Synthesis and X-Ray Crystal Structure of the Cluster Dianion, [Rh$_{10}$(CO)$_{21}$]$^{2-}$, containing a New Compact Array of Metal Atoms

Secondo Martinengo,*a Gianfranco Ciani,*b and Angelo Sironib

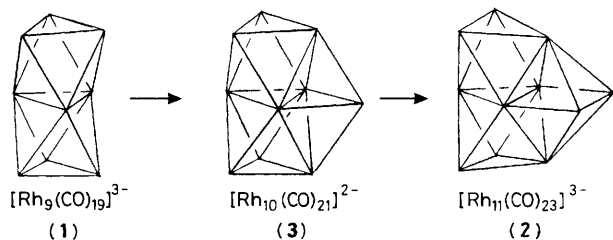a Centro del C.N.R. di Studio della Sintesi e Struttura dei Composti dei Metalli di Transizione nei Bassi Stati di Ossidazione, Via G. Venezian 21, 20133 Milano, Italy
b Istituto di Chimica Strutturistica Inorganica and Centro C.N.R., Via G. Venezian 21, 20133 Milano, Italy

The anion [Rh$_{10}$(CO)$_{21}$]$^{2-}$, obtained by reaction of [Rh$_9$(CO)$_{19}$]$^{3-}$ with the [Rh(CO)$_2$(NCMe)$_2$]$^+$ cation, contains a novel decanuclear metallic skeleton which is a fragment of hexagonal close-packed lattice formed by three superimposed layers (3/4/3 metals), with two octahedral and two tetrahedral condensed units as confirmed by X-ray crystallography.

A subject of interest in the field of cluster chemistry is the study of the process of cluster growth. The isolation and characterization of compounds with nuclearity 8—12 can help the understanding of the mechanism of metal atom aggregation in the passage from a simple octahedron to larger species, fragments of metallic lattices, which can contain fully encapsulated metals. We have recently described some rhodium cluster compounds of medium nuclearity, namely the anions [Rh$_9$(CO)$_{19}$]$^{3-}$ (**1**),[1] [Rh$_{11}$(CO)$_{23}$]$^{3-}$ (**2**),[2] and the neutral [Rh$_{12}$H$_2$(CO)$_{25}$],[3] all with metallic skeletons based on condensed face-sharing octahedral units. We report here a new intermediate species, the [Rh$_{10}$(CO)$_{21}$]$^{2-}$ (**3**) anion. Other decanuclear clusters are known, mostly containing interstitial main group elements, as [Rh$_{10}$E(CO)$_{22}$]$^{n-}$ (E = P, As, n = 3;[4] E = S, n = 2[5]), [Ru$_{10}$C$_2$(CO)$_{24}$]$^{2-}$,[6] [Os$_{10}$C(CO)$_{24}$]$^{2-}$ and related species,[7] or interstitial hydrides as [Os$_{10}$H$_4$(CO)$_{24}$]$^{2-}$,[7] or exhibiting non-compact geometries as [Pd$_{10}$(CO)$_{12}$(PBu$_3$)$_6$][8] or [Fe$_4$Pt$_6$(CO)$_{22}$]$^{2-}$.[9] The present anion, which shows a novel cluster geometry, is the first example of a compact close-packed decanuclear species without interstitial atoms.

Anion (**3**) has been prepared by treatment of (**1**) with the [Rh(CO)$_2$(NCMe)$_2$]$^+$ cation in MeOH;† the entering metal atom binds to the central triangle of the parent anion, thus giving a larger fragment of hexagonal close-packing (**3**), whose possible role of intermediate between compounds (**1**) and (**2**) is illustrated in Scheme 1. The intermediate role of anion (**3**) is also confirmed by its chemical behaviour: it can be converted back into (**1**) by treatment with halide ions in MeCN with release of a [Rh(CO)$_2$X$_2$]$^-$ unit, or it can react with the [Rh(CO)$_4$]$^-$ anion in methanolic solution to give (**2**) in good

yields. Crystals of the [PPh$_4$]$^+$ salt of (**3**) have been investigated by X-ray diffraction.‡

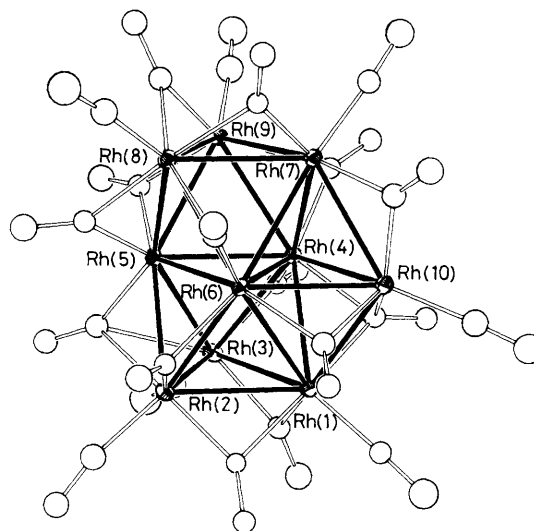Figure 1. A view of one of the two independent anions [Rh$_{10}$(CO)$_{21}$]$^{2-}$ (anion A). The metal–metal bond distances (Å) (in square brackets those of anion B) are as follows: 1–2 2.801(2) [2.788(3)], 1–3 2.840(2) [2.838(3)], 1–4 2.736(2) [2.706(2)], 1–6 2.903(2) [2.885(2)], 1–10 2.821(2) [2.828(2)], 2–3 2.797(2) [2.774(2)], 2–5 2.750(2) [2.772(2)], 2–6 2.744(2) [2.719(2)], 3–4 2.731(2) [2.723(2)], 3–5 2.738(2) [2.716(2)], 4–5 2.731(2) [2.730(2)], 4–6 2.828(2) [2.816(2)], 4–7 2.783(2) [2.770(2)], 4–9 2.730(2) [2.726(2)], 4–10 2.902(2) [2.963(2)], 5–6 2.740(2) [2.748(2)], 5–8 2.761(2) [2.745(2)], 5–9 2.712(2) [2.722(2)], 6–7 2.876(2) [2.852(2)], 6–8 2.796(2) [2.790(2)], 6–10 2.745(2) [2.740(2)], 7–8 2.794(2) [2.796(2)], 7–9 2.851(2) [2.837(2)], 7–10 2.783(2) [2.775(2)], 8–9 2.796(2) [2.792(2)].

