

Preliminary communication

Transformation of a coordinated carbon monoxide into an oxyethyl bridging group in a hydrido-carbonyl rhenium cluster. Synthesis and crystal structure of the anion $[\text{Re}_3(\mu\text{-H})_3(\text{CO})_9\{\mu_3\text{-}\eta^2\text{-C(H)(Me)O}\}]^{2-}$

Tiziana Beringhelli, Giuseppe D'Alfonso ^{*}, Maria Freni

Dipartimento di Chimica Inorganica e Metallorganica e Centro C.N.R., Via G. Venezian 21, 20133 Milano (Italy)

Gianfranco Ciani ^{*}, Massimo Moret and Angelo Sironi

Istituto di Chimica Strutturistica Inorganica e Centro C.N.R., Via G. Venezian 21, 20133 Milano (Italy)

(Received March 27th, 1991)

Abstract

The reaction of the unsaturated anion $[\text{Re}_3(\mu\text{-H})_4(\text{CO})_{10}]^-$ with LiMe at low temperature gives the unsaturated acyl derivative $[\text{Re}_3(\mu\text{-H})_4(\text{CO})_9\{\text{C(Me)O}\}]^{2-}$, which is slowly converted, as the temperature is raised, into a saturated species in which a hydride ligand has migrated from the cluster to the acylic carbon atom to give $[\text{Re}_3(\mu\text{-H})_3(\text{CO})_9\{\mu_3\text{-}\eta^2\text{-C(H)(Me)O}\}]^{2-}$. Variable temperature ¹H-NMR spectroscopy has shown the existence of an unexpected equilibrium between the two anions.

We are currently studying the reductive hydrogenation of CO and of unsaturated organic molecules using small hydrido-carbonyl clusters of rhenium, as the unsaturated anion $[\text{Re}_3(\mu\text{-H})_4(\text{CO})_{10}]^-$ (**1**) [1]. We previously reported on the reduction of tropylium ion [2], acetone [3] and isonitriles [4] brought about by **1**. We also showed that coordinated carbon monoxide in compound **1** can be reduced in a two step process involving initially reaction with Li[BH(^sBu)₃] to give the rather unstable formyl intermediate $[\text{Re}_3(\mu\text{-H})_4(\text{CO})_9(\text{CHO})]^{2-}$, which is followed by migration of a hydride from the cluster to the formyl C atom to produce the saturated anion $[\text{Re}_3(\mu\text{-H})_3(\text{CO})_9\{\mu_3\text{-}\eta^2\text{-CH}_2\text{O}\}]^{2-}$ [5] containing an oxymethyl bridging group.

We now present the results of a preliminary study of the reaction of **1** with LiMe, which has revealed that the reduction of one CO ligand to a bridging-C(Me)-(H)O-group takes place.

¹H-NMR monitoring of the reaction between **1** and a slight excess of methyl-lithium at -30 °C in THF-*d*₈ shows the quantitative formation of the novel unsaturated acyl species $[\text{Re}_3(\mu\text{-H})_4(\text{CO})_9\{\text{C(Me)O}\}]^{2-}$ (**2**), as indicated by the

appearance of three hydridic resonances (δ -7.8, -8.0, -11.0 ppm, ratio 1:1:2), typical of the $[\text{Re}_3(\mu\text{-H})_4(\text{CO})_9\text{L}]^-$ unsaturated anions, of idealized C_3 symmetry [6] (the acyclic methyl group gives a signal at δ 2.27 ppm). The acyl product **2** is quite stable compared with the formyl intermediate observed in the reaction of **1** with $\text{Li}[\text{BH}(\text{}^t\text{Bu})_3]$, but as the temperature is raised to 10 °C the signals of **2** slowly decrease, and three new signals, in a ratio 1:1:1, appear at δ -9.40, -12.64, -13.04 ppm; the spectrum also shows a broad quartet at δ 5.65 ppm (intensity 1), coupled with a doublet at δ 1.95 ppm (intensity 3, $J(\text{HH}) = 7$ Hz). The data are consistent with the transformation of **2** into the novel saturated anion $[\text{Re}_3(\mu\text{-H})_3(\text{CO})_9\{\mu_3\text{-}\eta^2\text{-C(H)(Me)O}\}]^{2-}$ (**3**), by attack of a cluster hydride of **2** on the acyl carbon atom.

