New Carbide Clusters in the Cobalt Subgroup. Part II.[1] Crystallographic Characterization of the Di-μ_3-carbonyl-hexa-μ-carbonyl-carbido-undecacarbonyl-*polyhedro*-octarhodium

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The title compound crystallizes in the triclinic space group $P\bar{1}$ with cell constants $a = 9{\cdot}18(1)$, $b = 17{\cdot}76(2)$, $c = 10{\cdot}46(1)$ Å, $\alpha = 75°\ 57'(6')$, $\beta = 69°\ 4'(6')$, $\gamma = 92°\ 22'(6')$, $Z = 2$. The structure was determined by Patterson and Fourier methods from *X*-ray single-crystal counter data and refined by block-diagonal least-squares calculations to R 0·0234 for 3423 significant reflections.

The molecule has C_1 symmetry. The Rh_8 metal atom cluster can be described as a monocapped prism plus one edge-bridging atom; Rh–Rh distances range from 2·699 to 2·913(3), mean 2·81 Å. The carbide atom occupies the centre of the prism with mean Rh–C 2·127 Å. The carbonyl groups are distributed on the cluster surface: two triple bridging, six-edge-bridging, and eleven linearly; their bonding parameters are as expected. The cluster geometry and the ligand stereochemistry suggest the most probable mechanism of formation of the molecule to consist in the insertion of two $[Rh(CO)_2]^+$ groups on the $[Rh_6(CO)_{15}C]^{2-}$ anion.

We have recently reported synthesis and structure[1] of a new polynuclear carbonyl anion of rhodium, $[Rh_6(CO)_{15}C]^{2-}$. This anion is novel in many respects: it is the first known cluster compound with trigonal prismatic geometry of the metal atoms and the first carbido-derivative in the cobalt subgroup with an isolated carbon atom placed in the centre of the cluster.

Convinced that $[Rh_6(CO)_{15}C]^{2-}$ is only the first species of a new family of cluster compounds we are devoting our efforts to the preparation and characterization of related species such as $[Co_6(CO)_{15}C]^{2-}$ and of other complexes derived from these anions.[2] We have been particularly attracted by the possibility of obtaining the related neutral carbido-carbonyl by oxidation of the rhodium dianion with iron(III) ion in water; in fact this proved to be a very complicated reaction. The initial oxidation product separates as a brown precipitate which we have not so far been able to characterize. After dissolution of this material in organic solvents different crystalline phases slowly separate dependant on the gaseous atmosphere and on time. Chemical analyses of these species are not conclusive: they merely give metal–ligand ratios higher than those for the dianion and suggest more complicated molecular structures.

We describe here the structural characterization by *X*-ray diffraction of the crystals obtained under carbon monoxide; the molecular formula of these crystals has proved to be $Rh_8(CO)_{19}C$. A preliminary account has already appeared,[2] and a full description of preparation and chemical characterization will be reported later.

EXPERIMENTAL

Crystal Data.—$C_{20}O_{19}Rh_8$, $M = 1367{\cdot}4$, Triclinic, $a = 9{\cdot}18(1)$, $b = 17{\cdot}76(2)$, $c = 10{\cdot}46(1)$ Å, $\alpha = 75°\ 57'\ (6')$, $\beta = 69°\ 4'(6')$, $\gamma = 92°\ 22'(6')$, $U = 1528{\cdot}77$ Å^3, $D_m = 3{\cdot}01(2)$ (by flotation), $Z = 2$, $D_c = 2{\cdot}97$ g/cm^3, $F(000) = 1264$. Space group $P\bar{1}$ (No. 2). Unit-cell dimensions were determined by precession photographs, Mo-K_α radiation [$\lambda = 0{\cdot}7107$ Å, $\mu(\text{Mo-}K_\alpha) = 41{\cdot}62$ cm^{-1}].

Intensity Measurements.—A prismatic crystal, with dimensions $0{\cdot}14 \times 0{\cdot}16 \times 0{\cdot}33$ mm, was mounted on a PAILRED linear equi-inclination diffractometer. Twelve levels of the reciprocal lattice, $hk0$—11, were collected within the sphere $2\theta \leqslant 50°$ 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 5875 reflections were measured with the w-scan method at a scan rate of 1° min^{-1}, background was counted for 40 s at the extreme points of the scan range. During data collection the intensities of four well spaced zero-level reflections were measured after completion of each layer, but no significant crystal decay was observed. The 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.[3] The absorption correction was computed by the method of refs. 4 and 5, a sampling of $8 \times 8 \times 8$ points being used. Transmission factors ranged from 0·55 to 0·68. No extinction corrections were made since no significant effects were observed. A final set of 4323 independent reflections was obtained after removal of all those with $\sigma(I)/I > 0{\cdot}25$.

