Synthesis and Crystallographic Characterization of the Carbidopentadecacarbonylhexarhodate Dianion in its Bis(benzyltrimethylammonium) Salt, the First Example of a Trigonal Prismatic Cluster of Metal Atoms

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Carbidopentadecacarbonylhexarhodate dianion has been obtained by reaction of dodecacarbonyltetrarhodium with methanolic sodium hydroxide under carbon monoxide with successive addition of chloroform. The structural characterization has been carried out on the salt $[NMe_3(CH_2Ph)]_2[Rh_6(CO)_{15}C]$, which crystallizes in the monoclinic space group $C2/c$ with a = 22·17(2), b = 11·46(1), c = 18·51(2) Å, β = 112° 43′ (6′), Z = 4. Diffractometer data have been refined by least-squares methods to a final R of 0·033 for 1654 statistically significant reflections. The anion $[Rh_6(CO)_{15}C]^{2-}$ has precise C_2 and idealized D_{3h} symmetry. The six rhodium atoms define a trigonal prism whose edges are associated with symmetrical bridging CO groups, the remaining six carbonyl ligands are linearly bonded one per each rhodium atom. The carbide atom occupies the centre of the prism. The mean basal and inter-basal Rh–Rh distances are 2·776(3) and 2·817(2) Å respectively; mean Rh–C(carbide) 2·134(6) Å. The mean Rh–C and C–O distances for linear, basal bridging, and inter-basal bridging CO groups are 1·89(1), 1·13(1); 2·12(1), 1·14(2); and 2·04(1), 1·17(2) Å.

ISOLATED carbon atoms of the carbide type have been found to date in five polynuclear metal carbonyls, *viz.* $Fe_5(CO)_{15}C$ (ref. 1), $[Fe_5(CO)_{14}C]^{2-}$ (ref. 2), $[Fe_6(CO)_{16}C]^{2-}$ (ref. 3), $Ru_6(CO)_{14}$(arene)C,[4,5] and $Ru_6(CO)_{17}C$.[6] The first two compounds are the only known derivatives having a square pyramidal arrangement of the metal atoms, the others falling in the more populated class with octahedral clusters.

In this paper we report the preparation and structure determination of the rhodium anionic species $[Rh_6(CO)_{15}C]^{2-}$, which has proved to be the first carbidocarbonylderivative in the cobalt triad and, at the same time, the first hexanuclear metal atom cluster having a trigonal prismatic geometry.

The compound, previously formulated as $[NMe_3(CH_2Ph)][Rh_3(CO)_{10}]$, had been obtained by reaction of tetracarbonyldichlorodirhodium and potassium hydroxide in methanol, but further research proved to be impossible because further attempts at preparation had systematically failed; the compound could be obtained only as a minor by-product during the preparation of the anion $[Rh_7(CO)_{16}]^{3-}$.[7] We thus decided to undertake a crystallographic characterization which has led not only to the correct formulation of the complex, but also to a new method of its preparation. In fact, as soon as the presence of a carbon atom at the centre of the cluster was apparent, we assumed that this carbon might originate from minor amounts of chloroform in the methanol. This hypothesis proved to be correct and the compound is now readily available in good yields. Hence it is now possible to study some of the chemistry of this anion, which will be reported later[8] together with further details regarding its synthesis.

The synthesis of this novel cluster confirms the versatility of rhodium, among the Group VIII metals, in giving a variety of cluster geometries. In fact, together with the compounds which are known for rhodium and for the other elements, syntheses and structures have been reported for $[Rh_{12}(CO)_{30}]^{2-}$ (refs. 9 and 10) and $[Rh_7(CO)_{16}]^{3-}$ (refs. 11 and 12), which exhibit metal polyhedrons at present peculiar to this metal.