Crystals of compound **3**, as its NEt_4^+ salt, suitable for X-ray analysis* were grown by slow diffusion of n-pentane vapour into a THF solution at 5 °C.

The structure of the anion is illustrated in Fig. 1. It is very similar to that of the analogous $[\text{Re}_3(\mu\text{-H})_3(\text{CO})_9\{\mu_3\text{-}\eta^2\text{-CH}_2\text{O}\}]^{2-}$ anion [5], and contains an isosceles Re_3 triangle, with two longer metal-metal edges [Re1-Re2 3.171(1) Å, Re1-Re3 3.176(1) Å], and one shorter edge [Re2-Re3 2.945(1) Å]. Each rhenium atom bears three terminal carbonyls, and the three hydrides were shown (by use of the Orpen energy-minimization program [7]) to occupy bridging positions on the three triangular edges, in agreement with the ligand stereochemistry.

The bridging MeC(H)O group exhibits bond parameters (see caption to Fig. 1) very similar to the corresponding ones in $[\text{Re}_3(\mu\text{-H})_3(\text{CO})_9\{\mu_3\text{-}\eta^2\text{-CH}_2\text{O}\}]^{2-}$ [5]. Though the ligand might be viewed as an acetaldehyde molecule interacting with the metallic triangle, it is correctly described as an oxyethyl group. In fact, the C-O bond distance [1.496(15)] is clearly indicative of a single bond (in true aldehyde complexes substantially shorter values are observed [8]) and the bond angles at the carbon atom have the values expected for sp^3 hybridization.

The reaction of **1** with LiMe here reported shows interesting differences from that with $\text{Li}[\text{BH}(\text{}^t\text{Bu})_3]$ previously described [5], the most remarkable one being the reversibility of the conversion of **2** into the $\mu_3\text{-}\eta^2$ -oxyethyl compound **3** (at least in the reaction mixtures). Thus, variable temperature $^1\text{H-NMR}$ monitoring shows that the ratio R between the two species (**2/3**) varies, reversibly, from $R = 3.0$ at 50 °C, to $R = 1.5$ at 25 °C, to $R = 1.1$ at 10 °C. These data allow a rough estimate of ΔH^\ominus and ΔS^\ominus for the equilibrium $\mathbf{3} \rightleftharpoons \mathbf{2}$ (4.5 ± 0.5 kcal mol $^{-1}$ and 16 ± 2 cal K $^{-1}$ mol $^{-1}$, respectively). The reversibility of this transformation, which seems to be

* IR spectrum $\nu(\text{CO})$ (THF): 2003m 1977s, 1886s, 1872s cm $^{-1}$.

Crystal data. $\text{C}_{27}\text{H}_{47}\text{N}_2\text{O}_{10}\text{Re}_3$, $M = 1118.3$, monoclinic, space group $P2_1/n$ (non-standard of No. 14), $a = 9.897(4)$, $b = 22.720(5)$, $c = 15.840(4)$ Å, $\beta = 96.77(3)^\circ$, $U = 3536.9$ Å 3 , $Z = 4$, $D_c = 2.100$ g cm $^{-3}$, $F(000) = 2112$, Mo- K_α radiation ($\lambda = 0.71073$ Å), $\mu(\text{Mo-}K_\alpha) = 104.3$ cm $^{-1}$. The structure was solved by Patterson and Fourier methods and refined by full matrix least squares, on the basis of 3043 significant [$I > 3\sigma(I)$] independent reflections, collected within the limit $2\theta < 48^\circ$ on an Enraf-Nonius CAD4 diffractometer. One of the independent tetraethylammonium cations lies in general position while two other half-cations lie on inversion centres and are, therefore, disordered. All the anionic atoms were treated anisotropically, while isotropic thermal factors were assigned to the cationic atoms. The hydrogen atoms within the anion were located in idealized positions. The final values of the agreement indices R and R_w were 0.040 and 0.047, respectively. Tables of atomic coordinates, bond distances and angles, and structure factors moduli have been deposited at the Cambridge Crystallographic Data Centre, and lists of thermal parameters and structure factors are available from the authors.