Preliminary communication

A REACTIVE AND VERSATILE TRIRHENIUM CARBONYL CLUSTER OBTAINED BY OXIDATION OF $[Re_3(\mu-H)_4(CO)_{10}]^-$. SYNTHESIS, X-RAY CHARACTERIZATION AND REACTIVITY OF $Re_3(\mu-H)_3(CO)_{10}(NCMe)_2$

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Summary

Oxidation of $[\text{Re}_3(\mu-H)_4(\text{CO})_{10}]^-$ with $\text{CF}_3\text{SO}_3\text{H}$ in acetonitrile gives the new complex $\text{Re}_3(\mu-H)_3(\text{CO})_{10}(\text{NCMe})_2$. This contains a triangle of metal atoms with the edges bridged by the hydrides (mean Re—Re 3.266 Å). The acetonitrile ligands, bound to two metals in a *trans*-diaxial manner, are easily replaced, giving a variety of derivatives.

The unsaturated cluster anion $[\text{Re}_3(\mu-H)_4(\text{CO})_{10}]^-$ (I) is a very reactive compound, owing to the hydridic nature of the hydrogens bridging the short (formally double) Re—Re bond [1]. Nevertheless it does not react readily with two-electron donor ligands (CO, PR₃ or unsaturated hydrocarbons), unlike the related triosmium compound Os₃(μ -H)₂(CO)₁₀, probably because of its anionic charge. This seemed to rule out the possibility that I could furnish an entry to the field of organic chemistry of trirhenium clusters, such as that well developed for triosmium clusters [2]. Attempts were made therefore, to obtain a neutral reactive derivative of compound I. Previous studies showed that most of its reactions follow eq. 1, where XY represents

 $[\text{Re}_{3}(\mu-\text{H})_{4}(\text{CO})_{10}]^{-} + XY \rightarrow [\text{Re}_{3}(\mu-\text{H})_{3}(\mu-\text{Y})(\text{CO})_{10}]^{-} + HX$ (1)

an acid [3] or a halogen molecule [4]. This process formally involves two processes: (i) H abstraction (as H^-) by an electrophilic X^+ species, (ii) coordination, in bridging position, of the nucleophilic Y^- species. The two processes

are concerted, since the first one would lead to a "super-unsaturated" unit (44 valence electrons) $[\text{Re}_3(\mu-H)_3(\text{CO})_{10}]$, whose existence is very speculative (an isoelectronic "Os₃(CO)₁₀" unit has been suggested as a reactive intermediate in many reactions of Os₃(μ -H)₂(CO)₁₀ [5]). However, on treating compound I with a strong acid having a non-coordinating anion (such as CF₃SO₃H) in acetonitrile solution, we succeeded in isolating the $[\text{Re}_3(\mu-H)_3(\text{CO})_{10}]$ unit in a form stabilized by two weakly bonded solvent molecules, $\text{Re}_3(\mu-H)_3(\text{CO})_{10}(\text{NCMe})_2$ (II), which might represent the desired neutral reactive species suitable for further reactions with organic systems, as in the case of the related compound Os₃(CO)₁₀(NCMe)₂ [5].

The reaction (eq. 2) is almost quantitative. The evolved H₂ was identified $[\text{Re}_{3}(\mu-\text{H})_{4}(\text{CO})_{10}]^{-} + \text{CF}_{3}\text{SO}_{3}\text{H} + 2 \text{ MeCN} \rightarrow \text{Re}_{3}(\mu-\text{H})_{3}(\text{CO})_{10}(\text{NCMe})_{2} + H_{2} + \text{CF}_{3}\text{SO}_{3}^{-}$ (2)

by GLC. Colourless crystals of the compound were investigated by X-ray analysis*.

The structure of the compound, of idealized C_2 symmetry, consists of an almost equilateral triangle of rhenium atoms, bearing ten terminal carbonyl groups and two terminal acetonitrile molecules, as illustrated in Fig. 1. The two solvent molecules are bound in axial direction, on opposite sides of the Re₃ plane. The hydride ligands, not directly located, are assumed to be bridging on the metal—metal edges, on the basis of the values of the Re–Re bond lengths and the stereochemistry of the other ligands.

The Re–Re hydrogen-bridged bonds are in the range 3.251(2)–3.285(2) Å (overall mean value for the two independent molecules 3.266 Å), comparable with many similar interactions, e.g. 3.262 Å (mean value) in Re₃(μ -H)₃(CO)₁₁-(PPh₃) [6] and 3.292 Å (mean value) in Re₃(μ -H)₃(CO)₁₀(Py)₂ [7].

The mean values of the Re–C bond lengths within the Re(CO)₄ and the Re(CO)₃ moieties are 1.92 and 1.87 Å, respectively. The overall mean C–O bond length is 1.16 Å. The acetonitrile molecules are coordinated in an essentially linear way (Re–N–C 170(3)–179(3)°), with Re–N bond interactions in the range 2.09(5)–2.16(4) Å (mean 2.13 Å), comparable with the corresponding interaction in [ReBr₄(NO)(NCMe)]⁻ (2.153(11) Å) [8] and somewhat shorter than the Re–N(py) mean bond (2.22 Å) in Re₃(μ -H)₃(CO)₁₀(Py)₂. The mean bond lengths within the MeCN molecules are: N–C 1.15 Å and C–C 1.52 Å.

