New Carbide Clusters in the Cobalt Sub-group. Part 4.[1-3] Synthesis and Crystallographic Characterization of μ_3-Carbonyl-deca-μ-carbonyl-dicarbidotetradecacarbonyl-*polyhedro*-dodecarhodium

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The title complex crystallizes in the orthorhombic space group $P2_12_12_1$ with unit-cell dimensions a = 18.695(4), b = 18.604(4), c = 11.605(2) Å, and Z = 4. The structure has been determined by direct methods from X-ray single-crystal counter data and refined by least-squares calculations to R 0.037 for 3 450 significant diffraction intensities. The complex $[Rh_{12}C_2(CO)_{25}]$ is asymmetric and the metal-atom cluster is an irregular closed polyhedron which can be described in terms of layer packing of atoms (mean Rh–Rh 2.79 Å). The carbide carbon atoms occupy an irregular cavity as a C_2 unit [C–C 1.48(2) Å]; there are 14 Rh–C(carbide) contacts, nine short and five long (means 2.22 and 2.58 Å respectively). Of the carbonyl ligands, 14 are terminal, 10 are edge-bridging, and one is face-bridging.

THE well known versatility of rhodium in giving carbonyl clusters seems to be enhanced if carbon atoms are inserted into the interstices of the metal-atom polyhedron. We have already shown not only that carbide clusters can be obtained under mild conditions when carbonylic species react with $CHCl_3$ or CCl_4,[1] *e.g.* equation (1), but also that oxidation of $[Rh_6C(CO)_{15}]^{2-}$ leads to other species such as $[Rh_8(CO)_{19}]$ [2] and $[Rh_{15}C_2(CO)_{28}]^-$.[3] The last monoanion is rather unstable in solution and slowly gives a new crystalline material, $[Rh_{12}C_2(CO)_{25}]$, which has been characterized by the present crystallographic study.

$$6[Rh(CO)_4] + CCl_4 \xrightarrow[25\ ^\circ C]{Pr^iOH} [Rh_6C(CO)_{15}]^{2-} + 4Cl^- + 9CO \quad (1)$$

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

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

[3] Part 3, V. G. Albano, M. Sansoni, P. Chini, S. Martinengo, and D. Strumolo, *J.C.S. Dalton*, 1976, 970.

EXPERIMENTAL

All the operations were carried out under nitrogen, and the solvents were degassed and saturated with nitrogen.

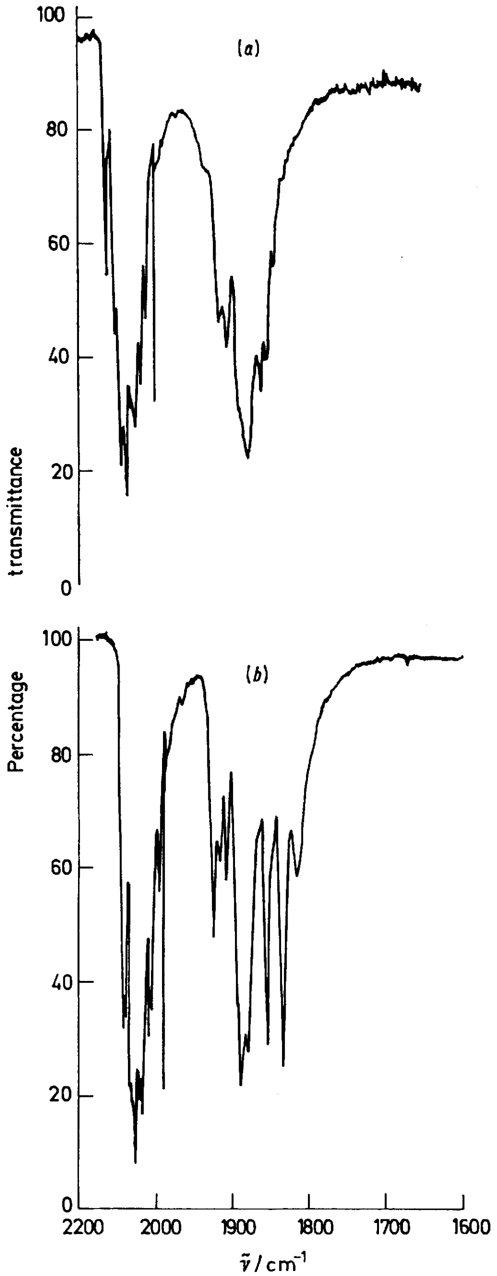

FIGURE 1 Infrared spectra of (*a*) $[H_3O][Rh_{15}C_2(CO)_{28}]$ and (*b*) $[Rh_{12}C_2(CO)_{25}]$