EXPERIMENTAL

Preparation of $[NMe_3(CH_2Ph)]_2[Rh_6(CO)_{15}C]$.—Dodecacarbonyltetrarhodium (1 g) was added to a solution of sodium hydroxide (2·14 g) in methanol (30 ml) under carbon monoxide. After 2 h the solution became deep green due to formation of the anion $[Rh_7(CO)_{16}]^{3-}$. Addition of $CHCl_3$ (2 ml) gave a slow transformation (2 days) into a yellow-green solution. After addition of excess of solid carbon dioxide the solution was evaporated to dryness and the residue was dissolved in water (25 ml). The filtered solution was saturated with solid KBr (*ca.* 10 g), and the yellow crystalline precipitate washed with a saturated solution of KBr, and vacuum dried. The pure potassium salt could be obtained by extraction with tetrahydrofuran in *ca.* 70% yields. The potassium salt (0·5 g) dissolved in ethanol (20 ml) was treated with a solution of benzyltrimethylammonium chloride (1 g) in ethanol (15 ml). The yellow precipitate was recrystallised from acetone–isopropanol; the yield is quantitative (Found: C, 32·25; H, 2·3; N, 1·90. Calc. for $C_{36}H_{32}N_2O_{15}Rh_6$: C, 32·0; H, 2·4; N, 2·05% †).

Crystal Data.—$C_{36}H_{32}N_2O_{15}Rh_6$, M = 675·04, Monoclinic, a = 22·17(2), b = 11·46(1), c = 18·51(2) Å, β = 112° 43′ (6′),

† Calc. for the original formulation $[NMe_3(CH_2Ph)][Rh_3(CO)_{10}]$: C, 32·5; H, 2·15; N, 1·9%.

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$U = 4337$ Å^3, $D_m = 2{\cdot}12(2)$ (by flotation), $Z = 4$, $D_c = 2{\cdot}07$, $F(000) = 2608$. Space group C_c (No. 9) or $C2/c$ (No. 15). Unit cell dimensions were determined by precession photographs and refined on a PAILRED diffractometer by use of silicon monochromatized Mo-$K_{\alpha 1}$ radiation [$\lambda = 0{\cdot}70930$ Å; μ(Mo-K_α) $= 22{\cdot}9$ cm^{-1}].

Intensity Measurements.—A thick-tabular crystal, with dimensions, $0{\cdot}074 \times 0{\cdot}223 \times 0{\cdot}307$ mm, was mounted on a PAILRED linear equi-inclination diffractometer. 21 levels of the reciprocal lattice, 0—20kl, were collected within the sphere $2\theta \leqslant 52°$. Outside this region only a small number of reflections were significantly above background. Integrated diffraction intensities for 2723 reflections were measured with the ω-scan method at a scan rate of 0·25° min^{-1}, the backgrounds were counted for 1 min at the extreme points of the scan range. During the data collection the intensities of four well spaced zero-level reflections were measured at regular intervals, and no significant decay was observed. The absorption correction was computed by the method of ref. 13, a sampling of $8 \times 8 \times 8$ points being used. The transmission factors were found to range from 0·70—0·85. The integrated intensities were reduced to F_o values by correction for Lorentz and polarization factors, the latter were evaluated by taking into account the partial polarization of the incident beam.[14] No correction for extinction was made since no significant effect was observed. A final set of 1654 independent reflections was obtained after removing all those with $\sigma(I)/I \geqslant 0{\cdot}25$.

Determination of the Structure.—A three-dimensional Patterson synthesis revealed interatomic vectors consistent with two triangular and parallel arrangements of rhodium atoms. The Rh···Rh distances in the triangles and between them were *ca.* 2·8 Å, and the overall geometry of the metal cluster proved to be that of a trigonal prism. The two Rh_3 units seemed to be related by a two-fold symmetry axis and consequently the $C2/c$ space group was postulated, and its choice confirmed by the successful refinement of the structure.

A three-dimensional Fourier synthesis, phased by the three independent rhodium atoms, showed the peaks of the atoms in the benzyltrimethylammonium cation and those of the carbonyl groups in the anion. Seven CO groups in general positions and one on the two-fold axis could be recognized, so the resulting formula appeared to be $[Rh_6(CO)_{15}]^{2-}$. However, there was one unexplainable peak at the centre of the cluster whose height was comparable with those of the carbon atoms. This peak remained very sharp in a difference-Fourier map, computed after preliminary refinement of the structure by least squares, and strongly suggested the presence of a light atom at the centre of the cluster. A carbon atom placed in this position, determined a significant lowering of the R factor and the soundness of the assumption was confirmed by the refinement.

