad\qquad\qquad\qquad\qquad\qquad (V)$$

$$[H_2Re_3(CO)_{10}I]^{2-} + [H_3Re_3(CO)_{10}I]^-$$

$$(IV) \qquad\qquad (III)$$

Dropwise addition of an equimolar amount of an ethanolic I_2 solution (0.1 M) to compound I in ethanol causes immediate change in the colour of the iodine solution from brown to yellow, followed by dissolution of the red compound I. No gas is evolved. On removing the solvent, a mixture of two compounds is obtained, and the ^1H NMR spectrum of the mixture shows four sharp singlets at high field. Two of these signals (τ 22.2 and 25.7) are due to compound III, which is also obtained as the sole product from the reaction of compound II with ethanolic I_2. The other two hydridic signals (τ 22.1 and 23.5) can be assigned to a second species of probable formulation $[H_2Re_3(CO)_{10}I]^{2-}$ (IV), which we were not able to isolate in the pure state. The reaction is probably:

$$2[H_3Re_3(CO)_{10}]^{2-} + 2\ I_2 \rightarrow [H_3Re_3(CO)_{10}I]^- + [H_2Re_3(CO)_{10}I]^{2-} + H^+ + 2\ I^- \quad (1)$$
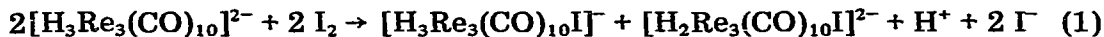
In the hope of obtaining compound IV only, according to reaction 2,

$$[H_3Re_3(CO)_{10}]^{2-} + I_2 \rightarrow [H_2Re_3(CO)_{10}I]^{2-} + H^+ + I^- \qquad\qquad (2)$$
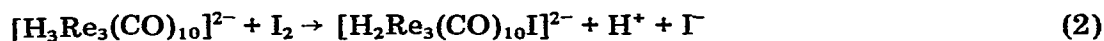
the iodine addition was carried out in presence of a substance with more basic properties than the parent anion I. Thus we treated compound I in ethanol with a solution of iodine in pyridine, but we isolated a crystalline non-electrolyte corresponding to $H_3Re_3(CO)_{10}(py)_2$ (V) (py = pyridine). The probable reaction is:

$$[H_3Re_3(CO)_{10}]^{2-} + I_2 + 2\ py \rightarrow H_3Re_3(CO)_{10}(py)_2 + 2\ I^- \qquad\qquad (3)$$

Compound V gives crystals which have been investigated by X-ray diffraction (see below).

When compound II is treated dropwise with an ethanolic solution (0.1 M) of iodine (molar ratio 1 : 1), a change of colour of the iodine solution takes place, followed by dissolution of the yellow compound II. No gas evolution occurs. On dropwise addition of water, yellow crystals separate in good yield, and these correspond to $[H_3Re_3(CO)_{10}I](NEt_4)$ (III). The reaction is:

TABLE 1

ANALYTICAL DATA

No.	Compound	Colour	M.p. (°C)	Analysis: found (calcd.) (%)			
				C	H	N	I
II	[$H_4Re_3(CO)_{10}$](NEt$_4$)	yellow	199	22.0(22.2)	2.5(2.46)	1.5(1.44)	—
III	[$H_3Re_3(CO)_{10}$I](NEt$_4$)	pale-yellow	222	19.3(19.6)	2.1(2.09)	1.3(1.27)	11.4(11.54)
V	$H_3Re_3(CO)_{10}$(py)$_2$	pale-yellow	175	24.2(24.0)	1.4(1.29)	2.7(2.79)	—

356

$$[H_4Re_3(CO)_{10}]^- + I_2 \rightarrow [H_3Re_3(CO)_{10}I]^- + H^+ + I^- \tag{4}$$
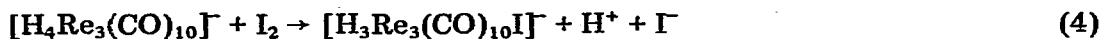
Unfortunately compound III does not give crystals suitable for an X-ray investigation.