Determination of the Structure.—A three-dimensional Patterson synthesis revealed interatomic vectors consistent with a trigonal prism, which was tentatively positioned in the cell. A Fourier synthesis phased by these atoms revealed the presence of two further rhodium atoms attached to the prism moiety. After preliminary refinement of the co-ordinates of these atoms a three-dimensional difference-Fourier synthesis showed the peaks of nineteen carbonyl groups and of one isolated carbon atom in the centre of the prism. The whole structure was refined by the least-squares method in the block-diagonal approximation (9×9 blocks), thermal motion being treated anisotropically for all atoms. The observations were weighted according to the formula $w = 1/(A + B \times F_o + C \times F_o^2)$ where, in the final cycles, A, B, and C had values 2·7, 0·04, and 0·0007 respectively and were chosen on the basis of an analysis of $\Sigma w(F_o - k|F_c|)^2$. Atomic scattering factors were taken from ref. 6 for all atoms, those for rhodium

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

[2] V. G. Albano, P. Chini, S. Martinengo, M. Sansoni, and D. Strumolo, *J.C.S. Chem. Comm.*, 1974, 299.

[3] W. L. Bond, *Acta Cryst.*, 1959, **12**, 375.

[4] W. R. Busing and H. A. Levy, *Acta Cryst.*, 1957, **10**, 180.

[5] G. Ciani, M. Manassero, and M. Sansoni, *J. Appl. Cryst.*, 1971, **4**, 173.

[6] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

being corrected[7] for the effects of anomalous dispersion. The function $\Sigma w(F_o - k|F_c|)^2$ was minimized until all shifts became $<0{\cdot}20\sigma$. Final values of reliability indices were R 0·0234 and R' 0·0299, where $R' = [\Sigma(F_o - k|F_c|)^2/\Sigma wF_o^2]^{1/2}$.

A final difference-Fourier synthesis revealed no errors in the structure; residual fluctuations did not exceed $\pm 0{\cdot}4$ eÅ^{-3} and were in the region of the metal atoms. Final positional and thermal parameters are reported in Table 1; final observed and computed structure factor moduli are in Supplementary Publication No. SUP 21186 (4 pp., 1 microfiche).*