The whole structure was refined by least squares in the block-diagonal approximation (9×9 blocks). The thermal motion was treated anisotropically for all atoms except those in the phenyl ring, constrained to rigid-body motion (D_{6h} symmetry, C–C taken as 1·392 Å), which was refined with individual isotropic thermal factors. The co-ordinates of the hydrogen atoms (C–H assumed 1·08 Å, C–C–H 120°) were computed at the end of each cycle, and their contributions to the structure factors were taken into account. The observations were weighted according to the formula $w = 1/(A + BF_o + CF_o^2)$, where, in the final cycles A, B, and C had values 27·0, 0·13, and 0·0002, and were chosen on the basis of an analysis of $\Sigma w\Delta^2$. The atomic scatterings factors were taken from ref. 15 for rhodium (corrected for the real and imaginary part of the anomalous dispersion), oxygen, nitrogen, and carbon, and from ref. 16 for hydrogen. The function $\Sigma w(F_o - k|F|_c)^2$ was minimized until all shifts became $< 0{\cdot}25\sigma$, the final values of the reliability indices were R 0·033 and R' 0·042 $\{R' = [\Sigma w(F_o - k|F|_c)^2/\Sigma wF_o^2]^{1/2}\}$.

A final difference-Fourier synthesis revealed no errors in the structure, the highest peaks did not exceed $\pm 0{\cdot}5$ eÅ^{-3} and were in the zones of the metal atoms. The results of the refinement are reported in Table 1, the final list of the observed and computed structure factors moduli are listed in Supplementary Publication No. 20553 (2 pp., 1 microfiche).*

Computations.—All computations were carried out on an IBM 7040 computer. For the absorption correction a local programme was used, in which the direction of primary and diffracted beams are evaluated as recently described.[17] Counter-data reduction and statistical analyses for weighting schemes were also based upon local versions of Fortran programmes. In addition, local versions of entries No. 7528, 7531, 7532, and 7535 in the 'International World List of Crystallographic Programs' were used for Fourier analysis, structure factor and least-squares calculation, Johnson's ORTEP for thermal ellipsoids plotting, and a programme by Domenicano and Vaciago for computation of the molecular parameters.

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

The crystal structure consists of discrete $[Rh_6(CO)_{15}C]^{2-}$ anions and $[NMe_3(CH_2Ph)]^+$ cations separated by normal van der Waal's contacts. The crystal packing is illustrated in Figure 1; the anions, which occupy the special positions e, are along the two-fold symmetry axes and the cations form piles around the screw axes. The baricentres of both anions and cations lie near the glide planes so that the structure can be described in terms of an AB sequence of layers, in which A and B are related by the $\frac{1}{2},\frac{1}{2},0$ displacement.

A perspective view of the dianion is shown in Figure 2. The rhodium atoms are at the corners of a trigonal prism, so that each is bonded to three others. The fifteen CO ligands adopt the most symmetrical arrangement, six are bonded linearly, one per metal atom, and the other nine form symmetrical bridges on the prism edges. The carbide atom is at the centre of the prism.

Bond distances and selected angles are listed in Tables 2 and 3; although the symmetry imposed by the space group is only C_2, the anion possesses D_{3h} symmetry within the limits of experimental errors. The Rh–Rh

* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

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distances fall into two sets, those within the basal triangles and those between them, the mean values being 2·776(3) and 2·817(2) Å respectively. These distances are comparable with those found in $Rh_6(CO)_{16}$ 2·776,[18] $[Rh_6(CO)_{15}I]^-$ 2·72—2·76,[19] $[Rh_{12}(CO)_{30}]^{2-}$ 2·68—2·85,[10] $[Rh_7(CO)_{16}]^{3-}$ 2·72—2·81,[12] $Rh_4(CO)_{12}$ 2·71—2·80,[20] $Rh_3(CO)_3(\pi\text{-}C_5H_5)_3$ 2·62,[21] $Rh_3(\pi\text{-}C_5H_5)_4H$ 2·70,[22] $Rh_2(CO)_3(\pi\text{-}C_5H_5)_2$ 2·68,[23] and in the metal 2·69 Å.[24] It can be seen that the transition from antiprismatic arrangement of metals in $Rh_6(CO)_{16}$ to prismatic in the present complex has had no effect on the basal Rh–Rh distances, and has caused only a moderate lengthening of the inter-basal ones; the distance between the basal planes is increased by 0·11 Å. The mean Rh–C(carbide) distance [**2·134(6)**] can be compared with the values found in $Ru_6(CO)_{14}$(arene)C (1·88—2·12),[5] and in $Ru_6(CO)_{17}C$ (2·05 Å).[6] If for rhodium in cluster compounds we deduce from the Rh–I distance in $[Rh_6(CO)_{15}I]^-$ (2·71 Å) [19] a covalent radius of 1·38 Å and take 0·77 Å for the carbide radius, their sum (2·15 Å) is found to be very near to the observed Rh–C distances. It might be inferred from this that the steric requirements of the central carbon atom have determined the metal-atom geometry; in fact the Rh–C distance observed in this structure could be obtained in octahedral geometry only by lengthening the Rh–Rh distances from 2·77 to *ca.* 3·0 Å. On the other hand the carbide atoms at the centres of octahedral Fe_6 and Ru_6 clusters imply the possibility of shorter radii for carbon, and indicate that steric factors alone do not justify the prismatic geometry of $[Rh_6(CO)_{15}C]^{2-}$. Very probably the determining factor is the impossibility of accommodating 90 outer valence-electrons in stable orbitals of an octahedral cluster (54 of rhodium atoms, 30 of carbonyl groups, 4 of the central carbon, and 2 anionic): in fact all the known octahedral carbonyl clusters possess only 86 electrons. Prismatic geometry and 90 valence electrons are therefore the peculiar characteristics of a novel family of cluster compounds. As the other clusters can be seen as small moieties of close-packed metal atoms, this new type of cluster can be connected to the structures of some carbides in which the carbon is prismatically

TABLE 1

Final positional and thermal [a] parameters [b] ($\times 10^4$)

Atom	x	y	z	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
Rh(1)	879(1)	2853(1)	3359(1)	17(1)	−6(1)	10(1)	63(1)	0(1)	23(1)
Rh(2)	−397(1)	2878(1)	3288(1)	20(1)	−4(1)	19(1)	62(1)	−5(1)	24(1)
Rh(3)	228(1)	773(1)	3323(1)	19(1)	0(1)	12(1)	59(1)	12(1)	26(1)
C(0)	0	2191(13)	2500	19(3)	0	10(5)	65(12)	0	15(4)
C(1)	1614(6)	3317(11)	4243(7)	30(3)	−34(10)	9(6)	78(11)	−7(12)	39(4)
O(1)	2056(5)	3593(9)	4773(6)	42(3)	−27(11)	−19(6)	144(11)	15(12)	49(4)
C(2)	−614(6)	3430(11)	4129(6)	36(3)	1(11)	35(5)	85(11)	−17(12)	38(4)
O(2)	−735(5)	3796(10)	4620(5)	61(3)	−15(11)	78(4)	185(13)	−65(10)	54(3)
C(3)	435(5)	−292(11)	4155(6)	22(3)	5(9)	14(6)	93(12)	31(11)	38(4)
O(3)	528(5)	−920(9)	4654(5)	53(3)	13(11)	34(5)	160(10)	105(10)	53(3)
C(4)	286(5)	4253(9)	3448(5)	21(2)	1(9)	19(4)	58(8)	−14(10)	31(3)
O(4)	326(4)	5222(7)	3572(5)	29(2)	−10(7)	41(5)	72(7)	−61(10)	91(4)
C(5)	−688(5)	1153(11)	3360(5)	30(3)	−4(9)	36(4)	90(11)	14(10)	29(3)
O(5)	−1110(4)	677(7)	3434(4)	36(2)	0(7)	54(3)	76(7)	17(8)	61(3)
C(6)	1217(5)	1097(10)	3508(6)	22(3)	10(9)	7(5)	66(10)	12(10)	32(4)
O(6)	1696(4)	593(7)	3653(5)	21(2)	24(6)	18(4)	85(7)	40(10)	71(4)
C(7)	1226(5)	3531(9)	2577(5)	18(2)	−8(8)	15(4)	65(9)	0(10)	27(3)
O(7)	1693(4)	4023(8)	2606(4)	20(2)	−40(6)	30(3)	124(8)	1(9)	52(3)
C(8)	0	−502(15)	2500	14(4)	0	−1(7)	90(15)	0	33(6)
O(8)	0	−1520(11)	2500	40(4)	0	36(6)	76(10)	0	57(5)
N	3523(5)	2352(9)	3404(6)	29(3)	−22(8)	39(5)	86(9)	−13(11)	58(4)
C(9)	2987(7)	1481(15)	3402(9)	43(4)	−55(13)	64(7)	135(16)	−38(18)	77(6)
C(10)	4129(7)	1672(14)	3454(9)	37(4)	54(14)	19(8)	142(16)	44(17)	59(6)
C(11)	3688(8)	3135(14)	4109(8)	57(5)	−28(14)	72(6)	128(16)	−61(15)	60(5)
C(12)	3275(7)	3127(12)	2672(8)	34(4)	−1(11)	26(7)	84(12)	17(14)	56(5)

