New Carbide Clusters in the Cobalt Sub-group. Part III.[1,2] Crystallographic Characterization of the Hydroxonium Salt of Tetradeca-μ-carbonyl-dicarbidotetradecacarbonyl-*polyhedro*-pentadecarhodate(1−)

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The title compound crystallizes in the orthorhombic space group *Pbcn*, with cell constants a = 15.01(2), b = 17.34(2), c = 18.85(2) Å, Z = 4. The structure was determined by direct methods from *X*-ray single-crystal counter data and refined by least-squares calculations to *R* 0.0267 for 2 387 significant reflections.

The $[Rh_{15}(CO)_{28}C_2]^-$ anion has precise C_2 symmetry idealizable to C_{2v}. The Rh_{15} metal atom cluster can be described as a centred and tetracapped pentagonal prism in which the central atom is twelve-co-ordinated in a non-crystallographic fashion, with Rh–Rh distances ranging from 2.738 to 3.332(3) Å. The two carbido-atoms occupy octahedral cavities, mean Rh–C 2.04 Å. The carbonyl ligands are bound on the cluster surface, fourteen linearly and fourteen edge-bridging such that all the metal atoms are thrice-connected to the ligands. The molecular architecture is discussed and a growth mechanism of the cluster is proposed.

CARBIDO–CARBONYL clusters of rhodium comprise a family of complexes related chemically and structurally. A major feature of these complexes seems to be their pronounced tendency towards clusters of high nuclearity: in fact, after isolation[1] of the dianion $[Rh_6(CO)_{15}C]^{2-}$, we have been able to obtain new and more complicated species.

By oxidation of the dianion in mild conditions a precipitate is obtained which when dissolved in organic solvents and set aside under carbon monoxide, gives crystals of the compound $[Rh_8(CO)_{19}C]$.[2] If the oxidation of the same dianion is carried out under nitrogen two new kinds of crystals are isolated, depending on the experimental conditions. We describe here the *X*-ray structure analysis of one of the species obtained under nitrogen, of formula $[H_3O][Rh_{15}(CO)_{28}C_2]$. A preliminary report has appeared[3] and details of preparation and chemical characterization will be reported later.

EXPERIMENTAL

Crystal Data.—$C_{30}H_3O_{29}Rh_{15}$, M = 2 370.91, Orthorhombic, a = 15.01(2), b = 17.34(2), c = 18.85(2) Å, U = 4 906.15 Å^3, D_m = 3.18(2) (by pycnometry), Z = 4, D_c = 3.21 g cm^{-3}, $F(000)$ = 4 327. Space group *Pbcn* (No. 60). Unit cell dimensions determined from precession photographs, Mo-K_α radiation, λ = 0.7107 Å; μ(Mo-K_α) = 48.4 cm^{-1}.

Intensity Measurements.—A prismatic crystal, with dimensions 0.125 × 0.110 × 0.237 mm, was mounted on a PAILRED linear equi-inclination diffractometer. The reciprocal lattice layers *hk*0—22 were collected within the limiting angles $3° < \theta < 28°$ and $0 < \mu < 24.5$ by use of graphite monochromatized Mo-K_α radiation. Outside this region only a small number of reflections were significantly above background. Integrated diffraction intensities for 9 427 reflections were measured with the ω-scan method at a scan rate of 1° min^{-1} and within an angular interval ($\Delta\omega$) varying, as a function of γ and μ, between 1.6 and 2.6°. Background was counted for 40 s at the extreme points of the scan range. During data collection the intensities of some reflections remeasured after completion of each layer, showed no significant decrease. Integrated intensities were reduced to F_o values by correction for Lorentz and polarization factors, the latter being evaluated by taking into account the partial polarization of the incident beam.[4] The absorption correction was computed by the method of refs. 5 and 6. Transmission factors were found to range from 0.663 to 0.715. No extinction corrections were made since no significant effects were observed. A final set of 2 387 independent reflections was obtained after removing all those with $\sigma(I)/I > 0.25$.

