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Preliminary communication

SYNTHESIS, X-RAY CRYSTAL STRUCTURE AND ^{13}C NMR STUDY OF THE ANION $[Re_6(\mu_3\text{-}H)_2C(CO)_{18}]^{2-}$: THE FIRST OCTAHEDRAL CARBONYL CLUSTER OF RHENIUM

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Summary

The novel high nuclearity carbido-carbonyl anion $[Re_6(\mu_3\text{-}H)_2C(CO)_{18}]^{2-}$, isolated from the pyrolysis of $[ReH_2(CO)_4](NEt_4)$ in n-tetradecane/decalin, contains an octahedral metal cluster, with Re—Re bond lengths in the range 2.939(2)—3.096(3) Å; the hydrogen atoms are assumed to bridge two faces of the octahedron which share an edge, as deduced from a comparative analysis of the X-ray structure and the ^{13}C NMR spectra at various temperatures.

Carbido-carbonyl clusters of rhenium can be obtained by pyrolysis of mono-, tri- or tetra-nuclear hydrido-carbonyl anions (as their tetraethylammonium salts) [1,2], at temperatures high enough to allow thermolysis of the CO ligands to give some reactive carbon radicals.

As we have previously reported, pyrolysis in boiling n-tetradecane (ca. 250°C) afforded two main products, $[Re_7C(CO)_{21}](NEt_4)_3$ [1] and $[Re_8C(CO)_{24}](NEt_4)_2$ [2]. On lowering the temperature at about 235°C (using a n-tetradecane/decalin mixture) the main product is a species (previously observed as a by-product) which we have isolated and characterized as the orange-brown salt $[Re_6(\mu_3\text{-}H)_2C(CO)_{18}]$-$(NEt_4)_2$ (yields of up to 35%)*.

The IR spectrum of the new species, in acetone, shows the following bands in the ν(CO) region: 1997sh, 1983s, 1925w and 1900m cm^{-1}. The compound is

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*The components of the reaction mixture can be easily separated owing to their differing solubilities: $[Re_7C(CO)_{21}](NEt_4)_3$ is insoluble in tetrahydrofuran and dichloromethane, $[Re_8C(CO)_{24}](NEt_4)_2$ is insoluble in dichloromethane, while $[Re_6(\mu_3\text{-}H)_2C(CO)_{18}](NEt_4)_2$ dissolves well in both solvents.

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diamagnetic and its ^1H NMR spectrum shows one hydridic resonance (δ −19.5 ppm) in addition to the cationic hydrogen signals, the intensity ratio being in agreement with the proposed formula. The ^{13}C NMR spectrum of a sample obtained by pyrolysis of ^{13}CO-enriched $[ReH_2(CO)_4](NEt_4)$ (^{13}CO ca. 30%) at room temperature, in tetrahydrofuran-d_8, consists of two resonances (with intensity ratio very close to the theoretical 1/18) attributable to the carbide (403.5 ppm, relative to the TMS) and to the carbonyls (195.7 ppm), respectively.

After many unsuccessful attempts to obtain crystals suitable for X-ray analysis with different cations $[(NEt_4)^+$, Cs^+, $(PPN)^+$, $(PPh_4)^+]$, we crystallized the novel anion in combination with the $(PPh_3Me)^+$ cation, because the structure of the analogous species $[Os_6(CO)_{18}](PPh_3Me)_2$ has been determined [3]. In spite of the poor diffraction at high θ values, the crystals were investigated by X-ray diffraction and found to be isomorphous to those of the osmium compound*.

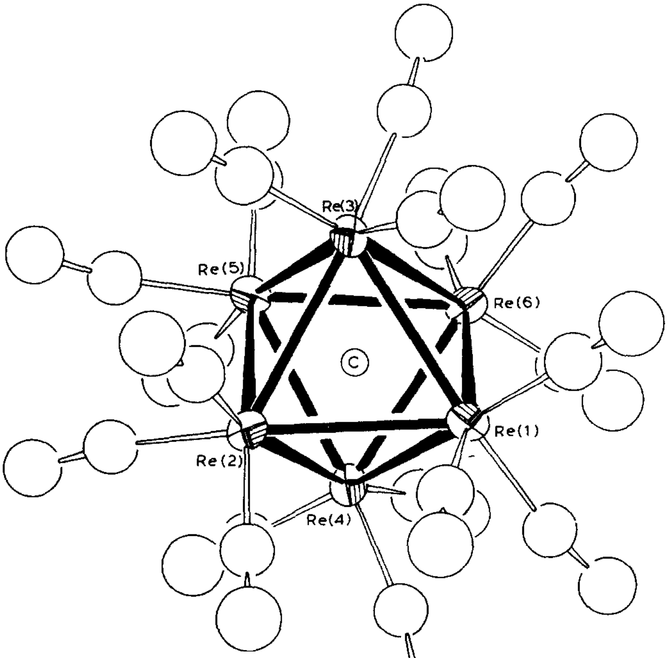

Fig. 1. A view of the $[Re_6(\mu_3\text{-}H)_2C(CO)_{18}]^{2-}$ anion down the z (C_3) axis. The rhenium atoms are all equivalent but, for clarity, they have been labelled from 1 to 6. The relevant bond lengths are: Re(1)—Re(2) 3.026(3), Re(1)—Re(4) 3.096(3), Re(1)—Re(6) 2.939(2), Re—C(carbide) 2.136(1) Å.