TABLE 1

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

Atom	x	y	z	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
Rh(1)	664(1)	2458(1)	5467(1)	56(1)	13(1)	−32(1)	24(1)	−13(1)	65(1)
Rh(2)	3083(1)	3334(1)	5745(1)	75(1)	19(1)	−45(1)	18(1)	−19(1)	59(1)
Rh(3)	2722(1)	1670(1)	6537(1)	90(1)	15(1)	−49(1)	19(1)	−4(1)	63(1)
Rh(4)	4826(1)	1746(1)	3862(1)	80(1)	25(1)	−63(1)	17(1)	−19(1)	70(1)
Rh(5)	2551(1)	2481(1)	2798(1)	66(1)	19(1)	−52(1)	20(1)	−20(1)	63(1)
Rh(6)	5015(1)	3377(1)	3014(1)	60(1)	15(1)	−35(1)	16(1)	−12(1)	58(1)
Rh(7)	2112(1)	3925(1)	3489(1)	71(1)	30(1)	−57(1)	18(1)	−14(1)	73(1)
Rh(8)	4462(1)	1573(1)	1313(1)	117(1)	23(1)	−56(1)	22(1)	−33(1)	75(1)
C(0)	3187(6)	2493(3)	4540(6)	49(6)	4(5)	−30(9)	13(1)	−11(5)	75(6)
C(1)	−1493(8)	2528(5)	5896(8)	81(8)	24(8)	−53(13)	43(3)	−35(8)	112(8)
O(1)	−2788(6)	2569(5)	6131(9)	66(6)	55(8)	−85(13)	99(4)	−75(11)	251(11)
C(2)	2726(8)	3953(4)	7064(7)	146(9)	38(8)	−84(12)	30(2)	−39(6)	85(7)
O(2)	2492(7)	4277(3)	7897(6)	252(10)	85(7)	−150(13)	44(2)	−98(5)	152(7)
C(3)	2243(9)	890(4)	8331(7)	147(10)	18(8)	−81(13)	27(2)	−10(7)	89(7)
O(3)	1968(8)	456(4)	9385(6)	257(11)	12(9)	−119(13)	47(2)	40(7)	114(7)
C(4)	6276(7)	1104(4)	2984(7)	113(8)	32(7)	−100(12)	25(2)	−47(6)	119(7)
O(4)	7232(7)	743(3)	2575(7)	205(8)	139(6)	−194(14)	51(2)	−127(6)	240(9)
C(5)	1922(7)	2387(5)	1292(7)	79(8)	11(8)	−53(12)	46(3)	−18(8)	87(7)
O(5)	1357(6)	2349(4)	498(6)	172(7)	83(8)	−164(9)	93(3)	−107(6)	112(5)
C(6)	6626(7)	4114(3)	1408(7)	91(7)	20(6)	−110(10)	22(2)	−21(6)	105(6)
O(6)	7557(6)	4510(3)	410(5)	131(7)	−30(6)	−3(11)	33(2)	9(5)	88(6)
C(7)	3146(7)	4988(3)	2935(6)	93(7)	34(6)	−77(10)	25(2)	−32(5)	73(6)
O(7)	3738(6)	5605(3)	2632(6)	169(8)	−5(6)	−81(11)	25(1)	−21(5)	134(6)
C(8)	497(7)	4153(4)	2738(7)	85(7)	19(7)	−83(11)	25(2)	1(7)	111(7)
O(8)	−402(6)	4323(4)	2263(7)	139(6)	25(7)	−226(10)	49(2)	−9(7)	217(8)
C(9)	2849(9)	694(4)	2482(8)	134(10)	46(8)	−57(15)	35(2)	−48(7)	118(9)
O(9)	1912(8)	172(4)	3114(9)	179(10)	−10(8)	2(19)	34(2)	−23(8)	235(11)
C(10)	5362(9)	1062(4)	−96(8)	157(10)	6(8)	−87(14)	27(2)	−50(6)	110(7)
O(10)	5923(8)	781(3)	−970(6)	256(12)	27(8)	−41(16)	48(2)	−120(5)	158(7)
C(11)	5979(8)	2484(4)	134(7)	154(10)	37(8)	−86(13)	26(2)	−46(6)	101(7)
O(11)	6912(8)	2993(3)	−612(6)	218(10)	−5(8)	−21(14)	34(2)	−30(6)	120(7)
C(12)	230(8)	1818(4)	7427(8)	92(8)	13(8)	−63(12)	39(3)	−6(8)	98(7)
O(12)	−715(7)	1599(4)	8562(6)	108(7)	35(9)	12(13)	85(3)	44(9)	105(7)
C(13)	3590(6)	2517(3)	7190(6)	63(6)	12(6)	−28(9)	23(2)	0(5)	46(5)
O(13)	4164(5)	2493(3)	8011(5)	130(6)	22(5)	−103(8)	36(1)	−20(5)	81(4)
C(14)	6631(7)	2614(3)	3016(7)	80(7)	13(6)	−68(10)	17(1)	−9(6)	89(6)
O(14)	7977(5)	2657(3)	2778(6)	78(5)	30(5)	−111(10)	31(1)	−41(6)	222(8)
C(15)	4768(7)	1118(4)	5758(7)	122(8)	48(7)	−87(11)	26(2)	−21(6)	85(6)
O(15)	5448(6)	705(3)	6261(6)	184(7)	117(6)	−148(10)	55(2)	1(7)	137(7)
C(16)	542(8)	1746(4)	4134(7)	105(8)	20(7)	−56(12)	27(2)	−17(6)	81(7)
O(16)	−359(6)	1252(3)	4236(6)	132(7)	−43(6)	−56(11)	38(2)	−51(6)	162(7)
C(17)	5364(7)	3854(3)	4506(6)	95(7)	−10(6)	−46(10)	19(2)	−13(5)	69(6)
O(17)	6330(6)	4229(3)	4596(5)	138(7)	−52(6)	−37(9)	51(2)	−50(5)	92(5)
C(18)	761(8)	3833(4)	5530(7)	116(9)	48(7)	−29(13)	32(2)	−26(6)	72(7)
O(18)	−150(6)	4105(3)	6301(6)	152(7)	94(6)	−54(11)	48(2)	−48(6)	110(6)
C(19)	3580(7)	3674(3)	1529(6)	80(7)	16(6)	−26(10)	24(2)	−15(6)	64(6)
O(19)	3977(5)	3994(2)	338(5)	129(6)	40(5)	−71(8)	31(1)	−14(4)	75(4)

* In the form: $\exp -(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)$.