Determination of the Structure.—A Fourier synthesis, phased by direct methods as previously described,[7] revealed the presence of seven rhodium atoms in general positions and one on a two-fold symmetry axis; the entire metal atom cluster contained fifteen atoms arranged in a polyhedron of crystallographic C_2 symmetry. After preliminary refinement of the metal–atom parameters a difference-Fourier synthesis revealed the presence of fourteen independent carbonyl groups and of one independent carbide atom; the molecular formula of the complex therefore seemed to be $Rh_{15}(CO)_{28}C_2$. The Fourier map showed an isolated peak of electron density slightly lower than that of a carbon atom, which remained for the moment unexplained. The structure was refined by block-diagonal least-squares (9 × 9 blocks) up to *R* 0.0316. A difference-Fourier synthesis computed at this level was rather flat; the interference peaks did not exceed ±0.5 eÅ^{-3}, but the peak which had been disregarded remained very sharp with height 2 eÅ^{-3} clearly indicating the presence of a light atom. This was tentatively interpreted as being oxygen but its refinement was not satisfactory since the thermal factor became unrealistically high. The discrepancy disappeared by halving the occupancy factor of this atom. There was therefore one isolated oxygen atom for each $Rh_{15}(CO)_{28}C_2$ unit, pointing to the presence of either an H_2O or $[H_3O]^+$ species. The latter interpretation was accepted when the crystals were found to be diamagnetic and the cluster was consequently formulated as a monoanion. The alternative interpretation of the cation as being NH_4^+ was discarded as being chemically unlikely.

In the refinement of the structure by least-squares techniques, weights were applied according to $w = 1/(A +$

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[1] Part I, V.G. Albano, M. Sansoni, P. Chini, and S. Martinengo, *J.C.S. Dalton*, 1973, 651.

[2] Part II, V. G. Albano, M. Sansoni, P. Chini, S. Martinengo, and D. Strumolo, *J.C.S. Dalton*, 1975, 305.

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$BF_0 + CF_0^2$) where in the final cycles A, B, and C had values 100.0, −0.89, and 0.0027 and were chosen on the basis of an analysis of $\Sigma w\Delta^2$. Atomic scattering factors were taken from ref. 8 for rhodium (corrected for the real and imaginary part of the anomalous dispersion), oxygen, and carbon. The function $\Sigma w(F_o - kF_c)^2$ was minimized until all shifts became $< 0.25\sigma$; final values of the reliability indices were R 0.0267 and R' 0.0305. Final atom positions are reported in Table 1; final observed and computed structure factors and temperature factors are given in Supplementary Publication No. SUP 21691 (4 pp., 1 microfiche).*

TABLE 1

Final positional parameters ($\times 10^4$), with estimated standard deviations in parentheses

