

# A High Nuclearity Carbonyl Cluster of Rhenium stabilized by an Interstitial Carbide; Synthesis and X-Ray Crystal Structure of the Anion $[\text{Re}_7\text{C}(\text{CO})_{21}]^{3-}$

Gianfranco Ciani,\* Giuseppe D'Alfonso,\* Maria Freni, Pierfrancesco Romiti, and Angelo Sironi  
 Centro del C.N.R. di Studio della Sintesi e Struttura dei Composti dei Metalli di Transizione nei Bassi Stati di Ossidazione e Istituto di Chimica Generale ed Inorganica, Via G. Venezian 21, 20133 Milano, Italy

The trianion  $[\text{Re}_7\text{C}(\text{CO})_{21}]^{3-}$ , isolated from the pyrolysis of  $[\text{ReH}_2(\text{CO})_4][\text{NEt}_4]$  in *n*-tetradecane, has been characterized by an X-ray crystal structural analysis of the  $[\text{PPh}_4]^+$  salt, and shown to contain a monocapped octahedral arrangement of rhenium atoms with an encapsulated carbon atom.

While Group 8 transition metals are known to form many high nuclearity carbonyl cluster compounds,<sup>1</sup> in the manganese subgroup the homonuclear carbonyl clusters as yet characterized contain a maximum number of four metal atoms only.

We have previously attempted to obtain larger rhenium clusters by pyrolysis of  $[\text{ReH}_2(\text{CO})_4][\text{NEt}_4]$  in long-chain hydrocarbons up to *n*-nonane, but we obtained mixtures from which only known tri- and tetra-nuclear clusters were separated.<sup>2</sup> We have now performed the pyrolysis of the same parent compound in *n*-tetradecane and, from the reaction mixture, we have been able to isolate and characterize the novel carbido carbonyl cluster anion  $[\text{Re}_7\text{C}(\text{CO})_{21}]^{3-}$ , which contains a metallic monocapped octahedron and is iso-electronic with other similar cluster species, such as  $[\text{Rh}_7(\text{CO})_{16}]^{3-}$  (ref. 3) and  $[\text{Os}_7(\text{CO})_{21}]^{4-}$ .

In a typical pyrolysis 0.5 g of  $[\text{ReH}_2(\text{CO})_4][\text{NEt}_4]$ , suspended in 10 ml of *n*-tetradecane, was heated under nitrogen up to the b.p. of the hydrocarbon (*ca.* 250 °C), and then refluxed for a few minutes. A gas was evolved and the colour of the solid turned progressively from cream to black. After removing the *n*-tetradecane, the mixture was treated with acetone, affording a deep-red solution and a black residue. The solution was evaporated to dryness, giving a mixture of products, which, when treated with tetrahydrofuran, left the insoluble red species  $[\text{Re}_7\text{C}(\text{CO})_{21}][\text{NEt}_4]_3$  (in yields of up to 50%). The i.r. spectrum, in acetone solution, shows the following bands in the  $\nu_{\text{CO}}$  region: 1977(sh), 1968(vs), 1940(mw), 1920(vw), 1890(m), and 1855(w)  $\text{cm}^{-1}$ . The compound is diamagnetic and the  $^1\text{H}$  n.m.r. spectrum, in the range  $\tau$  -40—+50, at room temperature, shows only the cationic hydrogen signals. Metathesis of the tetraethylammonium salt with  $\text{PPh}_4\text{Br}$  in methanol and crystallization from acetone-methanol gave crystals suitable for X-ray analysis.†

The structure of the anion is shown in Figure 1. The rhenium atoms form a monocapped octahedron of idealized  $C_{3v}$  symmetry, with an overall mean Re-Re bond length of 2.992 Å, similar to the normal Re-Re single bond in  $[\text{Re}_2(\text{CO})_{10}]$ , 3.041(1) Å,<sup>5</sup> and to the average metal-metal

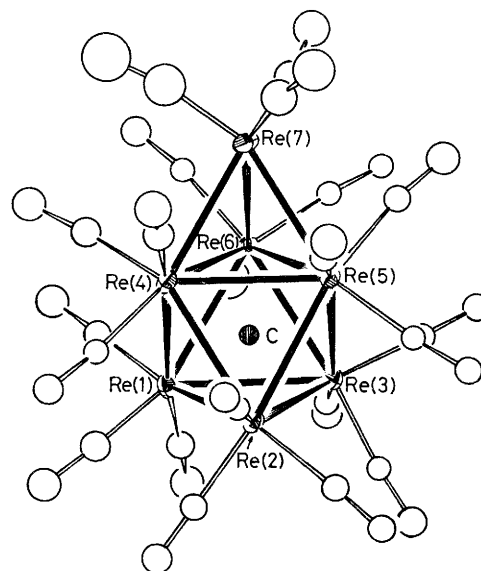


Figure 1. A view of the anion  $[\text{Re}_7\text{C}(\text{CO})_{21}]^{3-}$ . The individual Re-Re bond distances are as follows: (1)-(2) 3.069, (1)-(3) 3.084, (1)-(4) 2.981, (1)-(6) 3.015, (2)-(3) 3.086, (2)-(4) 3.012, (2)-(5) 2.981, (3)-(5) 3.022, (3)-(6) 2.969, (4)-(5) 2.955, (4)-(6) 2.957, (4)-(7) 2.943, (5)-(6) 2.952, (5)-(7) 2.927, and (6)-(7) 2.917 Å; e.s.d.s 0.001 Å.