Synthesis of $[Rh_{12}C_2(CO)_{25}]$.—*From* $K_2[Rh_6C(CO)_{15}]$. A 0.2 mol dm^{-3} aqueous solution of $Fe[NH_4][SO_4]_2 \cdot 12H_2O$ (10 cm^3) was added to a solution of $K_2[Rh_6C(CO)_{15}] \cdot 3thf$ (thf = tetrahydrofuran) (0.77 g, 0.58 mmol)[4] in water (15 cm^3). A brown precipitate was immediately formed and was extracted by shaking the suspension with CH_2Cl_2 (7 cm^3). The organic layer was separated and transferred to another tube where black crystals of $[Rh_{12}C_2(CO)_{25}]$ soon began to separate. After 48 h the precipitation was almost complete. The complex (0.45 g, 0.23 mmol) was filtered off, washed with cyclohexane (3 × 5 cm^3), and dried *in vacuo*, yield 79% (Found: C, 16.3; Rh, 62.8. Calc. for $C_{27}O_{25}Rh_{12}$: C, 16.5; Rh, 63.0%). The same procedure often leads to a different product, namely $[H_3O][Rh_{15}C_2(CO)_{28}]$, which has already been reported.[3] Contrary to

TABLE 1

Final positional parameters (× 10^4), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Rh(1)	−1 296(0)	−1 105(0)	4 159(1)
Rh(2)	665(0)	−62(0)	5 935(1)
Rh(3)	1 089(0)	−1 429(0)	5 775(1)
Rh(4)	110(0)	−1 426(0)	3 968(1)
Rh(5)	715(0)	526(0)	2 468(1)
Rh(6)	−537(0)	−248(0)	2 633(1)
Rh(7)	−708(0)	315(0)	6 356(1)
Rh(8)	−28(0)	937(0)	4 482(1)
Rh(9)	−1 434(0)	401(0)	4 266(1)
Rh(10)	672(0)	−949(0)	1 875(1)
Rh(11)	−457(0)	−1 149(0)	6 134(1)
Rh(12)	1 271(0)	−510(0)	3 935(1)
C(26)	−495(8)	−326(8)	4 822(13)
C(27)	186(8)	−231(8)	4 197(14)
C(1)	244(13)	−1 184(12)	447(21)
O(1)	34(10)	−1 392(10)	−378(17)
C(2)	−160(10)	−2 339(10)	4 448(17)
O(2)	−319(8)	−2 898(8)	4 702(13)
C(3)	1 467(13)	−2 290(12)	5 246(20)
O(3)	1 711(9)	−2 829(9)	4 928(15)
C(4)	1 341(11)	−1 617(11)	7 263(18)
O(4)	1 525(10)	−1 764(10)	8 204(16)
C(5)	−288(9)	−1 939(9)	7 149(15)
O(5)	−227(9)	−2 442(8)	7 723(14)
C(6)	1 263(11)	921(12)	1 280(19)
O(6)	1 558(9)	1 183(9)	551(16)
C(7)	−57(10)	400(10)	1 317(17)
O(7)	−270(8)	531(8)	378(14)
C(8)	785(11)	0(10)	7 522(17)
O(8)	908(10)	60(10)	8 490(17)
C(9)	795(10)	1 074(9)	5 684(16)
O(9)	1 136(8)	1 517(8)	6 049(15)
C(10)	−1 722(11)	514(11)	6 044(18)
O(10)	−2 261(9)	603(9)	6 506(14)
C(11)	1 707(10)	−363(11)	5 644(17)
O(11)	2 273(7)	−241(7)	6 029(12)
C(12)	−2 162(10)	−457(10)	4 211(17)
O(12)	−2 777(7)	−479(8)	4 240(12)
C(13)	1 700(9)	441(10)	3 381(15)
O(13)	2 199(8)	768(8)	3 480(13)
C(14)	465(9)	1 512(9)	3 241(15)
O(14)	634(8)	2 107(7)	3 048(13)
C(15)	−872(9)	−524(9)	7 461(15)
O(15)	−1 113(8)	−629(8)	8 338(13)
C(16)	−2 129(10)	1 143(10)	4 097(18)
O(16)	−2 505(10)	1 612(10)	3 982(18)
C(17)	−559(11)	1 733(10)	4 882(17)
O(17)	−867(9)	2 256(9)	5 101(15)
C(18)	−697(10)	975(10)	7 592(16)
O(18)	−736(10)	1 385(9)	8 306(16)
C(19)	−1 811(12)	−1 826(12)	3 413(21)
O(19)	−2 115(10)	−2 291(10)	2 989(17)
C(20)	689(9)	−1 913(9)	2 753(15)
O(20)	942(8)	−2 462(8)	2 553(13)
C(21)	−1 371(13)	460(13)	2 498(21)
O(21)	−1 668(9)	764(10)	1 746(16)
C(22)	2 132(10)	−991(11)	3 547(17)
O(22)	2 649(9)	−1 257(9)	3 323(16)
C(23)	−1 442(10)	−1 535(10)	5 727(17)
O(23)	−1 893(9)	−1 867(9)	6 218(16)
C(24)	−1 045(10)	−881(11)	1 676(17)
O(24)	−1 327(8)	−1 260(7)	1 031(13)
C(25)	1 572(11)	−1 058(11)	1 183(18)
O(25)	2 092(10)	−1 214(10)	713(18)