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

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

The contents of the unit cell are shown in Figure 1; the crystal consists of discrete molecules and the closest intermolecular approaches (C···C 3·4, C···O 3·1, and O···O 2·8 Å) indicate that there are no unusual intermolecular interactions. The molecule possesses C_1 symmetry and the two enantiomers are related in the crystal by inversion centres. A perspective view of $Rh_8(CO)_{19}C$ and of the metal atom cluster is shown in Figure 2; bond distances and relevant angles are listed in Table 2.

The Rh_8 cluster can be described as a monocapped trigonal prism, plus one edge-bridging atom. In fact, six atoms [Rh(1)—(6)] are arranged at the vertices of a trigonal prism: Rh(7) caps a rectangular face of the prism defining a tetragonal pyramid [Rh(1), Rh(2), and Rh(5)—(7)], and Rh(8) bridges the basal edge of the prism defined by Rh(4) and Rh(5). The carbide atom is approximately in the centre of the prism. This geometry indicates that the cluster is built up by the

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue.

[7] 'International Tables for *X*-Ray Crystallography,' vol. 3, Kynoch Press, Birmingham, 1962.

addition of two extra rhodium atoms to the preformed Rh_6C moiety. The same conclusion is suggested by the spatial arrangement of the fourteen carbonyl ligands bound to the prismatic skeleton. Apart from moderate distortions caused by the molecular overcrowding, these ligands exhibit the same stereochemistry as in $[Rh_6(CO)_{15}C]^{2-}$, in which each metal atom is linked to one terminal and three edge-bridging groups.[1] Only one edge-bridging group of the dianion has been lost, being replaced by the bridging Rh(8), while the two face-bridging ligands, C(18)-O(18) and C(19)-O(19), apparently linked in a different fashion, occupy practically the same positions of the corresponding basal bridging groups as in the dianion. The remaining five ligands are terminally bound two to Rh(7) and three to Rh(8). The co-ordination geometry about Rh(7) is similar to that existing in $Rh_6(CO)_{16}$.[8] For the subsequent discussion it is useful to note that an equivalent ligand geometry could be realized around Rh(7) by displacement of the linear groups orthogonally to actual position and obtaining the face-bridging ones from the adjacent interbasal bridging ligands C(16)-O(16) and C(17)-O(17). Finally, the edge-bridging Rh(8) is bound to three terminal ligands only and the resulting co-ordination geometry about it is distorted trigonal bipyramidal.

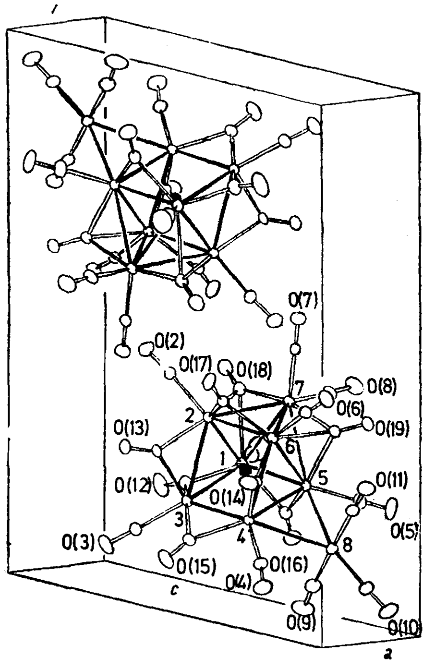

FIGURE 1 Perspective packing diagram showing the content of the unit cell and the atom-numbering scheme. Carbon atoms of the carbonyl ligands are not labelled

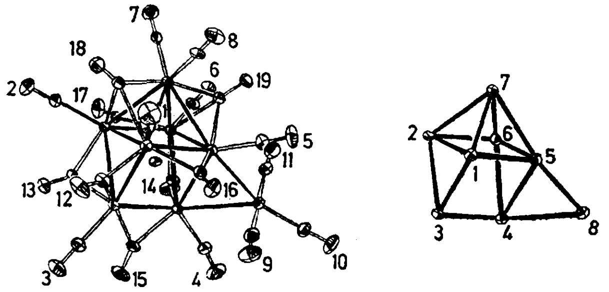

FIGURE 2 Perspective view of the molecular structure and of the metal-atom cluster. The ellipsoids of thermal motion enclose 20% of the electron density