Atom	x	y	z	B	Atom	x	y	z	B
C(13)	3051(5)	2447(8)	1902(4)	5·1(3)	H(14)	2058	2375	1812	7·0
C(14)	2399(4)	2144(9)	1544(5)	7·0(3)	H(15)	1676	1304	561	7·7
C(15)	2187(3)	1542(9)	841(5)	7·7(4)	H(16)	2462	778	−54	5·8
C(16)	2628(5)	1246(8)	496(4)	5·8(3)	H(17)	3623	1321	587	7·4
C(17)	3281(4)	1549(9)	853(5)	7·4(4)	H(18)	4004	2385	1838	5·6
C(18)	3492(3)	2148(9)	1557(5)	5·6(3)					

[a] The anisotropic temperature factors are given by exp $-(h^2b_{11} + k^2b_{22} + l^2b_{33} + hkb_{12} + hlb_{13} + klb_{23})$. [b] The estimated standard deviation in the last significant figure(s) is given in parentheses here and in the succeeding Tables.

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surrounded by metal atoms, *e.g.*, Fe_3C,[25] WC,[26] and Cr_2C_3.[27] One feature of this cluster is that it follows the

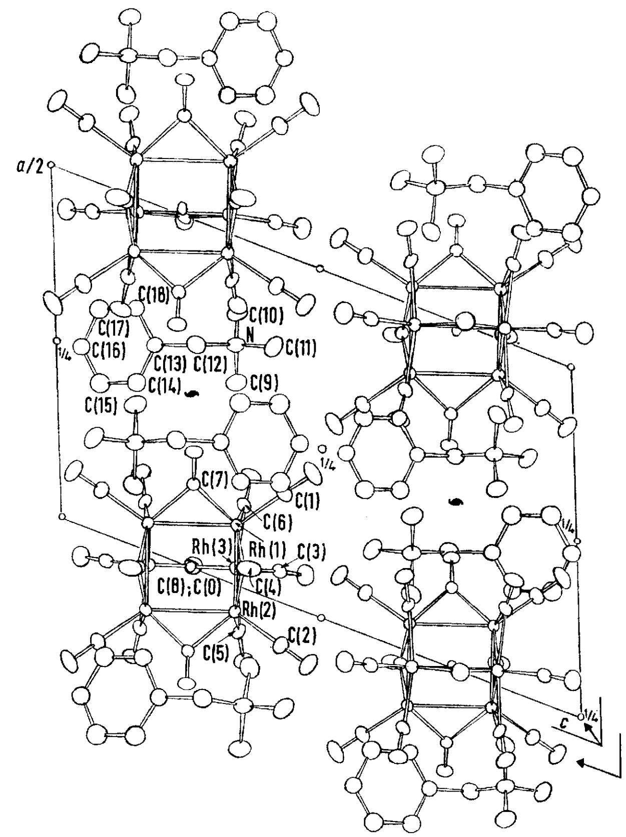

FIGURE 1 Perspective unit-cell drawing of the molecule projected on (010)

