

High Nuclearity Carbido Carbonyl Clusters of Rhenium. Synthesis, X-Ray Crystal Structure, and ^{13}C N.M.R. Study of the Anion $[\text{Re}_8\text{C}(\text{CO})_{24}]^{2-}$

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The novel high nuclearity carbido carbonyl anion $[\text{Re}_8\text{C}(\text{CO})_{24}]^{2-}$, isolated from the pyrolysis of $[\text{ReH}_2(\text{CO})_4]^-$ in *n*-tetradecane, has the metal atoms arranged as an octahedron capped on two opposite faces as shown by an X-ray crystal structure determination; ^{13}C n.m.r. analysis has confirmed the nature of the interstitial atom and shown that the solid-state structure of the anion is maintained in solution.

We have recently reported the synthesis and structure of the anion $[\text{Re}_7\text{C}(\text{CO})_{21}]^{3-}$, the first example of a high nuclearity carbido carbonyl cluster of rhenium.¹ We have now succeeded in isolating and characterizing a higher nuclearity member of the same family, namely the novel $[\text{Re}_8\text{C}(\text{CO})_{24}]^{2-}$ anion, which is isoelectronic with the bicapped octahedral $[\text{Os}_8(\text{CO})_{22}]^{2-}$ anion,² but differs from it in that the title complex contains a previously unknown *trans*-bicapped octahedral arrangement of metal atoms.

The pyrolysis of the monomer $[\text{ReH}_2(\text{CO})_4][\text{NEt}_4]$, under the conditions previously described,¹ afforded a mixture of products. Analogous mixtures were also obtained by pyrolysis of carbonyl clusters, such as $[\text{Re}_3\text{H}_3(\text{CO})_{10}][\text{NEt}_4]_2$,^{3a} $[\text{Re}_3\text{H}_4(\text{CO})_{15}][\text{NEt}_4]_2$,^{3b} or $[\text{Re}_4\text{H}_6(\text{CO})_{12}][\text{NEt}_4]_2$.^{3c} These mixtures were treated with tetrahydrofuran, giving a deep-red solution and a red residue of $[\text{Re}_7\text{C}(\text{CO})_{21}][\text{NEt}_4]_3$. Upon addition of *n*-hexane to the solution, a red precipitate was obtained, which, when crystallized from acetone-ethanol, gave red crystals of $[\text{Re}_8\text{C}(\text{CO})_{24}][\text{NEt}_4]_2$ (in yields of up to 30%), together with other as yet unidentified species. The i.r. spectrum, in acetone solution, showed the following bands in the $\nu(\text{CO})$ region: 2010sh, 2004s, 1950w, 1930mw, and 1890w cm^{-1} . The compound is diamagnetic and the ^1H n.m.r. spectrum, in the range $\tau -40$ to $+50$, at room temperature, showed only the cationic hydrogen signals.

The compound has been investigated by X-ray analysis.† The structure of the anion is shown in Figure 1. The metallic skeleton is a regular octahedron, capped on two opposite triangular faces by two other rhenium atoms, resulting in an idealized D_{3d} symmetry rhombohedron, hereafter referred to as a *trans*-bicapped octahedron. The Re-Re distances belong to two different classes: i, bonds within the octahedron, mean 2.993 Å, and ii, bonds involving the capping atoms, mean 2.970 Å. The overall mean of the Re-Re bond lengths is 2.985 Å, slightly smaller than the corresponding value of

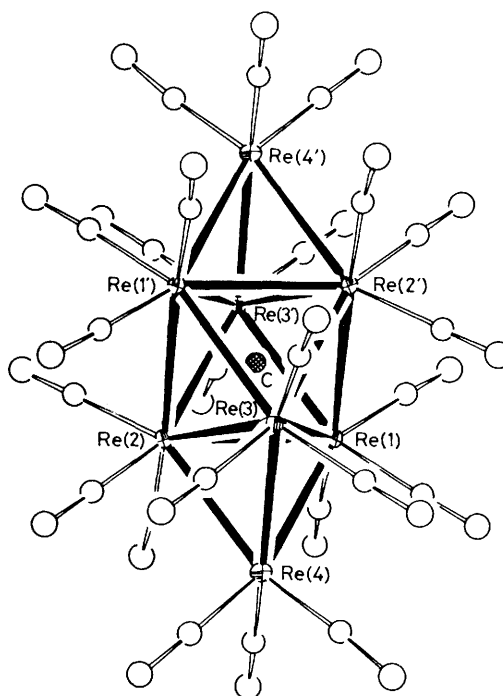


Figure 1. A view of the anion $[\text{Re}_8\text{C}(\text{CO})_{24}]^{2-}$. The carbide atom lies at the centre of the octahedral hole and the Re-C distances are in the range 2.110(1)–2.119(1) Å, with a mean value of 2.116 Å. Assuming a covalent radius of *ca.* 1.50 Å for the rhenium atom, the apparent radius of the interstitial carbon atom is 0.62 Å. Similar values have been assigned to all other 'carbide' atoms found in octahedral cavities.⁴