Properties

Compounds II, III and V are yellow, readily soluble in acetone, sparingly soluble in ethanol and insoluble in water and in non-polar organic solvents. They can be readily recrystallised from actone and ethanol. They are diamagnetic. Their melting points and analytical data are listed in Table 1. They appear to be quite stable in air in the solid state, but in solution they undergo very slow decomposition.

IR and NMR spectra

IR data for the region 1700—2200 cm^{-2} (in acetone) are shown in Table 2. No bands due to bridging carbonyl groups are observed. The complex nature of the spectra of these compounds in the CO stretching region indicates that they have a low symmetry, as is the case with I [1] and II [3].

The NMR peaks are listed in Table 3, with the relative intensities and the main assignments. The high field spectrum of compound II exhibits two single sharp resonances; from the intensity ratio we deduce that the numbers of the two types of hydridic hydrogen atoms are equal. The formation of II from I with acids, which occurs without gas evolution, agrees with its formulation, and the X-ray structure has shown the probable location of the four hydridic hydrogens [3]. The low τ values of these bridging hydride atoms are very close to those of the parent compound I and seem to be caused by the unsaturation of these species.

The intensity ratio (1 : 2) of the two sharp singlets at high field in the NMR spectrum of compound III agrees with the proposed structure depicted in Fig. 1. It has a bridging iodine atom bonded to the two previously unsaturated rhenium atoms, giving a triangular cluster with three Re—Re single bonds (48 valency electrons). The τ values of the bridging hydride ligands are higher than those of the parent compound II, in accord with the assumed absence of unsaturation.

The intensity ratio (1 : 1) of the two sharp singlets assignable to compound IV in the high field NMR spectrum of the mixture of III and IV is consistent with a structure having two non-equivalent hydrogen atoms.

The NMR spectrum of compound V shows the peaks of the pyridine ligands

TABLE 2

IR SPECTRA IN ACETONE

Compound	ν(C—O)
II	2090w, 2025m, 1998vs, 1948m, 1915s
III	2100vw, 2040sh, 1995vs, 1945m, 1930m, 1905s
IV [a]	2100vw, 2040sh, 1995vs, 1945m, 1930m, 1905s, 1865m
V	2100w, 2022vs, 1995s, 1960m, 1925s

[a] Mixture of compounds III and IV.

TABLE 3

NMR SPECTRA IN DEUTEROACETONE

Compound	Proton resonance (τ, ppm)	Relative intensity	Fine structure	Assignment
II	6.48	8	q	—CH₂—
	18.5	1	s	Re—H—Re
	23.4	1	s	Re—H—Re
III	6.48	8	q	—CH₂—
	22.1	1	s	Re—H—Re
	25.6	2	s	Re—H—Re
IV ᵃ	6.48	24	q	—CH₂—
	22.0	1	s	Re—H—Re
	22.1	1	s	Re—H—Re
	23.4	1	s	Re—H—Re
	25.6	2	s	Re—H—Re
V	0.94			CH (py)
	2.03			CH (py)
	2.40			CH (py)
	19.24	1	s	Re—H—Re
	23.00	2	s	Re—H—Re

ᵃ Mixture of compounds III and IV.

at low field and two sharp singlets (intensity ratio 1 : 2),at high field, due to three hydrido ligands, in agreement with the X-ray structure (see below). The τ values however are very low for bridging hydrides in a triangular cluster with three Re—Re single bonds (48 valency electrons); the possibility of structures different for this species in solution and in the solid state cannot be excluded.