bond distance in  $[\text{Re}_4(\text{CO})_{16}]^{2-}$ , 2.994 Å.<sup>6</sup> The Re-Re distances, however, belong to different classes: i, bonds within the Re(1), Re(2), Re(3) triangle, mean 3.080 Å; ii, bonds connecting the Re(1), Re(2), Re(3) and the Re(4), Re(5), Re(6) triangles, which are alternatively three longer (mean 3.017 Å) and three shorter (mean 2.977 Å); iii, bonds within the Re(4), Re(5), Re(6) triangle, mean 2.955 Å; iv, bonds involving the capping atom Re(7), mean 2.929 Å.

This anion is the first example of a carbido species in a carbonyl cluster compound of a metal not belonging to Group 8. The carbon atom lies at the centre of the octahedral hole, with Re-C distances in the range 2.11(1)—2.15(1) Å, mean 2.13 Å. The carbonyl ligands are all terminally bonded, three to each metal atom, and their stereochemistry resembles that present in the isoelectronic  $[\text{Os}_7(\text{CO})_{21}]^{4-}$ . This ligand geometry, which determines an idealized  $C_3$  symmetry for the whole anion, is probably responsible for the distribution of the metal-metal distances, very similar in both the osmium and rhenium species. The overall mean values of the Re-C and C-O bond lengths are 1.86 and 1.19 Å, respectively. The Re(7)-C bonds are somewhat shorter (mean 1.81 Å), probably owing to a higher localization of the anionic charge on the this metal atom, as suggested by a local electron count.

The presence of the interstitial carbon atom has a fundamental role in stabilizing this high nuclearity rhenium species.

† Crystal data:  $\text{C}_{94}\text{H}_{60}\text{O}_{21}\text{P}_3\text{Re}_7$ ,  $M = 2921.8$ , monoclinic, space group  $P2_1/n$  (No. 14),  $a = 18.851(4)$ ,  $b = 25.132(4)$ ,  $c = 19.138(4)$  Å,  $\beta = 95.31(2)^\circ$ ,  $Z = 4$ . The intensity data were recorded on an Enraf-Nonius CAD4 automated diffractometer, using graphite monochromated Mo- $K_\alpha$  radiation, within the range  $3 \leq \theta \leq 23^\circ$ . The structure was solved by direct methods and refined by least-squares using 7973 significant reflections [ $I \geq 3\sigma(I)$ ]. Anisotropic thermal parameters were assigned to the Re and P atoms. The current conventional  $R$  value is 0.049. 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.

The highest numbers of metal atoms found so far in carbonyl clusters of the Fe, Co, and Ni triads are, respectively: 10, in  $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$ ,<sup>7</sup> 22, in  $[\text{Rh}_{22}(\text{CO})_{87}]^{4-}$ ,<sup>8</sup> and  $[\text{Rh}_{22}(\text{CO})_{35}\text{H}_x]^{n-}$ ,<sup>9</sup> and 38, in  $[\text{Pt}_{38}(\text{CO})_{447}]^{2-}$ .<sup>1</sup> This trend can be rationalized by taking into account the fact that, with increasing nuclearity, the number of carbonyl groups on each metal atom must generally decrease, and this can better meet the electronic requirements of metals with higher numbers of valence electrons. In an octahedral cluster, for instance, with 86 valence electrons, the number of electrons which must be furnished by the ligands and/or anionic charges greatly increases on passing from the Ni (26) to the Mn subgroup (44). An octahedron of rhenium atoms requires, therefore, too many ligands, which are difficult to accommodate on the cluster surface, and such a species can be stabilized if some of the necessary electrons are supplied by interstitial atoms.

We thank the Italian C.N.R. for financial support.

Received, 4th December 1981; Com. 1397

## References

- 1 P. Chini, *J. Organomet. Chem.*, 1980, **200**, 37 and references cited therein.
- 2 G. Ciani, G. D'Alfonso, M. Freni, P. Romiti, and A. Sironi, *J. Organomet. Chem.*, 1978, **157**, 199.
- 3 V. G. Albano, P. L. Bellon, and G. Ciani, *Chem. Commun.*, 1969, 1024.
- 4 C. R. Eady, B. F. G. Johnson, J. Lewis, R. Mason, P. B. Hitchcock, and K. M. Thomas, *J. Chem. Soc., Chem. Commun.*, 1977, 385.
- 5 M. R. Churchill, K. N. Amoh, and H. J. Wasserman, *Inorg. Chem.*, 1981, **20**, 1609.
- 6 M. R. Churchill and R. Bau, *Inorg. Chem.*, 1968, **7**, 2606.
- 7 P. F. Jackson, B. F. G. Johnson, J. Lewis, M. McPartlin, and W. J. H. Nelson, *J. Chem. Soc., Chem. Commun.*, 1980, 224.
- 8 S. Martinengo, G. Ciani, and A. Sironi, *J. Am. Chem. Soc.*, 1980, **102**, 7564.
- 9 J. L. Vidal, R. C. Schoening, and J. M. Troup, *Inorg. Chem.*, 1981, **20**, 227.