TABLE 2

Bond distances (Å) and relevant angles (°)

(*a*) Distances

Rh(1)–Rh(2)	2·798(3)	C(4)–O(4)	1·13(1)
Rh(1)–Rh(3)	2·784(3)	C(5)–O(5)	1·14(1)
Rh(1)–Rh(5)	2·699(3)	C(6)–O(6)	1·13(1)
Rh(1)–Rh(7)	2·824(3)	C(7)–O(7)	1·12(1)
Rh(2)–Rh(3)	2·841(3)	C(8)–O(8)	1·12(1)
Rh(2)–Rh(6)	2·752(3)	C(9)–O(9)	1·13(1)
Rh(2)–Rh(7)	2·802(3)	C(10)–O(10)	1·12(1)
Rh(3)–Rh(4)	2·741(3)	C(11)–O(11)	1·13(1)
Rh(4)–Rh(5)	2·913(3)	C(12)–O(12)	1·15(1)
Rh(4)–Rh(6)	2·795(3)	C(13)–O(13)	1·15(1)
Rh(4)–Rh(8)	2·899(3)	C(14)–O(14)	1·16(1)
Rh(5)–Rh(6)	2·818(3)	C(15)–O(15)	1·14(1)
Rh(5)–Rh(7)	2·836(3)	C(16)–O(16)	1·14(1)
Rh(5)–Rh(8)	2·755(3)	C(17)–O(17)	1·13(1)
Rh(6)–Rh(7)	2·793(3)	C(18)–O(18)	1·15(1)
Rh(1)–C(O)	2·159(5)	C(19)–O(19)	1·15(1)
Rh(2)–C(O)	2·161(7)	Rh(1)–C(12)	1·976(8)
Rh(3)–C(O)	2·125(6)	Rh(3)–C(12)	2·195(7)
Rh(4)–C(O)	2·095(6)	Rh(2)–C(13)	2·025(6)
Rh(5)–C(O)	2·108(7)	Rh(3)–C(13)	2·040(7)
Rh(6)–C(O)	2·116(5)	Rh(4)–C(14)	1·997(6)
Rh(7) · · · C(O)	2·877(6)	Rh(6)–C(14)	2·050(7)
Rh(1)–C(1)	1·885(7)	Rh(3)–C(15)	2·144(7)
Rh(2)–C(2)	1·915(9)	Rh(4)–C(15)	2·007(7)
Rh(3)–C(3)	1·932(7)	Rh(1)–C(16)	2·124(9)
Rh(4)–C(4)	1·916(7)	Rh(5)–C(16)	2·033(6)
Rh(5)–C(5)	1·901(9)	Rh(2)–C(17)	2·058(6)
Rh(6)–C(6)	1·929(5)	Rh(6)–C(17)	2·059(8)
Rh(7)–C(7)	1·930(6)	Rh(1)–C(18)	2·458(8)
Rh(7)–C(8)	1·924(8)	Rh(2)–C(18)	2·404(8)
Rh(8)–C(9)	1·927(7)	Rh(7)–C(18)	2·012(7)
Rh(8)–C(10)	1·877(8)	Rh(7)–C(19)	2·177(7)
Rh(8)–C(11)	1·923(6)	Rh(5)–C(19)	2·171(6)
C(1)–O(1)	1·13(1)	Rh(6)–C(19)	2·355(8)
C(2)–O(2)	1·12(1)	Rh(8) · · · C(4)	2·831(9)
C(3)–O(3)	1·12(1)	Rh(8) · · · C(5)	2·796(8)