Structure of the species $H_3Re_3(CO)_{10}(py)_2$

A view of the compound is shown in Fig. 2. It contains a nearly equilateral Re₃ triangle, with one metal atom, Re(1), connected to four terminal CO groups and the other two metal atoms bearing three terminal CO and one N-bonded pyridine ligand. The two pyridine molecules are linked in axial direc-
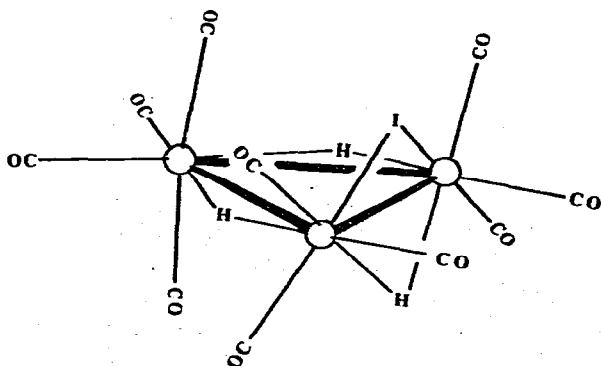

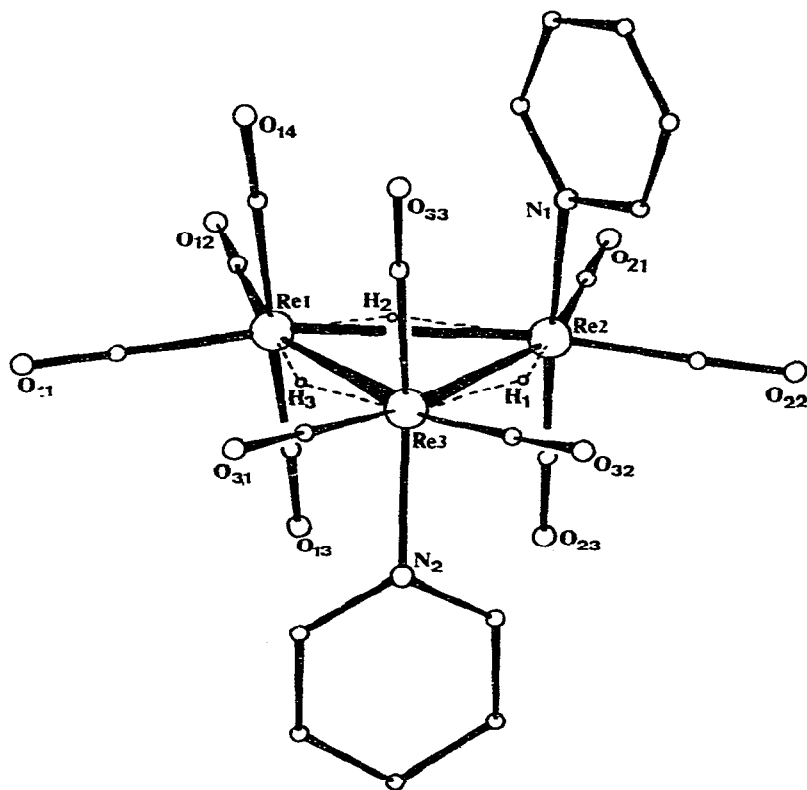Fig. 1. Suggested structure of the anion $[H_3Re_3(CO)_{10}I]^-$ (III).

Fig. 2. A view of the molecule $H_3Re_3(CO)_{10}(py)_2$ with the postulated hydridic atom positions.

tions, on opposite sides with respect to the Re_3 plane. The overall idealized symmetry of the molecule is C_2.

The metal—metal distances are in the range 3.272(7)—3.324(9) Å (mean value of the nine independent bonds 3.292 Å). These bonds are, as usual, longer than a normal Re—Re bond due to the presence of bridging hydrides on all the triangular edges, but the particularly high values are probably also a result of steric repulsions among the axial ligands. The mean values of the Re(1)—C and Re(2,3)—C bond lengths are 1.88 and 1.85 Å, respectively.

The Re—N(py) bonds (mean 2.22 Å) are comparable with other analogous bonds, e.g. 2.218(6) Å in $[ReCl_4(NO)(py)]^-$ [5]. The planes of the pyridine rings are approximately perpendicular to the plane of the metal atoms and their projections on this plane are nearly parallel to the opposite Re—Re edges. This orientation implies lower non-bonding interactions with the axial CO ligands.