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[4] S. Martinengo, D. Strumolo, and P. Chini, *Inorg. Synth.*, in the press.

what had been asserted previously,[3] it has not been yet possible to ascertain which reaction conditions favour which complex. Infrared spectra in Nujol (Figure 1) allowed the desired reaction product to be separated. The complex $[H_3O][Rh_{15}C_2(CO)_{28}]$ is quantitatively converted into $[Rh_{12}C_2(CO)_{25}]$ in the presence of CH_2Cl_2.

TABLE 2

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

Rh(1)–Rh(4)	2.707(2)	Rh(6)–C(24)	1.88(2)	Rh(11)–C(15)	2.08(2)
Rh(1)–Rh(6)	2.774(2)	Rh(7)–C(18)	1.89(2)	Rh(4)–C(20)	2.00(2)
Rh(1)–Rh(9)	2.818(2)	Rh(8)–C(17)	1.84(2)	Rh(10)–C(20)	2.06(2)
Rh(1)–Rh(11)	2.779(2)	Rh(9)–C(16)	1.91(2)	Rh(6)–C(21)	2.05(2)
Rh(2)–Rn(3)	2.671(2)	Rh(10)–C(1)	1.89(2)	Rh(9)–C(21)	2.06(3)
Rh(2)–Rh(4)	3.567(2)	Rh(10)–C(25)	1.88(2)	Rh(1)–C(23)	2.01(2)
Rh(2)–Rh(7)	2.708(2)	Rh(11)–C(5)	1.91(2)	Rh(11)–C(23)	2.03(2)
Rh(2)–Rh(8)	2.826(2)	Rh(12)–C(22)	1.89(2)	Rh(2)–C(11)	2.05(2)
Rh(2)–Rh(11)	2.924(2)	C(1)–O(1)	1.11(3)	Rh(3)–C(11)	2.30(2)
Rh(2)–Rh(12)	2.715(2)	C(2)–O(2)	1.12(3)	Rh(12)–C(11)	2.16(2)
Rh(3)–Rh(4)	2.783(2)	C(3)–O(3)	1.16(3)	C(7)–O(7)	1.19(3)
Rh(3)–Rh(11)	2.968(2)	C(4)–O(4)	1.18(3)	C(9)–O(9)	1.13(3)
Rh(3)–Rh(12)	2.758(2)	C(5)–O(5)	1.15(3)	C(10)–O(10)	1.15(3)