Atom	x	y	z
Rh(1)	5 000	1 875(0)	2 500
Rh(2)	3 586(0)	2 320(0)	3 411(0)
Rh(3)	4 054(0)	623(0)	3 383(0)
Rh(4)	3 744(0)	656(0)	1 843(0)
Rh(5)	4 746(0)	1 703(0)	1 017(0)
Rh(6)	3 333(0)	2 338(0)	1 940(0)
Rh(7)	2 505(0)	1 164(0)	2 798(0)
Rh(8)	4 889(0)	3 240(0)	1 767(0)
C(0)	3 817(7)	1 464(6)	2 630(5)
C(1)	1 298(8)	1 429(7)	3 006(8)
O(1)	589(7)	1 634(7)	3 118(7)
C(2)	2 362(8)	481(8)	1 965(7)
O(2)	1 824(7)	130(7)	1 658(7)
C(3)	2 687(8)	415(8)	3 571(7)
O(3)	2 316(6)	54(7)	4 000(6)
C(4)	3 801(9)	−414(7)	1 577(8)
O(4)	3 760(8)	−1 049(5)	1 466(7)
C(5)	4 231(9)	−447(7)	3 584(8)
O(5)	4 229(8)	−1 079(6)	3 669(8)
C(6)	4 428(9)	886(8)	4 374(8)
O(6)	4 237(8)	682(7)	4 941(5)
C(7)	3 697(8)	1 011(6)	804(6)
O(7)	3 218(7)	892(6)	351(5)
C(8)	4 681(8)	2 212(7)	134(6)
O(8)	4 676(8)	2 516(6)	−392(5)
C(9)	4 972(8)	4 317(7)	3 274(8)
O(9)	4 862(8)	4 949(5)	3 352(8)
C(10)	4 143(8)	3 214(7)	3 944(6)
O(10)	3 990(7)	3 570(5)	4 456(5)
C(11)	3 706(7)	3 252(6)	1 315(6)
O(11)	3 371(6)	3 629(5)	872(5)
C(12)	2 912(8)	3 027(7)	2 736(7)
O(12)	2 484(6)	3 605(6)	2 789(5)
C(13)	2 721(9)	2 276(9)	4 133(7)
O(13)	2 241(8)	2 284(8)	4 595(6)
C(13)	2 253(8)	2 282(7)	1 429(7)
O(14)	1 629(6)	2 245(6)	1 098(6)
O	951(14)	−35(13)	107(12)

Computations.—All computations were carried out on a UNIVAC 1106 computer at the computing centre of Milan University, with local programmes.

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

The crystal packing is shown in Figure 1; the unit cell contains four formula units $[H_3O][Rh_{15}(CO)_{28}C_2]$. The anions are disposed about locations of C_2 local symmetry, the H_3O^+ cations in general eight-fold position, consequently occupying only 50% of their locations; the packing is dominated by the large anions piled along the symmetry axes. Interanion distances are normal values, the shortest contacts being C · · · O 3.12 and O · · · O 2.90 Å. The shortest cation–anion contacts are in the range 2.82—2.92 Å, and indicate the presence of hydrogen bonds.

The disorder of the cations has no detectable effects on the anions since the Coulombic contribution to the lattice energy does not seem very dominant in a crystal containing such a large anion; at the same time, the cation distribution can be shown to be not completely random. As can be seen in Figure 1, the cation locations occur in pairs related by inversion centres whose mutual distance is as short as 2.89 Å; consequently the cation–cation repulsions make highly unlikely the existence of doubly occupied pairs of locations, and the disorder can be simply rationalized by attributing one $[H_3O^+]$ ion to every pair of locations. The occupancy can be considered random within each pair and uncorrelated to the neighbouring ones, which are separated by *ca.* 10 Å.

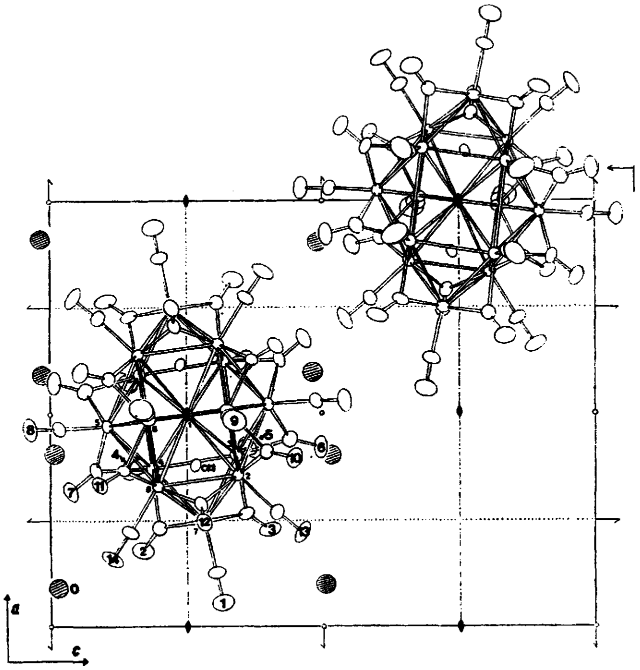

FIGURE 1 Partial view of the crystal packing down the b axis. Only the independent part of the anion is numbered and the carbon atoms are numbered according to the corresponding oxygen atom. Hatched circles indicate sites of disordered cations