(*b*) Angles

Rh(1)–C(1)–O(1)	178·9(9)	Rh(2)–C(17)–O(17)	138·0(6)
Rh(2)–C(2)–O(2)	176·0(6)	Rh(6)–C(17)–O(17)	138·1(5)
Rh(3)–C(3)–O(3)	178·0(9)	Rh(1)–C(18)–O(18)	127·8(5)
Rh(4)–C(4)–O(4)	171·1(9)	Rh(2)–C(18)–O(18)	128·0(7)
Rh(5)–C(5)–O(5)	171·0(6)	Rh(7)–C(18)–O(18)	146·2(6)
Rh(6)–C(6)–O(6)	174·9(7)	Rh(5)–C(19)–O(19)	133·9(5)
Rh(7)–C(7)–O(7)	179·0(6)	Rh(6)–C(19)–O(19)	131·3(5)
Rh(7)–C(8)–O(8)	176·4(6)	Rh(7)–C(19)–O(19)	134·4(5)
Rh(8)–C(9)–O(9)	177·1(9)	Rh(4)–Rh(8)–C(9)	88·5(3)
Rh(8)–C(10)–O(10)	177·6(6)	Rh(5)–Rh(8)–C(9)	87·1(3)
Rh(8)–C(11)–O(11)	175·8(7)	Rh(4)–Rh(8)–C(10)	137·9(3)
Rh(1)–C(12)–O(12)	144·4(7)	Rh(5)–Rh(8)–C(10)	160·1(3)
Rh(3)–C(12)–O(12)	132·0(7)	Rh(4)–Rh(8)–C(11)	92·4(3)
Rh(2)–C(13)–O(13)	138·6(6)	Rh(5)–Rh(8)–C(11)	90·6(2)
Rh(3)–C(13)–O(13)	132·7(5)	C(7)–Rh(7)–C(8)	97·2(3)
Rh(4)–C(14)–O(14)	135·3(5)	C(9)–Rh(8)–C(10)	92·9(2)
Rh(6)–C(14)–O(14)	136·9(5)	C(9)–Rh(8)–C(11)	176·8(3)
Rh(3)–C(15)–O(15)	135·5(6)	C(11)–Rh(8)–C(10)	88·5(3)
Rh(4)–C(15)–O(15)	141·9(6)	Rh(3)–Rh(4)–Rh(8)	133·2(1)
Rh(1)–C(16)–O(16)	133·9(5)	Rh(1)–Rh(5)–Rh(8)	141·1(1)
Rh(5)–C(16)–O(16)	144·8(5)		

The spatial distribution of the ligands suggests that the first step in the mechanism of formation of the molecule probably involves insertion of a $[Rh(CO)_2]^+$ group on one rectangular face of the $[Rh_6(CO)_{15}C]^{2-}$ anion. The

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[8] E. R. Corey, L. F. Dahl, and W. Beck, *J. Amer. Chem. Soc.*, 1963, **85**, 1202.

entering group is stabilized by four metal–metal and two metal–carbonyl interactions. The second step might parallel the first by insertion of another $[Rh(CO)_2]^+$ group on one of the remaining rectangular or triangular faces, but should be followed by an intramolecular rearrangement in which Rh(8) rotates from a face- to an edge-bridging position, displacing one carbonyl group which then migrates to a terminal position about Rh(8).

The mechanism of formation of this stable structure is substantiated by an inspection of the carbonyl–carbonyl contacts in $[Rh_6(CO)_{15}C]^{2-}$. Some carbon–carbon distances, reported in Figure 3, show the sizes of the empty zones above the faces of the Rh_6 prism. The holes on the rectangular faces are markedly elongated orthogonally to the three-fold axis of the prism and offer easy access to a $[Rh(CO)_2]^+$ group if it approaches the face in the proper orientation. This accounts for the aforementioned preferred ligand orientation about Rh(7). As can be seen in Figure 3, the attack on the triangular faces is not hindered, and cannot be excluded, considering that capped triangular faces have been found in $[Rh_7(CO)_{16}]^{3-}$ (ref. 9), $[Rh_7(CO)_{16}I]^{2-}$ (ref. 10), and in $Os_6(CO)_{18}$.[11] Very probably the cluster is unstable in a bicapped prismatic configuration because of strong non-bonded interactions among ligands, while the actual configuration, being less compact, allows more normal interligand contacts. Whatever may have determined the cluster geometry, it shows that isolated metal-atom aggregates are not necessarily fragments of closely packed atoms and that probably every kind of geometry could be stable in proper conditions.