Rh(4)–Rh(6)	2.943(2)	C(6)–O(6)	1.12(3)	C(12)–O(12)	1.15(3)
Rh(4)–Rh(10)	2.792(2)	C(8)–O(8)	1.15(3)	C(13)–O(13)	1.12(2)
Rh(4)–Rh(11)	2.776(2)	C(16)–O(16)	1.13(3)	C(14)–O(14)	1.17(2)
Rh(4)–Rh(12)	2.760(2)	C(17)–O(17)	1.16(3)	C(15)–O(15)	1.13(2)
Rh(5)–Rh(6)	2.757(2)	C(18)–O(18)	1.13(3)	C(20)–O(20)	1.15(2)
Rh(5)–Rh(8)	2.825(2)	C(19)–O(19)	1.15(3)	C(21)–O(21)	1.18(2)
Rh(5)–Rh(10)	2.832(2)	C(22)–O(22)	1.12(3)	C(23)–O(23)	1.19(3)
Rh(5)–Rh(12)	2.775(2)	C(24)–O(24)	1.15(3)	C(11)–O(11)	1.17(3)
Rh(6)–Rh(8)	3.221(2)	C(25)–O(25)	1.15(3)	Rh(1)–C(26)	2.22(2)
Rh(6)–Rh(9)	2.804(2)	Rh(5)–C(7)	1.98(2)	Rh(2)–C(26)	2.57(2)
Rh(6)–Rh(10)	2.755(2)	Rh(6)–C(7)	2.14(2)	Rh(4)–C(26)	2.54(2)
Rh(7)–Rh(8)	2.772(2)	Rh(2)–C(9)	2.15(2)	Rh(6)–C(26)	2.55(2)
Rh(7)–Rh(9)	2.784(2)	Rh(8)–C(9)	2.09(2)	Rh(7)–C(26)	2.18(2)
Rh(7)–Rh(11)	2.778(2)	Rh(7)–C(10)	1.96(2)	Rh(8)–C(26)	2.54(2)
Rh(8)–Rh(9)	2.822(2)	Rh(9)–C(10)	2.14(2)	Rh(9)–C(26)	2.31(2)
Rh(10)–Rh(12)	2.764(2)	Rh(1)–C(12)	2.02(2)	Rh(11)–C(26)	2.16(2)
Rh(1)–C(19)	1.86(2)	Rh(9)–C(12)	2.10(2)	Rh(2)–C(27)	2.23(2)
Rh(2)–C(8)	1.85(2)	Rh(5)–C(13)	2.13(2)	Rh(4)–C(27)	2.24(2)
Rh(3)–C(3)	1.85(2)	Rh(12)–C(13)	2.05(2)	Rh(5)–C(27)	2.64(2)
Rh(3)–C(4)	1.82(2)	Rh(5)–C(14)	2.10(2)	Rh(6)–C(27)	2.26(2)
Rh(4)–C(2)	1.86(2)	Rh(8)–C(14)	2.02(2)	Rh(8)–C(27)	2.24(2)
Rh(5)–C(6)	1.87(2)	Rh(7)–C(15)	2.05(2)	Rh(12)–C(27)	2.12(2)
				C(26)–C(27)	1.48(2)