Figure 2 shows the anion, and Figure 3 two views of the metal-atom cluster. Although the precise molecular symmetry is C_2, bond distances and angles (Table 2) do not deviate significantly from C_{2v} symmetry. An idealized geometrical description of the cluster could be that of a centred and tetracapped pentagonal prism with the capping atoms positioned on the bases and on two side faces. From a chemical and structural standpoint the cluster is better described as a system of two octahedra sharing one vertex [Rh(1)] plus four extra atoms [Rh(5), Rh(5′), Rh(8), and Rh(8′)] forming tetrahedra fused with

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1975, Index issue. (Items less than 10pp. are supplied as full-sized copies.)

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the octahedra and with themselves. The carbide atoms occupy the octahedral cavities.

The cluster geometry, at first sight very different from that of the parent prismatic anion $[Rh_6(CO)_{15}C]^{2-}$, can be rationalized by a growth mechanism (Figure 4). The first step consists in the insertion of a rhodium atom on a rectangular face of the prismatic unit (1). In a second step the monocapped prism (2) undergoes isomerization to a monocapped octahedron (3) by shifting the metal atoms defining the edge opposite to the capped face. This isomerization should not require high activation energy, as no metal–metal bonds are stretched and two new bonds are formed. At this point the growth mechanism of the cluster would imply a step leading to a system of two octahedra sharing one vertex. This step could take place through the insertion of the monocapped octahedron (3) (oriented as shown in Figure 4) on a rectangular face of the prism (1), giving the intermediate (4) with six new metal–metal interactions; (4) could isomerize the prismatic moiety to monocapped octahedron and rearrange to (5) by rotation of a rhodium atom from the capping position on the newly formed octahedron to the interoctahedral position on the *aa'* axis. The polyhedron (5) could accept two further metal atoms on one of the interoctahedral cavities and, in order to make room for the entering atoms, rotate the octahedra about the *aa'* axis up to the final configuration.

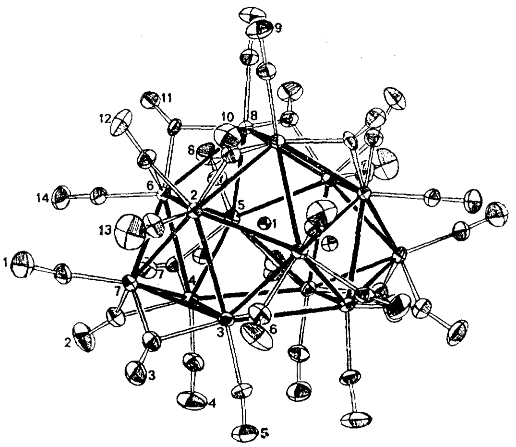

FIGURE 2 Perspective drawing of the anion. Heavy lines define the metal-atom cluster; the central rhodium and carbido-atoms are not connected to the neighbouring ones for sake of clarity

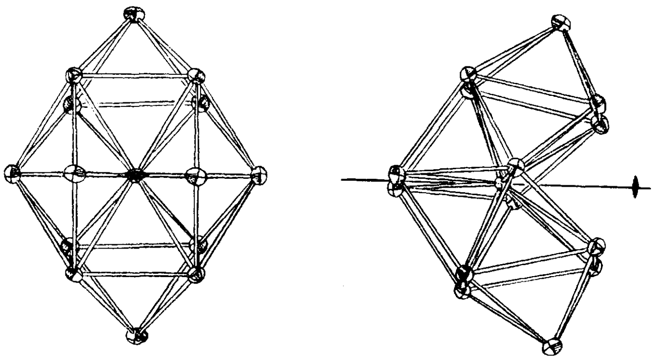

FIGURE 3 Two views of the metal-atom cluster in which only bonding rhodium–rhodium interactions are drawn (see text)