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*Crystal data. $C_{57}H_{32}O_{18}P_2Re_6$, M = 2190.1, trigonal, space group $P\bar{3}1c$ (No. 163), $a = b = 12.327(1)$, c = 24.812(3) Å, Z = 2, D_c 2.23 g cm^{-3}, μ(Mo-K_α) 113.4 cm^{-1}; Mo-K_α radiation λ 0.71073 Å. The data were collected on an ENRAF—NONIUS CAD-4 automated diffractometer, within the range $3 < \theta < 23°$. An empirical absorption correction was applied (normalized transmission factors in the range 1.00—0.72). After mediation of equivalent reflections a set of 466 significant ($I > 2.5\sigma(I)$) independent reflections were used in the solution and refinement of the structure, up to a current conventional R value of 0.053.

The structure of the anion is shown in the Fig. 1. It is the first example of an octahedral carbonyl cluster of rhenium, having the carbide atom inside the octahedral cavity. Each metal atom bears three terminal carbonyl groups and the required number of valence electrons (86) is achieved by the presence of two hydridic ligands, which are assumed to bridge two faces sharing an edge (see below). The anion has a crystallographically imposed 32 (D_3) symmetry. The two equilateral triangular faces, normal to C_3, have Re—Re distances of 3.026(3) Å, while the edges connecting such faces have alternately three shorter (2.939(2) Å) and three longer (3.096(3) Å) distances. This twisting of opposite faces, to give short and long interfacial interactions, is also present, although to a minor extent, in the $[Os_6(CO)_{18}]^{2-}$ (2.814 and 2.886 Å) [3] and $[Re_7C(CO)_{21}]^{3-}$ (2.977 and 3.017 Å) [1] anions. In the latter the Re—Re bond distances range from 2.929 to 3.080 Å, and so all the distances found in $[Re_6(\mu_3\text{-}H)_2C(CO)_{18}]^{2-}$ can be considered normal and not indicative of a particular location of the two hydride ligands.

The high temperature factors for the metal atoms and for the carbonyl ligands suggest the presence of some kind of disorder, and probably the refined positional parameters correspond to the mean value obtained from overlapping different orientations of a less symmetrical (probably C_2) anion, as also indicated by the rather scattered values of the Re—C(carbonyl) and C—O bond lengths (mean 1.87 and 1.20 Å, respectively). This makes it difficult to derive the hydride atom locations from the stereochemistry of the carbonyl ligands*. From computed contacts, however, we can exclude for the hydrogen atoms double-bridging locations on cluster edges, while all the faces are available to permit them to be triple-bridging. In order to clarify the stereochemistry of the hydridic ligands, we have examined the ^1H and ^{13}C NMR spectra at low temperatures. The hydridic signal remains a singlet down to −105°C, while the ^{13}C signal due to the carbonyls at −90°C collapses and at −105°C splits into six signals, of intensities 6/4/2/2/2/2, relative to the carbido signal. This pattern indicates a low symmetry of the anion, and immediately excludes the possibility that the two hydr-

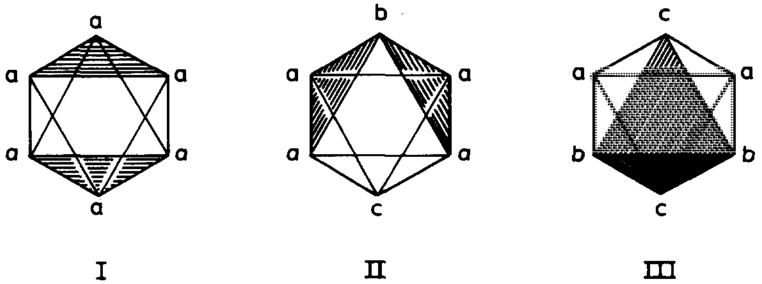

Fig. 2. The three possible isomers of $[Re_6(\mu_3\text{-}H)_2C(CO)_{18}]^{2-}$ (shaded faces are hydrogen-bridged).

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*The X-ray structure of the p-xylylenebis(triphenylphosphonium) salt of the same anion (Monoclinic $P2_1/n$, a 26.309(4), b 10.348(2), c 27.099(4) Å, β 118.3(1)°, Z = 4), although based on data of poorer quality, shows a substantially similar cluster geometry (Re—Re in the range 2.958(3)—3.129(4) Å, mean 3.011 Å), and similar carbonyl disposition (involving the same kind of disorder), in spite of the fact that the anion is not in a specific position.

ogen atoms are bridging to opposite faces, as in the isoelectronic species $[Ru_6(\mu_3\text{-}H)_2(CO)_{18}]$ [4] (isomer I in Fig. 2). Of the two other possible isomers (II and III of Fig. 2), only III possesses a two-fold axis, passing through the midpoint of opposite edges, compatible with the disordered structure found in the solid state. The observed intensity pattern seems not be derived from isomer II but rather from isomer III, assuming that the scrambling of the hydrogens on the faces of the octahedron is frozen out at low temperature and that of the carbonyls localized about each Re atom, is fixed only for the CO groups bound to the rhenium atoms bridged by the hydridic ligands (b and c in Fig. 2, giving the signals of intensities 2/2/2 and 4/2, respectively), while the carbonyls bound to rhenium atoms of type a remain equivalent and give the signal of intensity 6. No $^{13}C—^{1}H$ coupling was detected, even at low temperature.

We are studying the reactivity of $[Re_6(\mu_3\text{-}H)_2C(CO)_{18}]^{2-}$, and have observed that with strong acids it gives a novel compound, of probable formulation $[Re_6H_3C(CO)_{18}]^{-}$; the reaction has been reversed upon dissolving the product in basic solvents.

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