Rh(10)–C(1)–O(1)	172(2)	Rh(1)–C(12)–O(12)	141(2)
Rh(4)–C(2)–O(2)	178(2)	Rh(9)–C(12)–O(12)	132(2)
Rh(3)–C(3)–O(3)	179(2)	Rh(5)–C(13)–O(13)	137(2)
Rh(3)–C(4)–O(4)	177(2)	Rh(12)–C(13)–O(13)	140(2)
Rh(11)–C(5)–O(5)	175(2)	Rh(5)–C(14)–O(14)	133(2)
Rh(5)–C(6)–O(6)	176(2)	Rh(8)–C(14)–O(14)	140(2)
Rh(2)–C(8)–O(8)	175(2)	Rh(7)–C(15)–O(15)	139(2)
Rh(9)–C(16)–(16)	176(2)	Rh(11)–C(15)–O(15)	136(2)
Rh(8)–C(17)–O(17)	176(2)	Rh(4)–C(20)–O(20)	140(2)
Rh(7)–C(18)–O(18)	175(2)	Rh(10)–C(20)–O(20)	133(2)
Rh(1)–C(19)–O(19)	177(2)	Rh(6)–C(21)–O(21)	136(2)
Rh(12)–C(22)–O(22)	178(2)	Rh(9)–C(21)–O(21)	137(2)
Rh(6)–C(24)–O(24)	176(2)	Rh(1)–C(23)–O(23)	137(2)
Rh(10)–C(25)–O(25)	171(2)	Rh(11)–C(23)–O(23)	136(2)
Rh(5)–C(7)–O(7)	147(2)	Rh(2)–C(11)–O(11)	138(2)
Rh(6)–C(7)–O(7)	129(2)	Rh(3)–C(11)–O(11)	127(2)
Rh(2)–C(9)–O(9)	137(2)	Rh(12)–C(11)–O(11)	136(2)
Rh(8)–C(9)–O(9)	139(2)	C(3)–Rh(3)–C(4)	93(1)
Rh(7)–C(10)–O(10)	142(2)	C(1)–Rh(10)–C(25)	89(1)
Rh(9)–C(10)–O(10)	133(2)		

From $[H_3O][Rh_{15}C_2(CO)_{28}]$. Dichloromethane (3 cm³) was added to crystalline $[H_3O][Rh_{15}C_2(CO)_{28}]$ (100 mg) and the mixture was left to stand. After 5 d a crystalline precipitate (85.2 mg) had formed and was filtered off, washed with cyclohexane, and dried *in vacuo*. Its i.r. spectrum in Nujol was identical to that of $[Rh_{12}C_2(CO)_{25}]$.

Crystal Data.—$C_{27}O_{25}Rh_{12}$, $M = 1\,959.2$, Orthorhombic, $a = 18.695(4)$, $b = 18.604(4)$, $c = 11.605(2)$ Å, $U = 4\,036.2$ Å³, $D_m = 3.17$ (by pycnometry), $Z = 4$, $D_c = 3.22$ g cm⁻³, $F(000) = 3\,608$, space group $P2_12_12_1$ (no. 19), Mo-K_α radiation, $\lambda = 0.710\,7$ Å, μ(Mo-K_α) = 47.1 cm⁻¹.

Intensity Measurements.—A crystal of dimensions 0.18 × 0.08 × 0.09 mm was mounted on a Philips PW 1100 four-circle diffractometer. Diffraction intensities were collected in the range $4 < 2\theta < 55°$ by the ω-scan method with scan width 0.8° and speed 0.05° s⁻¹. Background was measured on both sides of each reflection for half the peak-scanning time. About 5 300 reflections were measured, 3 450 of which were significantly above background $[I > 4\sigma(I)]$ and were used in the structure determination and refinement. Three standard reflections were measured every 60 min during data collection and showed no significant decrease in intensity. Integrated intensities were reduced to F_o values by correction for Lorentz and polarization.

The absorption correction was computed and the transmission factors found were in the range 0.53—0.70.

Determination and Refinement of the Structure.—The structure was solved by direct methods using the MULTAN [5] program. The Fourier synthesis, computed with the most promising set of phases of 312 reflections, showed 12 strong peaks attributable to rhodium atoms. After a preliminary refinement of the heavy-atom parameters a second Fourier map revealed 25 carbonyl groups on the cluster surface and two carbon atoms inside the metal-atom polyhedron; the molecular formula of the complex was therefore $[Rh_{12}C_2(CO)_{25}]$. The structure was refined by block-diagonal least squares (9 × 9 and 4 × 4 blocks) to R 0.037 and R' 0.045. A difference-Fourier synthesis computed after refinement revealed only interference peaks in the range ±0.5 e Å^{-3}. Weightings were applied to the observations according to $w = 1/(A + BF_o + CF_o^2)$; in the final cycles A, B, and C had values of 61.4, −0.45, and 0.001 5 and were chosen on the basis of an analysis of $\Sigma w\Delta^2$. Atomic scattering factors were taken from ref. 6, and the real and imaginary part of the rhodium anomalous dispersion was taken into account.