TABLE 2

Bond distances (Å) and relevant angles (°) * with estimated standard deviations in parentheses

Rh(1)–Rh(2)	2.837(3)	Rh(2)–C(10)	2.03(1)
Rh(1)–Rh(3)	3.082(3)	Rh(8')–C(10)	1.98(1)
Rh(1)–Rh(4)	3.091(3)	Rh(6)–C(11)	2.05(1)
Rh(1)–Rh(6)	2.831(3)	Rh(8)–C(11)	1.97(1)
Rh(1)–Rh(5)	2.836(3)	Rh(4)–C(7)	2.05(1)
Rh(1)–Rh(8)	2.745(3)	Rh(5)–C(7)	2.02(1)
Rh(2)–Rh(3)	3.024(3)	Rh(2)–C(12)	2.04(1)
Rh(2)–Rh(6)	2.800(3)	Rh(6)–C(12)	2.02(1)
Rh(2)–Rh(5')	2.925(3)	Rh(3)–C(3)	2.11(1)
Rh(2)–Rh(8')	2.809(3)	Rh(7)–C(3)	1.97(1)
Rh(2)–Rh(7)	2.826(3)	Rh(4)–C(2)	2.11(1)
Rh(3)–Rh(4)	2.942(3)	Rh(7)–C(2)	1.98(1)
Rh(3)–Rh(5')	2.833(3)	C(1)–O(1)	1.14(2)
Rh(3)–Rh(7)	2.738(3)	C(4)–O(4)	1.12(2)
Rh(4)–Rh(5)	2.826(3)	C(5)–O(5)	1.11(2)
Rh(4)–Rh(6)	2.988(3)	C(8)–O(8)	1.13(2)
Rh(4)–Rh(7)	2.734(3)	C(9')–O(9')	1.12(2)
Rh(5)–Rh(6)	2.956(3)	C(13)–O(13)	1.13(2)
Rh(5)–Rh(8)	3.024(3)	C(14)–O(14)	1.13(2)
Rh(6)–Rh(7)	2.883(3)	C(2)–O(2)	1.17(2)
Rh(6)–Rh(8)	2.829(3)	C(3)–O(3)	1.16(2)
Rh(8)–Rh(8')	2.780(6)	C(6)–O(6)	1.16(2)
Rh(3) · · · Rh(4')	3.332(3)	C(7)–O(7)	1.14(2)
Rh(2)–C(13)	1.88(1)	C(10)–O(10)	1.17(2)
Rh(3)–C(15)	1.92(1)	C(11)–O(11)	1.17(2)
Rh(4)–C(4)	1.92(1)	C(12)–O(12)	1.20(2)
Rh(5)–C(8)	1.89(1)	C(0)–Rh(1)	1.93(1)
Rh(6)–C(14)	1.89(1)	C(0)–Rh(2)	2.12(1)
Rh(7)–C(1)	1.91(1)	C(0)–Rh(3)	2.07(1)
Rh(8)–C(9')	1.88(1)	C(0)–Rh(4)	2.04(1)
Rh(3)–C(6)	2.00(2)	C(0)–Rh(6)	2.12(1)
Rh(5')–C(6)	2.02(2)	C(0)–Rh(7)	2.06(1)
Rh(2)–C(13)–O(13)	175(1)	Rh(6)–C(11)–O(11)	136(1)
Rh(3)–C(5)–O(5)	171(1)	Rh(8)–C(11)–O(11)	134(1)
Rh(4)–C(4)–O(4)	173(1)	Rh(4)–C(7)–O(7)	133(1)
Rh(5)–C(8)–O(8)	177(1)	Rh(5)–C(7)–O(7)	139(1)
Rh(6)–C(14)–O(14)	177(1)	Rh(2)–C(12)–O(12)	136(1)
Rh(7)–C(1)–O(1)	176(1)	Rh(6)–C(12)–O(12)	137(1)
Rh(8)–C(9')–O(9')	174(1)	Rh(3)–C(3)–O(3)	132(1)
Rh(3)–C(6)–O(6)	136(1)	Rh(7)–C(3)–O(3)	143(1)
Rh(5')–C(6)–O(6)	134(1)	Rh(4)–C(2)–O(2)	135(1)
Rh(2)–C(10)–O(10)	137(1)	Rh(7)–C(2)–O(2)	142(1)
Rh(8')–C(10)–O(10)	134(1)		

* Primed atoms are symmetry-equivalent to the unprimed ones.