As expected, the solvent molecules are rather labile and can be easily replaced, (within a few hours) by a variety of ligands at room temperature. Reactions 3-10 are so far investigated.

^{*}Crystal data. C_{14} H₉N₂O₁₀Re₃, Mol.wt. 923.8, orthorhombic, space group *Pbca* (No. 61), with a 12.948(3), b 16.718(4) and c 40.279(11) Å, D_c 2.81 g cm⁻³ for Z = 16. The structure was solved by Patterson and Fourier methods, on the basis of 1720 significant counter data, and refined by full-matrix least-squares up to a current R value of 0.042. There are two independent molecules in the asymmetric unit. (The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain). Any request should be accompanied by a full literature citation for this communication.)



Fig. 1. A view of one of the two independent molecules $\operatorname{Re}_{3}(\mu-H)_{3}(\operatorname{CO})_{10}(\operatorname{NCMe})_{2}$, with the postulated hydridic atoms positions.

TABLE 1

IR AND NMR DATA

Compound	IR $(cm^{-1})^a$ v(C-O)	¹ H NMR ^b			
		Proton resonance (τ)	Relative intensity	Fine structure	Assignment
Re ₃ (μ-H) ₃ (CO) ₁₀ (NCMe) ₂	2098mw, 2039sh,	7,71	6	Singlet	сн,
(11)	2028vs, 2000sh,	22.0	1	Singlet	Re—H—Re
	1991s, 1961m, 1938s, 1921m.	24.52	2	Singlet	Re—H—Re
Re ₃ (µ-H) ₃ (CO) ₁₀ (PPh ₃) ₂ (V)	2095m, 2028vs,	2.50	30	Multiplet	C ₆ H ₅
	2000s, 1987ms, 1957vs, 1935vs, 1927s, 1910s.	25.07	2	Doublet (J(P—H) 15.4 Hz)	Re—H—Re
	·	25.93	1	Triplet (J(P—H) 7.8 Hz)	Re—H—Re
[Re3(µ-H)3(µ-OMe)(CO)10] (VIII)	2096w, 2020m,	6.13	3	Singlet	OCH3
	2000vs, 1985sh,	19.65	1	Singlet	Re—H—Re
	1957vs, 1935vs, 1888s.	23.84	2	Singlet	Re—H—Re
Re ₃ (µ-H) ₃ (CO) ₁₁ (NCMe) (IX)	2113mw, 2090mw,	7.65	3	Singlet	СН3
	2038m, 2022s,	24.56	2	Singlet	Re—H—Re
	2003vs, 1971m, 1936m, 1921sh.	27.26	1	Singlet	Re—H—Re

^a IR spectra were recorded on a Perkin-Elmer 781 spectrophotometer, in toluene solution (II and IX), in KBr disk (V) and in dichloromethane solution (VIII). ^b NMR spectra were recorded on a Bruker-80 in CDCl₃ solution (II, V, and IX) and in CD_2Cl_2 (VIII).

$$(3) Py \qquad Re_{3}(\mu-H)_{3}(CO)_{10}(Py)_{2} \qquad [7]$$

$$(III)$$

$$(4) dppm \qquad Re_{3}(\mu-H)_{3}(CO)_{10}(dppm) \qquad [9]$$

$$(IV)$$

$$(5) PPh_{3} \qquad Re_{3}(\mu-H)_{3}(CO)_{10}(PPh_{3})_{2}$$

$$(V)$$

$$(6) \Gamma \qquad [Re_{3}(\mu-H)_{3}(\mu-I)(CO)_{10}]^{-} \qquad [3a]$$

$$(VI)$$

$$Re_{3}(\mu-H)_{3}(CO)_{10}(NCMe)_{2} \qquad (7) CH_{3}COO^{-} \qquad [Re_{3}(\mu-H)_{3}(\mu-O_{2}CCH_{3})(CO)_{10}]^{-} \qquad [3b]$$

$$(VII)$$

$$(8) CH_{3}O^{-} \qquad [Re_{3}(\mu-H)_{3}(\mu-O_{2}CCH_{3})(CO)_{10}]^{-}$$

$$(VII)$$

$$(9) CO (1 atm) \qquad Re_{3}(\mu-H)_{3}(CO)_{11}(NCMe)$$

$$(IX)$$

$$(10) CO (10 atm) \qquad Re_{3}(\mu-H)_{3}(CO)_{12} \qquad [10]$$

In the case of the reaction with CO, at atmospheric pressure only the monosubstituted derivative is formed: this is another interesting species, able to give many derivatives of the type $\operatorname{Re}_3(\mu-H)_3(\operatorname{CO})_{11}L$. For example, by reaction with Γ , the known $[\operatorname{Re}_3(\mu-H)_3\operatorname{I(CO)}_{11}]^-$ [11] is readily formed. Compounds II and IX thus provide an easy and selective route to a number of derivatives of $\operatorname{Re}_3(\mu-H)_3(\operatorname{CO})_{12}$, offering an alternative to the direct syntheses which require more drastic conditions and generally lead to complex structure of products. Furthermore compound II allows the synthesis of anionic species of the type $[\operatorname{Re}_3(\mu-H)_3(\mu-X)(\operatorname{CO})_{10}]^-$ (as the methoxo derivative VIII), which cannot be obtained directly by reaction of compound I with HX, unless HX is markedly acidic.

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