[Rh$_9$(CO)$_{19}$]$^{3-}$ [Rh$_{10}$(CO)$_{21}$]$^{2-}$ [Rh$_{11}$(CO)$_{23}$]$^{3-}$
(**1**)   (**3**)   (**2**)

Scheme 1

The structure of the novel anion is shown in Figure 1. It contains a Rh_{10} metallic array which is a fragment of hexagonal close-packing of idealized C_{2v} symmetry, formed by three superimposed layers (3/4/3 metals), exhibiting two octahedral and two tetrahedral condensed units. The tenth rhodium atom, instead of assuming a capping position on one of the outer triangles of the parent anion (1), shows the preference for a cluster site which allows the attainment of a larger number of metal–metal bonds. This was already observed, for instance, on capping the trigonal prismatic nitride $[Rh_6N(CO)_{15}]^-$ with the anions $[M(CO)_4]^-$ (M = Co, Rh, Ir), the entering metal being bound on a square face of the prism.[10] From the point of view of the metal–metal connectivities five of the Rh atoms exhibit four bonds, two five bonds, one six bonds, and two seven bonds. One of the metal–metal interactions, Rh(4)–Rh(6), is inside the cluster.

The bond parameters in the two independent anions‡ are very similar. The 25 Rh–Rh bonds are in the range 2.712(2)—2.903(2) Å (mean 2.788 Å) in one anion and 2.706(2)—2.963(2) Å (mean 2.782 Å) in the second one. The scattering of the metal–metal bonds seems related to the asymmetry of the ligand distribution, while there is no clear distinction between bridged and unbridged edges.

The ligand stereochemistry is such that the whole anion does not present any symmetry element. Of the 21 carbonyl ligands 7 are terminally bonded, one per metal atom except the central metals Rh(4), Rh(5), and Rh(6), with mean Rh–C and C–O bond lengths of 1.86 and 1.16 Å, respectively. The other 14 CO groups span very different bridging situations: 12 are double-bridging, six of them almost symmetric, four slightly asymmetric (mean difference Rh–C long/Rh–C short 0.20 Å), and two quite asymmetric (mean difference Rh–C long/Rh–C short 0.41 Å). Two carbonyls are triple-bridging, one [on face Rh(1,4,10)] with one long (mean 2.44 Å) and two short (mean 2.07 Å) Rh–C bonds, and the second [on face Rh(2,3,5)] with one short (mean 1.92 Å) and two long (mean 2.51 Å) such distances.

Finally, the anion possesses 134 valence electrons, corresponding to 67 cluster valence molecular orbitals (CVMOs), in accord both with the results of an MO calculation on the bare cluster and with the suggestion of a number of $6N_{metals}$ + 7 CVMOs as the more probable for a compact close-packed cluster.[11]

References

1 S. Martinengo, A. Fumagalli, R. Bonfichi, G. Ciani, and A. Sironi, *J. Chem. Soc., Chem. Commun.*, 1982, 825.

2 A. Fumagalli, S. Martinengo, G. Ciani, and A. Sironi, *J. Chem. Soc., Chem. Commun.*, 1983, 453.

3 G. Ciani, A. Sironi, and S. Martinengo, *J. Chem. Soc., Chem. Commun.*, 1985, 1757.

4 J. L. Vidal, W. E. Walker, and R. C. Schoening, *Inorg. Chem.*, 1981, 20, 238; J. L. Vidal, *ibid.*, 1981, 20, 243.

5 G. Ciani, L. Garlaschelli, A. Sironi, and S. Martinengo, *J. Chem. Soc., Chem. Commun.*, 1981, 563.

6 C. T. Hayward, J. R. Shapley, M. R. Churchill, C. Bueno, and A. L. Rheingold, *J. Am. Chem. Soc.*, 1982, 104, 7347.

7 P. F. Jackson, B. F. G. Johnson, J. Lewis, W. J. H. Nelson, and M. McPartlin, *J. Chem. Soc., Dalton Trans.*, 1982, 2099; D. Braga, J. Lewis, B. F. G. Johnson, M. McPartlin, W. J. H. Nelson, and M. D. Vargas, *J. Chem. Soc., Chem. Commun.*, 1983, 241, and references therein.

8 E. G. Mednikov, N. K. Eremenko, V. A. Mikhailov, J. P. Gubin, Y. L. Slovokhotov, and Y. T. Struchkov, *J. Chem. Soc., Chem. Commun.*, 1981, 989.

9 G. Longoni, M. Manassero, and M. Sansoni, *J. Am. Chem. Soc.*, 1980, 102, 7973.

10 S. Martinengo, G. Ciani, and A. Sironi, *J. Chem. Soc., Chem. Commun.*, 1984, 1577.

11 G. Ciani and A. Sironi, *J. Organomet. Chem.*, 1980, 197, 233.