2.992 Å found in the $[\text{Re}_7\text{C}(\text{CO})_{21}]^{3-}$ anion.¹ The carbon atom lies at the centre of the octahedral hole and the Re-C distances are in the range 2.110(1)–2.119(1) Å, with a mean value of 2.116 Å. Assuming a covalent radius of *ca.* 1.50 Å for the rhenium atom, the apparent radius of the interstitial carbon atom is 0.62 Å. Similar values have been assigned to all other 'carbide' atoms found in octahedral cavities.⁴

The carbonyl ligands are all terminally bonded, three per metal atom, and their stereochemistry conforms to the idealized D_{3d} symmetry of the metal cluster. From a local electron count the anionic charges can be formally localized on the capping atoms and this is reflected in the Re-C(carbonyl) and C-O mean bond distances, 1.85 and 1.19 Å respectively, for the carbonyl groups bound to the capping atoms and 1.91 and 1.16 Å respectively for the remainder.

A ^{13}C n.m.r. analysis has been performed on a ^{13}C enriched sample of $[\text{Re}_8\text{C}(\text{CO})_{24}][\text{NEt}_4]_2$ {obtained from *ca.* 20% ^{13}C enriched $[\text{ReH}_2(\text{CO})_4][\text{NEt}_4]$ } at different temperatures in $[\text{C}_2\text{H}_5]_2\text{O}$.

In the range $+40$ to -50 °C the anion spectra consisted of three signals at 431.3, 204.0, and 191.3 p.p.m., relative to

† Crystal data: $\text{C}_{41}\text{H}_{40}\text{N}_2\text{O}_{24}\text{Re}_8$, $M = 2434.4$, triclinic, space group $\bar{P}1$ (No. 2), $a = 12.047(4)$, $b = 12.188(4)$, $c = 9.811(3)$ Å, $\alpha = 91.10(3)$, $\beta = 97.59(3)$, $\gamma = 109.58(3)^\circ$, $Z = 1$. The intensity data were recorded on an Enraf-Nonius CAD4 automated diffractometer, using graphite-monochromated $\text{Mo-K}\alpha$ radiation, within the range $3 < \theta < 27^\circ$. The absorption coefficient $\mu(\text{Mo-K}\alpha)$ was 190.6 cm^{-1} and the application of an empirical correction based on ψ -scan led to correction factors (on F) in the range 1.00–0.67. The structure was solved by conventional Patterson and Fourier methods and refined by least-squares, using 3150 significant reflections [$I > 3\sigma(I)$]. The anion lies in a special position, with the carbide atom on an inversion centre. The cation shows disorder, with the C atoms bound to N doubled in an almost cubic arrangement of half atoms. The current conventional R value is 0.044. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

tetramethylsilane (intensity ratio 1:6:18). On lowering the temperature to $-100\text{ }^{\circ}\text{C}$, the most intense signal splits, giving a spectrum consisting of four resonances (intensity ratio 1:6:12:6). The resonance at 431.3 p.p.m., to our knowledge the lowest-field ^{13}C n.m.r. signal ever found, is attributable to the interstitial carbon atom, since it is known⁵ that such atoms give very low-field resonances. The anion $[\text{Re}_7\text{C}(\text{CO})_{21}]^{3-}$ also shows an analogous signal at 423.6 p.p.m. The intensity ratio with respect to the CO signals clearly indicates that the carbon atom originates from a CO group of $[\text{ReH}_2(\text{CO})_4]^-$.

The low temperature spectrum is fully consistent with the structure found in the solid state, where three types of equivalent carbonyl ligands are present. The lower field CO signal is attributable to the six ligands bound to the capping metals; the higher field signal is due to the six CO groups bound to the octahedral moiety and lying on the mirror planes (σ_d in the idealized D_{3d} symmetry); the other signal, of double intensity, can be ascribed to the remaining twelve CO groups. On raising the temperature, the eighteen carbonyls of the octahedral moiety become dynamically equivalent and this can be rationalized in terms of a localized scrambling on each rhenium atom.

There are three different isomers for a bicapped octahedral cluster, since the capped triangular faces can be opposite $\{[\text{Re}_8\text{C}(\text{CO})_{24}]^{2-}\}$, share a vertex $\{[\text{Os}_8(\text{CO})_{22}]^{2-}\}$,² or share an edge (no example). From Wade's rules⁶ and M.O. calculations of cubic close packed clusters^{7,8} the different isomers all have the same number of valence electrons, although differences are present in the pattern of the metal-metal connectivities.

Three factors seem to be important in determining the carbonyl cluster geometry: i, the total number of valence

electrons; ii, the principle of charge equalization; iii, the ratio between carbonyl ligands and metal atoms. A metal like rhenium, with fewer valence electrons than group 8 metals and little tendency to support bridging carbonyls, not only requires the carbide as an 'inner' ligand, but also requires three carbonyls for each Re atom, a feature consistent with *trans* rather than other isomers. For the same reasons, a rhenium cluster containing an octahedron with three or more capping metal atoms seems to be improbable, although higher nuclearity poly-carbide species are not excluded.

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