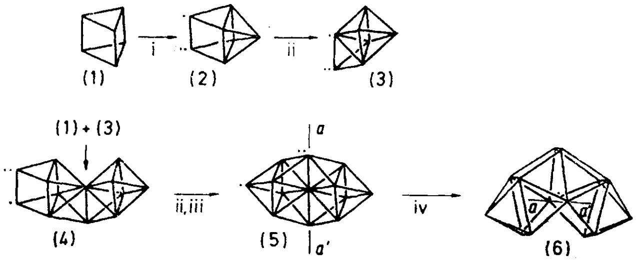

FIGURE 4 Schematic representation of our suggested growth mechanism for $Rh_{15}C_2$. Dots show the atom displacements in the isomerization steps. Carbido-atoms present in the prismatic and octahedral cavities are not shown. i, +Rh; ii, isomerization; iii, rotation; and iv, insertion of 2 Rh and isomerization about *aa'*

This growth mechanism has an experimental basis in the chemical evidence that the starting material is the preformed Rh_6C cluster, and in the ascertained easy insertion of a rhodium atom on a rectangular face of the prism.[2] This scheme is probably an oversimplification and ignores the role played by the ligands, but we feel that the determining steps are not far from those of our model which explains three main features of the cluster: (i) the position of the carbido-atoms by the prism-octahedron isomerization, (ii) the formation of fused octahedra, and (iii) the presence of strain in some Rh–Rh interactions (see later). The unusual cluster geometry is certainly a consequence of the fact that the anion $[Rh_6(CO)_{15}C]^{2-}$ as a whole participates to the growth of the molecular architecture.

The most singular feature of the cluster is the twelve-co-ordination about the central atom which is not metal-like, *i.e.* a close packing of atoms in which all the metal-metal contacts are equal in length. This particular type of twelve-co-ordination has been already suggested [9] in terms of sphere packing but has never before been found. Some discussion seems necessary in order to rationalize this structure. Non-crystallographic twelve-co-ordinations cannot be realized with equal surface and inner distances, for example in the highly symmetrical icosahedral co-ordination the central atom should be 10% smaller than the surface ones. Rotational isomerization of the icosahedron leads to bicapped pentagonal prisms in which again, if the size of the central atom is supposed equal to the surface ones, deformations are necessary. A possible configuration consists of a 10 + 2 co-ordination in which the distances of the two pyramidal apices from the centre and the interbasal edges of the prism are 5% longer than the other contacts. A second configuration preserves the equivalence of the centre–surface distances through the stretching of two basal edges of the prism which become 10% longer than the others. The latter is the type of configuration adopted by the present cluster, but further minor deviations from ideal geometry are imposed by the intermetal interactions and will be discussed later.