Final atom positions are in Table 1, bond distances and angles in Table 2; observed and computed structure factors and thermal parameters are given in Supplementary Publication No. SUP 22205 (15 pp.).* All the calculations were carried out on a UNIVAC 1106 computer at the computing centre of Milan University, using local programs.

DISCUSSION

The structure consists of discrete $[Rh_{12}C_2(CO)_{25}]$ molecules held together by normal van der Waals interactions. The molecular stereochemistry (Figure 2) is asymmetric and the crystals contain molecules of the same chirality, enantiomorphous molecules crystallizing in enantiomorphous crystals. The geometry of the metal-atom cluster cannot be easily described, the only kind of regularity being the disposition of the rhodium atoms in three nearly parallel layers containing four, five, and three atoms arranged in a rhomb, an irregular pentagon, and a triangle respectively (Figure 3). The average separation of the layers is 2.2 Å (value in the metal, 2.3 Å). The faces of the polyhedron are all triangular except two which are rhombic. A more regular packing of the metal atoms seems to be hindered by the presence of the two carbide atoms which are not disposed in two separate interstices, as in $[Rh_{15}C_2(CO)_{28}]^-$, but occupy a unique irregular cavity as a C_2 unit. The cavity is derived from two fused polyhedra, a trigonal prism, and a tetragonal antiprism sharing the face defined by Rh(2),Rh(4),Rh(6),Rh(8). Two edges of the shared face, Rh(2)–Rh(4) and Rh(6)–Rh(8), are remarkably stretched since the carbide atoms are not equidistant from the central layer of metal atoms but are deeply immersed in the antiprismatic moiety of the cavity; in fact C(26) and C(27) are 1.3 below and 0.2 Å above this plane respectively. The C–C(carbide) distance [1.48(2) Å] is shorter than that expected for a single bond (1.54 Å) but greater than the range of values found in a series of compounds containing the dicarbide anion $[C_2]^{2-}$ (1.19—1.35 Å).[7] The actual distance indicates a strong carbon–carbon bond but can hardly be discussed in terms of bond order as the carbon orbitals are employed in delocalized cluster orbitals.

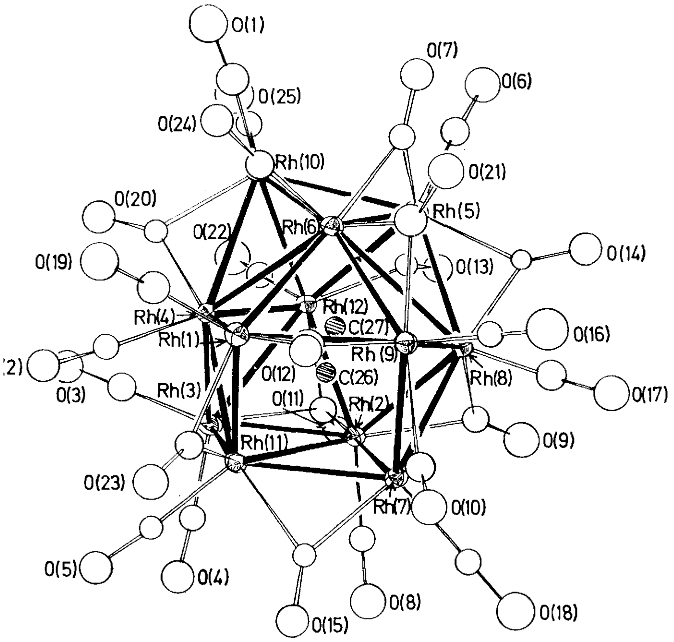

FIGURE 2 Molecular structure of $[Rh_{12}C_2(CO)_{25}]$

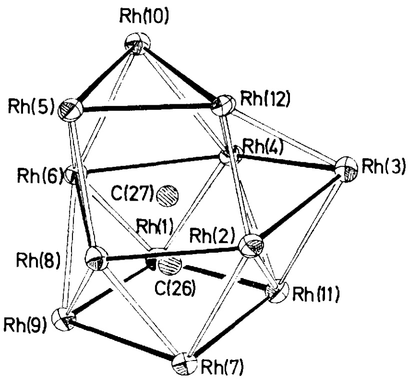

FIGURE 3 View of the $Rh_{12}C_2$ cluster showing its rationalization in terms of the layers of metal atoms. Filled bonds join the atoms within each layer