The average bond angles are listed in Table 4. The carbonyl arrangement in the equatorial plane clearly indicates the presence of edge-bridging hydrides. A comparison with the equatorial moiety of the non-hydridic $Ru_3(CO)_{12}$ [6] of D_{3h} symmetry shows that the Re—Re—C(cis) (mean 106°) are larger than the Ru—Ru—C(cis) angles (mean 99°), while the C—Re—C (mean 89°) are smaller than the C—Ru—C angles (mean 103°), because of steric hindrance by the hydrido ligands.

TABLE 4

SELECTED MEAN BOND ANGLES (deg.) WITHIN THE MOLECULE $H_3Re_3(CO)_{10}(py)_2$

Re(2)—Re(1)—C(11)	166(2)	C(21)—Re(2)—C(22)	90(3)
Re(2)—Re(1)—C(12)	103(2)	C(21)—Re(2)—C(23)	91(3)
Re(2)—Re(1)—C(13)	82(2)	C(21)—Re(2)—N(1)	92(4)
Re(2)—Re(1)—C(14)	100(2)	C(22)—Re(2)—C(23)	87(3)
Re(3)—Re(1)—C(11)	109(2)	C(22)—Re(2)—N(1)	89(4)
Re(3)—Re(1)—C(12)	162(2)	C(23)—Re(2)—N(1)	174(3)
Re(3)—Re(1)—C(13)	93(2)	Re(1)—Re(3)—C(31)	105(2)
Re(3)—Re(1)—C(14)	91(2)	Re(1)—Re(3)—C(32)	164(2)
C(11)—Re(1)—C(12)	88(3)	Re(1)—Re(3)—C(33)	85(2)
C(11)—Re(1)—C(13)	91(4)	Re(1)—Re(3)—N(2)	93(2)
C(11)—Re(1)—C(14)	87(4)	Re(2)—Re(3)—C(31)	166(2)
C(12)—Re(1)—C(13)	88(5)	Re(2)—Re(3)—C(32)	104(2)
C(12)—Re(1)—C(14)	88(5)	Re(2)—Re(3)—C(33)	89(2)
C(13)—Re(1)—C(14)	172(3)	Re(2)—Re(3)—N(2)	92(3)
Re(1)—Re(2)—C(21)	101(2)	C(31)—Re(3)—C(32)	90(2)
Re(1)—Re(2)—C(22)	169(2)	C(31)—Re(3)—C(33)	89(2)
Re(1)—Re(2)—C(23)	89(2)	C(31)—Re(3)—N(2)	89(3)
Re(1)—Re(2)—N(1)	95(4)	C(32)—Re(3)—C(33)	90(3)
Re(3)—Re(2)—C(21)	158(2)	C(32)—Re(3)—N(2)	92(3)
Re(3)—Re(2)—C(22)	111(2)	C(33)—Re(3)—N(2)	175(3)
Re(3)—Re(2)—C(23)	97(2)		
Re(3)—Re(2)—N(1)	83(3)		

Experimental

IR spectra were recorded on a Beckmann IR 33 spectrometer in acetone and in Nujol mulls in the region 4000—600 cm^{-1}, and with a Perkin-Elmer Model 621 in the range 600—250 cm^{-1}. NMR spectra were recorded at 38°C on a Varian XL 100 instrument at 100 MHz, with saturated solutions in deutero-acetone containing TMS as internal standard.

Tetraethylammonium tetrahydridodecacarbonyltrirhenate (II)
Compound I (0.1 g) in 1.4 ml of acetone is treated drop by drop with 1 ml of an 0.1 M acetone solution of HClO$_4$ (molar ratio 1 : 1). The red colour of the solution changes to yellow, and on addition of water yellow crystals separate (52 mg, yield 70%). Compound II is soluble in acetone, ethanol and methanol and is insoluble in non-polar organic solvents and in water.