The Rh–Rh distances range from 2.738 to 3.332 Å, and the mean value of the bonding interactions (see later; 2.87 Å) is significantly longer than those found in $[Rh_6(CO)_{15}C]^{2-}$ (2.79) [1] and in $[Rh_8(CO)_{19}C]$ (2.81 Å),[2] indicating some degree of destabilization of the cluster. The range of Rh–Rh distances can be compared with those found in other polyhedral cluster compounds of rhodium.[1,2,10-15] Five independent distances in the present cluster exceed the longest value reported and the character of the longest interactions [Rh(3)–Rh(4′) and its equivalent Rh(3′)–Rh(4)] which correspond to the stretched edges of the ideal polyhedron is questionable. If our suggested growth mechanism of the cluster is almost correct these distances can be considered as very short non-bonding contacts and the appreciable lengthening of some distances [Rh(1)–Rh(3), Rh(1)–Rh(4), Rh(2)–Rh(3), and Rh(4)–Rh(6)] and the compression of others [Rh(3)–Rh(7) and Rh(4)–Rh(7)] is probably a consequence of repulsive interactions between the couples Rh(3) ··· Rh(4′) and Rh(3′) ··· Rh(4). The non-bonding character of these interactions is confirmed by the fact that they are 16% longer than the means of the others, while the ideal value is only 10% longer. This excessive lengthening is also responsible for the misalignment of the Rh(5)–Rh(1)–Rh(5′) atoms, which are collinear in the ideal model.

The carbido-atoms, which are located in the octahedral cavities of the cluster, have Rh–C distances 1.93—2.12, mean 2.04 Å, strictly comparable with those found in $[Ru_6(CO)_{17}C]$ (2.05) [16] and $[Ru_6(CO)_{14}(arene)C]$ (2.04 Å),[17] in which the carbon atoms are in octahedral cavities. Significantly longer distances are found for the carbon in prismatic cavities: 2.13 Å in both $[Rh_6(CO)_{15}C]^{2-}$ and $[Rh_8(CO)_{19}C]$.[1,2]

The twenty-eight carbonyl ligands are distributed on the cluster surface, fourteen terminally, one per metal atom, and fourteen edge-bridging, such that there are two bridging connections per metal atom. Mean Rh–C and C–O values for the terminal groups are 1.89 and 1.12 Å, which compare well with those found in other carbido-derivatives {1.89 and 1.13 in $[Rh_6(CO)_{15}C]^{2-}$ (ref. 1) and 1.91 and 1.13 Å in $[Rh_8(CO)_{19}C]^{2}$} but differ significantly from corresponding values in other carbonyl clusters of rhodium {*e.g.* 1.86 and 1.15 in $[Rh_6(CO)_{16}]$,[11] 1.85 and 1.15 in $[Rh_6(CO)_{15}I]^-$,[12] 1.88 and 1.14, and 1.82 and 1.20 in $[Rh_{12}(CO)_{30}]^{2-}$,[13] and 1.82 and 1.17 Å in $[Rh_7(CO)_{16}I]^{2-}$ (ref. 15)}. The comparison shows that, in spite of the lower ligand–metal ratio, the metal–carbonyl interactions in the carbido-derivatives of rhodium exhibit lower metal–ligand back-bonding, possibly because the carbido-atoms withdraw electronic charge towards the core of the cluster. An alternative explanation could be that this is a result of the high number of bridging groups.

The bridging ligands exhibit moderate asymmetries which find strict correspondence in groups related by the non-crystallographic mirror planes; mean Rh–C and C–O distances are 2.02 and 1.17 Å.

Intramolecular carbon–carbon contacts are in the range 2.6—3.3 Å indicating that, although the ligand–metal ratio is the lowest found for cluster carbonyls, the ligand overcrowding is not alleviated. An explanation is that as the metal polyhedron becomes bigger the curvature of its surface diminishes and a lower sector of the outer space per cluster atom remains available for the ligands. Steric effects may become the determining

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factor for the stability of big clusters and the existence of $[Rh_{15}(CO)_{28}C_2]^-$ can be attributed not only to the strengthening effects of the interstitial carbons on the rhodium–rhodium interactions but also to the ability of these atoms to supply four electron pairs to the cluster orbitals, without steric hindrance and without accumulation of negative charge.

In the light of these observations one could speculate that stable clusters of high nuclearity require not only strong homophilicity of the metals but also low ligand–metal ratios, as confirmed by the known species $[Pt_{15}(CO)_{30}]^{2-}$,[18] $[Au_{11}X_3L_9]$ ($X = I^-$ or SCN^-, L = phosphines),[19] and finally $[Bi_9]^{5+}$.[20]

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