The bonding Rh–Rh distances (2.67—2.97 Å, mean 2.79 Å) are normal and in good agreement with those found in $[Rh_6C(CO)_{15}]^{2-}$ (2.79 Å) [1] and $[Rh_8C(CO)_{19}]$ (2.81 Å),[2] but significantly shorter than in $[Rh_{15}C_2(CO)_{28}]^-$ (2.87 Å).[3] The metal–metal contacts range from four to six and there is no correlation between bond distances and formal co-ordination numbers.

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

[5] P. Main, M. M. Woolfson, and G. Germain, 'MULTAN, A Computer Programme for the Automatic Solution of Crystal Structures,' Centre Européen de Calcul Atomique et Moleculaire, Orsay, France, 1971.

[6] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 231.

[7] A. F. Wells, 'Structural Inorganic Chemistry,' Clarendon Press, Oxford, 1975, p. 759.

The Rh–C(carbide) interactions are not very regular. C(27) is six-co-ordinate with five short (mean 2.22 Å) and one long contact (2.64 Å). The co-ordination geometry about this atom can be compared to that found in $[Rh_6C(CO)_{15}]^{2-}$. C(26) is eight-co-ordinate with four short and four long distances (means 2.22 and 2.55 Å respectively), the antiprismatic cavity occupied by this atom being similar to that present in $[Co_8C(CO)_{18}]^{2-}$.[8] The short distances can be compared with those found in the prismatic cavities of $[Rh_6C(CO)_{15}]^{2-}$ and $[Rh_8C(CO)_{19}]$ (2.13 Å),[1,2] and with the value in the octahedral cavities of $[Rh_{15}C_2(CO)_{28}]^-$ (2.04 Å).[3]

Of the carbonyl ligands, 14 are terminal, 10 are edge-bridging, and one is face-bridging. The mean Rh–C and C–O values for the three types of ligands are: 1.87, 1.14; 2.06, 1.16; and 2.17, 1.17 Å respectively. Nine out of the 12 rhodium atoms are three-co-ordinate, one is two-co-ordinate [Rh(4)], and two are four-co-ordinate [Rh(5) and Rh(9)]. A sharp correlation between the number of rhodium–rhodium interactions and the number and type of rhodium–carbonyl interactions has not been found, but one should note that: (*i*) the minimum number of metal–carbonyl interactions (two) is realised by Rh(4), the only atom with six metal–metal distances < 3 Å; (*ii*) the metal atoms possessing two terminal ligands, Rh(3) and Rh(10), are the only ones not connected with the carbide atoms; (*iii*) an overall electron count, based on localized Rh–Rh bonds, shows that there is a formal excess of only one electron pair in the molecule (local computations, on the other hand, indicate a nearly regular charge distribution among the cluster atoms, the electrons attributed to the rhodium atoms ranging from 17.7 to 18.6). From these facts it can be inferred that the ligand stereochemistry is dictated both by the non-bonded contacts on the cluster surface and by the need for an even distribution of the valence electrons among the metal atoms.

This molecule possesses the most irregular stereochemistry ever found in cluster compounds and contradicts a well documented preference of metal-atom clusters for polyhedra that can be considered as fragments of continuous packings of spheres. The metal-atom polyhedron is completely unexpected and cannot be easily rationalized. The only explanation for the existence of such a molecule is that, in agreement with the chemical data, it is a product of partial decomposition of $[Rh_{15}C_2(CO)_{28}]^-$. The presence of two carbide carbon atoms in the cluster fits this hypothesis very well and the proposal is strengthened by the fact that the molecular architecture of $[Rh_{15}C_2(CO)_{28}]^-$ is destabilized by some short non-bonded contacts between rhodium atoms (see ref. 3).

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