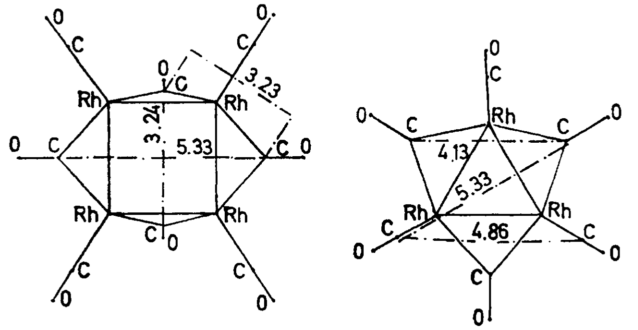

FIGURE 3 Some non-bonded C · · · C contacts, illustrating the shape and size of the empty zones above the faces of the prismatic cluster in the anion $[Rh_6(CO)_{15}C]^{2-}$

The fifteen rhodium–rhodium distances range from 2·699 to 2·913(3) Å; their mean is 2·81 Å but more significant means are obtained if the distances are grouped in the following sets: interbasal distances in the prism 2·730; basal distances in the prism, except Rh(4)–Rh(5), 2·807; pyramidal distances 2·814; distances of the edge-bridging Rh(8) 2·822, and bridged Rh(4)–Rh(5) 2·913 Å. Excepting the Rh(4)–Rh(5) interaction, the distances in the prism are inversely related to the corresponding values in $[Rh_6(CO)_{15}C]^{2-}$, in which the interbasal and basal mean values are 2·817 and 2·776 Å. The co-ordination numbers about the metal atoms are different [five for Rh(8), eight for Rh(3), Rh(4), and Rh(7), nine for the remaining atoms], but there is no apparent correlation between bond distances and co-ordination numbers. The Rh(4)–Rh(5) distance is 0·2 Å longer than the other basal distances in the prism, and this effect may be ascribed to the substitution of the bridging carbonyl group by the bridging Rh(8) and shows the substantially different bonding mechanisms of the two species. In fact, the bond of the double-bridging carbonyl may be described in terms of three-centre orbitals[12] which strengthen the metal–metal bond,[13] while the linkage of the bridging rhodium atom probably adds only non-bonded contributions to the Rh(4)–Rh(5) interaction.

The trigonal bipyramidal co-ordination about Rh(8) exhibits irregularities. The Rh(8)–Rh(4) distance is 0·144 Å longer than the Rh(8)–Rh(5), and Rh(4)–Rh(8)–C(10) is 22·2° less than Rh(5)–Rh(8)–C(10). The two distances were not expected to be equivalent, because of the different co-ordination about Rh(4) and Rh(5). The angular deformation, on the other hand, is not explainable in terms of abnormally short non-bonded contacts because a careful examination of the intermolecular distances reveals only normal values. The rotation of the equatorial carbonyl away from the shorter rhodium–rhodium bond may indicate non-equivalent repulsions between the electron pairs of these bonds.

Electron counts, with the assumption of electron-pair bonds for the metal–metal interactions, show that the molecule as a whole follows the noble-gas rule (72 electrons for rhodiums, 38 for CO groups, 4 for the central carbon, and 15 rhodium–rhodium bonds contributing 30, total 154, *i.e.* 18 electrons per rhodium atom). Local counts for single atoms are less significant, for example Rh(8) would attain 17 electrons in this way and consequently the complex should be paramagnetic. The observed diamagnetism shows the slight significance of such counts and indicates that the bonds in these polyhedral complexes should be described only in terms of delocalized molecular orbitals.

The mean Rh–C(carbide) distance (2·127 Å) agrees well with the corresponding (2·134 Å) value in $[Rh_6(CO)_{15}C]^{2-}$. The eleven Rh–C and C–O distances for the terminal groups are substantially equivalent, mean values 1·914 and 1·127 Å. The differences between the values here and those found in the dianion (1·89 and 1·13 Å) are barely significant, but are in keeping with the dianionic character of the latter. The six edge-bridging groups are not strictly symmetrical, and the mean of the Rh–C distances is 2·064 Å. The

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two face-bridging ligands are strongly asymmetric with Rh–C distances in the range 2·012—2·458 Å. The mean C–O distance for all the bridging groups is 1·147 Å.

An examination of the Rh–C–O angles of the linear groups reveals that the mean value for nine groups is 176·7° while for the remaining two, Rh(4)–C(4)–O(4) and Rh(5)–C(5)–O(5), it is 171°. The latter value may be viewed as an incipient bending of the ligands towards bridging positions on the metal–metal bonds Rh(4)–Rh(8) and Rh(5)–Rh(8), as confirmed by the short contacts of these carbons with Rh(8) (see Table 2).

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