New Carbide Clusters in the Cobalt Sub-group. Part 10.[1-9] Preparation and Crystallographic Characterization † of Dicarbido-octa-μ-carbonyl-hexadecacarbonyl-*polyhedro*-dodecarhodate(2−) as its Bis(triphenylphosphine)iminium Salt, $[N(PPh_3)_2]_2[Rh_{12}C_2(CO)_{24}]$

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The title compound has been prepared by heating at 70 °C the dianion $[Rh_6C(CO)_{15}]^{2-}$ and H_2SO_4 in propan-2-ol. Its molecular structure has been determined by single-crystal *X*-ray crystallography: triclinic, space group $P\bar{1}$, with a = 17.190(4), b = 13.049(4), c = 11.581(3) Å, α = 103.24(1), β = 88.69(1), γ = 102.24(1)°, and Z = 1. The structure has been solved from 3 421 diffraction intensities, collected by counter methods, and refined by least-squares calculations to R = 0.050. The dianion has idealized D_{2h}-*mmm* symmetry and contains a Rh_{12} polyhedron based on a square–rhomb–square sequence of layers arranged in such a way as to form two prismatic cavities sharing one edge. Two carbon atoms are encapsulated in these cavities. Relevant average bond distances are Rh−C(carbide) 2.12 and Rh−Rh 2.81 Å. Eight CO ligands bridge the edges of the square layers and 16 are terminal, one per metal atom in the outer squares and two for each atom of the central rhomb. The Rh−C and C−O average distances are 1.89, 1.10, and 2.04, 1.17 Å for terminal and bridging groups, respectively.

After the discovery of a facile synthesis of the carbido-carbonyl clusters $[M_6C(CO)_{15}]^{2-}$ (M = Co or Rh) we have developed the chemistry of these anions under various chemical and physical conditions. The use of preformed carbon-containing clusters as starting material allowed the preparation of higher nuclearity species often containing two interstitial atoms. For example, oxidation of $[Rh_6C(CO)_{15}]^{2-}$ with iron(III) has led to $[Rh_8C(CO)_{19}]$,[2] $[Rh_{15}C_2(CO)_{28}]^-$,[3] and $[Rh_{12}C_2(CO)_{25}]$.[4]

Now we have heated $[Rh_6C(CO)_{15}]^{2-}$ in propan-2-ol at 70 °C in the presence of a stoicheiometric amount of H_2SO_4 and isolated the new species $[Rh_{12}C_2(CO)_{24}]^{2-}$. The stoicheiometry suggests that this anion is built up by condensation of two prismatic units. The reaction implies the intermediate formation of a reactive monohydride [10] which dimerizes with evolution of hydrogen and carbon monoxide [equation (1)].

$$2[Rh_6C(CO)_{15}]^{2-} + 2H^+ \longrightarrow 2[Rh_6C(CO)_{15}H]^- \longrightarrow [Rh_{12}C_2(CO)_{24}]^{2-} + H_2 + 6CO \quad (1)$$

The presence of the hydrogen ion is essential because it acts as an oxidizing agent.‡ Under the same physical conditions, but without acid, only the reversible conversion of the prismatic dianion into octahedral $[Rh_6C(CO)_{13}]^{2-}$ takes place after brief refluxing,[7] while at longer times the $[Rh_{12}C_2(CO)_{23}]^{4-}$ anion is formed.[12] In this paper we describe the preparation and structural characterization of the dianion $[Rh_{12}C_2(CO)_{24}]^{2-}$ as its $[N(PPh_3)_2]^+$ salt.

Experimental

The solvents were distilled and dried by the usual methods. All the operations were carried out in an inert atmosphere. The salt $K_2[Rh_6C(CO)_{15}]$ was prepared as described.[13] Infrared spectra were recorded on a Perkin-Elmer 457 spectrophotometer.

Synthesis of $[N(PPh_3)_2]_2[Rh_{12}C_2(CO)_{24}]$.—A solution of $K_2[Rh_6C(CO)_{15}]$ (0.618 g, 0.55 mmol) in propan-2-ol (20 cm³), with H_2SO_4 (0.33 mmol) in slight excess with respect to the stoicheiometric ratio of 1 : 1, was heated at 70 °C under nitrogen for about 30 min, until the i.r. spectrum only showed bands at 2 040(sh), 2 020s, 1 975(sh), 1 875w, 1 840m, and 1 815w cm⁻¹. The anion $[Rh_{12}C_2(CO)_{24}]^{2-}$ was separated as its potassium salt by concentration *in vacuo* to 3 cm³, adding a solution of KCl (0.75 g, 10 mmol) in water (30 cm³), and evaporating the residual alcohol by stirring *in vacuo*. The salt first separated as an oil, which solidified when the last traces of alcohol were eliminated. The powder was then filtered off, washed four times with 10 cm³ of a solution of KCl in water (2 g in 100 cm³), and dried *in vacuo*. The yield based on Rh was 80—90%. Tetra-alkylammonium and $[N(PPh_3)_2]^+$ salts were obtained by metathesis in alcohol. Crystals of the $[N(PPh_3)_2]^+$ salt suitable for *X*-ray analysis were obtained by recrystallization from tetrahydrofuran and propan-2-ol by the slow diffusion technique (Found: C, 38.6; H, 2.00; N, 0.85. Calc. for $C_{98}H_{60}N_2O_{24}P_4Rh_{12}$: C, 39.1; H, 2.00; N, 0.95%). The same anion could be obtained at room temperature by reaction of $[N(PPh_3)_2]_2[Rh_6C(CO)_{15}]$ with CF_3CO_2H in excess weakly basic solvents such as CH_2Cl_2. In this case it was possible to demonstrate the intermediate formation of hydridic species by n.m.r. spectroscopy.[10] The final product did not show hydridic signals. The i.r. spectrum of the $[N(PPh_3)_2]^+$ salt in tetrahydrofuran in the carbonyl-stretching region