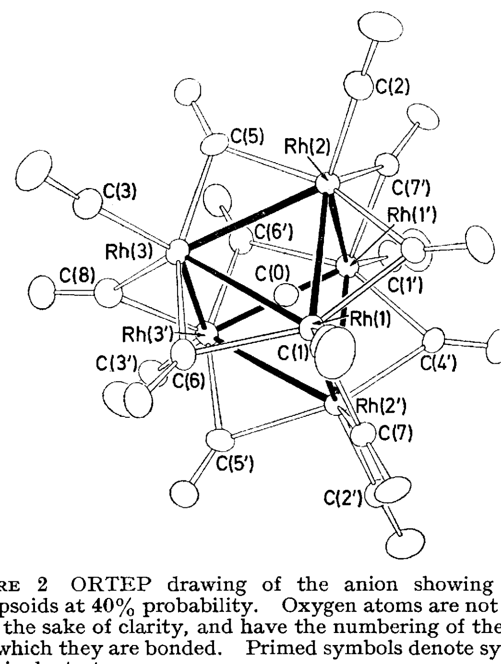

FIGURE 2 ORTEP drawing of the anion showing thermal ellipsoids at 40% probability. Oxygen atoms are not labelled, for the sake of clarity, and have the numbering of the carbons to which they are bonded. Primed symbols denote symmetry-equivalent atoms

'inert-gas rule,' which is formally violated in the octahedral family.

This compound can be logically connected to the other carbonyl clusters on the basis of a general correlation existing between polyhedron geometry and number of valence electrons in the skeleton orbitals. Wade [28] has shown this connection for the boron hydrides and has extended the rationalization to the metal clusters assuming, as for boranes, that each metal atom contributes three orbitals to the skeleton molecular orbitals.

TABLE 2

Bond distances (Å) within the anion and cation

Rh(1)–Rh(2)	2·783(2)	Rh(1)–C(7)	2·04(1)
Rh(1)–Rh(3)	2·773(2)	Rh(2)'–C(7)	2·06(1)
Rh(2)–Rh(3)	2·772(2)	Rh(3)–C(8)	2·03(1)
Rh(1)–Rh(2)'	2·817(2)	C(1)–O(1)	1·13(1)
Rh(3)–Rh(3)'	2·817(2)	C(2)–O(2)	1·12(2)
Rh(1)–C(0)	2·124(6)	C(3)–O(3)	1·13(2)
Rh(2)–C(0)	2·127(6)	C(4)–O(4)	1·13(1)
Rh(3)–C(0)	2·150(6)	C(5)–O(5)	1·14(2)
Rh(1)–C(1)	1·89(1)	C(6)–O(6)	1·15(2)
Rh(2)–C(2)	1·90(2)	C(7)–O(7)	1·16(2)
Rh(3)–C(3)	1·88(1)	C(8)–O(8)	1·17(2)
Rh(1)–C(4)	2·12(1)	N–C(9)	1·55(2)
Rh(2)–C(4)	2·13(1)	N–C(10)	1·53(2)
Rh(2)–C(5)	2·10(1)	N–C(11)	1·51(2)
Rh(3)–C(5)	2·11(1)	N–C(12)	1·53(2)
Rh(1)–C(6)	2·13(1)	C(12)–C(13)	1·53(2)
Rh(3)–C(6)	2·12(1)		