Tetraethylammonium trihydridoiododecacarbonyltrirhenate (III)
a) Compound I (0.184 g) in 1 ml of ethanol is treated dropwise with 1.3 ml of an 0.15 M ethanolic iodine solution (molar ratio 1 : 1). No evolution of gas is observed and white crystals of NEt$_4$I separate. The filtered solution is evaporated to dryness. The residue is shown to contain a mixture of compounds III and IV.
b) Compound II (0.060 g) in 1 ml of ethanol is treated dropwise with 0.5 ml of an ethanolic iodine solution (0.15 M) (molar ratio 1 : 1). No gas evolution is observed. The yellow solution becomes pale-green and on addition of water, pale yellow crystals of III separate (yield 30%). Compound III soluble in

acetone, ethanol and trichloromethane, and insoluble in water and in non-polar organic solvents;

Trihydridododecacarbonyldipyridinetrirhenium (V)

Compound I (0.050 g) in 2 ml of ethanol is treated with 1 ml of a 0.05 M iodine solution in pyridine with stirring until the red crystals dissolve. The solution is evaporated to dryness and the residue is treated with 1 ml of acetone. The solution is filtered, and hexane is added. Pale-yellow crystals separate. Compound V is soluble in acetone and ethanol, and insoluble in non-polar organic solvents.

Single-crystal X-ray data

$C_{20}H_{13}N_2O_{10}Re_3$, Mol. wt. 999.9, monoclinic, space group Pc (No. 7), a 10.81(1), b 25.43(2), c 17.17(1) Å, β 123.20(5)°, U 3949.5 Å^3, D_m 2.50(3), D_c 2.52 g cm^{-3} for Z 6.

The intensities were collected on an automatic diffractometer using graphite monochromatized Mo-K_α radiation (λ 0.7107 Å), within the limits $3.5° < \theta < 23°$. The total number of collected reflections was 5849. After rejection of all data having $\sigma(I)/I > 0.25$ a set of 3183 independent reflections was used in the solution and refinement of the structure.

The structure was solved by conventional Patterson and Fourier methods which showed the presence of three independent molecules in the asymmetric unit of the non-centrosymmetric Pc space group. The refinements were carried out by block-matrix least-squares with the carbonyl ligands constrained to linearity (with a fixed C—O distance of 1.20 Å) and the pyridine ligands constrained in a rigid-body motion with an ideal geometry. Anisotropic thermal factors were assigned to the Re atoms only. The current value of the concentional R factor is 13.1%. One of the three independent molecules shows a high disorder of the ligands and it was impossible to refine most of them. This led to high agreement indices and to high standard deviations for the refined parameters.

Acknowledgement

References

1 A. Bertolucci, M. Freni, P. Romiti, G. Ciani, A. Sironi and V.G. Albano, J. Organometal. Chem., 113 (1976) C61.
2 M. Freni, P. Romiti and G. D'Alfonso, J. Organometal. Chem., 140 (1977) 195.
3 G. Ciani, G. D'Alfonso, M. Freni, P. Romiti, A. Sironi and A. Albinati, J. Organometal. Chem., 136 (1977) C49.
4 (a) V.F. Allen, R. Mason and P.B. Hitchcock, J. Organometal. Chem., 140 (1977) 297; (b) M.R. Churchill, F.J. Hollander and J.P. Hutchinson, Inorg. Chem., 16 (1977) 2697; (c) A.G. Orpen, A.V. Rivera, E.G. Bryan, D. Pippard, G.M. Sheldrick and K.D. Rouse, J. Chem. Soc. Chem. Commun., (1978) 723.
5 G. Ciani, D. Giusto, M. Manassero and M. Sansoni, J. Chem. Soc. Dalton, (1978) 798.
6 R. Mason and A.I.M. Rae, J. Chem. Soc. (A), (1968) 778.