TABLE 3

Bond angles (°) within the anion and cation

Rh(1)–Rh(2)–Rh(3)	59·9(1)	C(0)–Rh(1)–C(1)	170·5(5)
Rh(2)–Rh(3)–Rh(1)	60·3(1)	C(0)–Rh(2)–C(2)	170·3(5)
Rh(3)–Rh(1)–Rh(2)	59·8(1)	C(0)–Rh(3)–C(3)	171·4(5)
Rh(1)–Rh(2)'–Rh(1)'	90·2(1)	C(1)–Rh(1)–Rh(2)	124·1(5)
Rh(1)–Rh(2)'–Rh(3)'	89·6(1)	C(1)–Rh(1)–Rh(3)	122·0(4)
Rh(2)–Rh(1)–Rh(2)'	89·8(1)	C(1)–Rh(1)–Rh(2)'	140·9(5)
Rh(3)–Rh(1)–Rh(2)'	90·4(1)	C(1)–Rh(1)–C(4)	94·2(5)
Rh(1)–Rh(3)–Rh(3)'	89·6(1)	C(1)–Rh(1)–C(6)	90·6(5)
Rh(3)–Rh(3)'–Rh(2)'	90·4(1)	C(1)–Rh(1)–C(7)	94·1(5)
Rh(1)–C(1)–O(1)	180(1)	C(2)–Rh(2)–Rh(1)	122·5(4)
Rh(2)–C(2)–O(2)	177(1)	C(2)–Rh(2)–Rh(3)	123·5(4)
Rh(3)–C(3)–O(3)	176(1)	C(2)–Rh(2)–Rh(1)'	141·1(3)
Rh(1)–C(4)–O(4)	139·2(11)	C(2)–Rh(2)–C(4)	91·8(5)
Rh(2)–C(4)–O(4)	138·7(11)	C(2)–Rh(2)–C(5)	94·6(5)
Rh(1)–C(4)–Rh(2)	81·9(4)	C(2)–Rh(2)–C(7)'	94·9(5)
Rh(2)–C(5)–O(5)	138·4(11)	C(3)–Rh(3)–Rh(1)	125·4(4)
Rh(3)–C(5)–O(5)	139·0(10)	C(3)–Rh(3)–Rh(2)	123·1(4)
Rh(2)–C(5)–Rh(3)	82·4(5)	C(3)–Rh(3)–Rh(3)'	139·4(4)
Rh(1)–C(6)–O(6)	139·1(10)	C(3)–Rh(3)–C(5)	92·3(5)
Rh(3)–C(6)–O(6)	139·2(10)	C(3)–Rh(3)–C(6)	94·1(5)
Rh(1)–C(6)–Rh(3)	81·6(4)	C(3)–Rh(3)–C(8)	93·3(5)
Rh(1)–C(7)–O(7)	136·6(8)	C(9)–N–C(10)	109·2(11)
Rh(2)'–C(7)–O(7)	136·4(9)	C(9)–N–C(11)	108·3(13)
Rh(1)–C(7)–Rh(2)'	86·9(5)	C(9)–N–C(12)	111·0(9)
Rh(3)–C(8)–O(8)	136·1(3)	C(10)–N–C(11)	109·7(10)
Rh(3)–C(8)–Rh(3)'	87·8(7)	C(10)–N–C(12)	110·8(12)
Rh(1)–C(0)–Rh(2)	81·8(3)	C(11)–N–C(12)	107·7(10)
Rh(2)–C(0)–Rh(3)	80·8(1)	N–C(12)–C(13)	113·8(10)
Rh(1)–C(0)–Rh(3)	80·9(1)		

Wade's theories for electron-deficient polyhedra have later been extended by Mingos [29] to apply to electron-precise and electron-rich ones (electron-precise polyhedra being defined as those in which the number of

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27 D. Meinhardt and O. Krisemat, *Z. Naturforsch.*, 1960, *A*, **15**, 880.
28 K. Wade, *Chem. Comm.*, 1971, 792.
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electron pairs in the skeleton molecular orbitals are equal to the number of polyhedron edges).

In order to rationalize the $[Rh_6(CO)_{15}C]^{2-}$ structure, its 45 valence-electron pairs can be allocated following the scheme used for $[Co_6(CO)_{15}]^{2-}$ (ref. 30), *i.e.* 24 electron pairs in molecular orbitals obtained by interactions of the tetrahedral-like hybrid orbitals of the metals and the terminal and bridging carbonyl groups, 12 electron pairs in essentially cluster non-bonding atomic orbitals, the d_{xy} and $d_{x^2-y^2}$ ones, if local coordinates on the rhodium atoms are chosen so that the *z* axes point towards the central carbido-atoms and the *y* axes lie in the symmetry planes of the prism. The remaining nine electron pairs must be distributed in the skeleton molecular orbitals built up by the metal orbitals d_{xz}, d_{yz}, d_{z^2}, and the *sp* ones of the carbide atom. According to Mingos' classification, nine electron pairs in a hexanuclear cluster should generate an electron-precise polyhedron, *i.e.* the trigonal prism, therefore this compound is the first experimental example of an electron-precise polyhedron with six skeleton atoms.

With regard to rhodium–carbonyl interactions the Rh–C and C–O distances for linear, basal bridging, and inter-basal bridging CO groups have the following mean values: 1·89(1), 1·13(1), 2·12(1), 1·14(2), and 2·04(1), 1·17(2) Å. The bond angles indicate strictly linear interactions for the terminal groups with mean Rh–C–O 178°. The bridging groups are highly symmetrical, the mean Rh–C–O and Rh–C–Rh angles being 138·9(5) and 82·0(3), and 136·4(5) and 87·3(3)° for the basal and inter-basal groups.

Lastly the cation geometry is as expected, with mean N–C distances 1·53(1) Å and mean C–N–C angles 109·4(5)°.

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