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† *Supplementary data available* (No. SUP 23455, 24 pp.): thermal parameters, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

‡ The method of growing clusters by oxidative dimerization of smaller cluster anions upon protonation is well known and has been applied in many other cases.[11]

Table 1. Final positional parameters ($\times 10^4$) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Rh(1)	641(1)	−465(1)	2 254(1)
Rh(2)	1 508(1)	−904(1)	153(1)
Rh(3)	1 745(1)	1 245(1)	46(1)
Rh(4)	891(1)	1 679(1)	2 142(1)
Rh(5)	117(1)	1 067(1)	−53(2)
Rh(6)	−725(1)	369(1)	1 773(3)
Rh(5P)	235(2)	1 897(3)	−156(7)
Rh(6P)	−416(3)	201(4)	1 014(9)
C(0)	832(6)	287(8)	800(14)
C(1)	375(10)	−1 051(15)	3 633(24)
O(1)	232(8)	−1 383(11)	4 374(16)
C(2)	2 007(8)	−1 999(11)	−541(17)
O(2)	2 319(6)	−2 698(9)	−993(13)
C(3)	2 485(8)	2 060(11)	−816(17)
O(3)	2 932(7)	2 577(9)	−1 254(13)
C(4)	775(7)	2 891(10)	3 359(17)
O(4)	670(6)	3 616(8)	4 049(12)
C(5)	540(20)	2 120(19)	−968(26)
O(5)	853(9)	2 861(12)	−1 194(17)
C(6)	−81(18)	2 465(15)	750(32)
O(6)	−283(9)	3 232(12)	1 074(17)
C(7)	−1 001(7)	1 591(9)	2 711(16)
O(7)	−1 182(7)	2 266(9)	3 249(14)
C(8)	−1 220(11)	−573(14)	2 700(18)
O(8)	−1 551(8)	−993(11)	3 293(16)
C(9)	1 608(7)	−1 117(10)	1 804(21)
O(9)	2 039(6)	−1 475(8)	2 343(12)
C(10)	2 498(7)	268(9)	195(15)
O(10)	3 190(5)	363(6)	272(11)
C(11)	2 005(7)	2 281(10)	1 672(16)
O(11)	2 559(6)	2 971(8)	2 090(12)
C(12)	1 268(8)	945(10)	3 379(17)
O(12)	1 729(7)	1 148(8)	4 101(14)
P(1)	5 601(2)	3 391(2)	−3 311(4)
P(2)	7 218(2)	3 737(2)	−4 332(5)
N	6 472(5)	3 936(7)	−3 556(12)
C(13)	5 552(5)	2 460(6)	−2 368(8)
C(14)	6 233(5)	2 094(6)	−2 175(8)
C(15)	6 205(5)	1 375(6)	−1 443(8)
C(16)	5 497(5)	1 022(6)	−903(8)
C(17)	4 816(5)	1 388(6)	−1 096(8)
C(18)	4 843(5)	2 107(6)	−1 829(8)
C(19)	4 995(5)	2 685(7)	−4 631(9)
C(20)	4 694(5)	1 576(7)	−4 866(9)
C(21)	4 244(5)	1 058(7)	−5 902(9)
C(22)	4 095(5)	1 649(7)	−6 704(9)
C(23)	4 396(5)	2 759(7)	−6 469(9)
C(24)	4 846(5)	3 277(7)	−5 432(9)
C(25)	5 136(4)	4 431(6)	−2 494(8)
C(26)	4 326(4)	4 399(6)	−2 629(8)
C(27)	3 980(4)	5 186(6)	−1 910(8)
C(28)	4 444(4)	6 005(6)	−1 056(8)
C(29)	5 254(4)	6 037(6)	−921(8)
C(30)	5 600(4)	5 251(6)	−1 640(8)
C(31)	7 089(5)	2 422(5)	−5 273(9)
C(32)	7 359(5)	1 597(5)	−4 931(9)
C(33)	7 222(5)	567(5)	−5 674(9)
C(34)	6 816(5)	363(5)	−6 760(9)
C(35)	6 456(5)	1 188(5)	−7 101(9)
C(36)	6 683(5)	2 218(5)	−6 358(9)
C(37)	8 052(4)	3 922(7)	−3 363(11)
C(38)	7 972(4)	4 268(7)	−2 142(11)
C(39)	8 621(4)	4 423(7)	−1 372(11)
C(40)	9 350(4)	4 233(7)	−1 824(11)
C(41)	9 430(4)	3 888(7)	−3 044(11)
C(42)	8 781(4)	3 732(7)	−3 814(11)
C(43)	7 463(4)	4 697(5)	−5 215(8)
C(44)	7 207(4)	5 665(5)	−4 869(8)
C(45)	7 450(4)	6 475(5)	−5 487(8)
C(46)	7 948(4)	6 316(5)	−6 450(8)
C(47)	8 204(4)	5 347(5)	−6 795(8)
C(48)	7 962(4)	4 358(5)	−6 178(8)
H(1)	6 782(5)	2 368(6)	−2 593(8)
H(2)	6 733(5)	1 092(6)	−1 293(8)
H(3)	5 475(5)	465(5)	−336(8)
H(4)	4 267(5)	1 114(6)	−679(8)
H(5)	4 316(5)	2 390(6)	−1 978(8)
H(6)	4 810(5)	1 118(7)	−4 245(9)
H(7)	4 011(5)	199(7)	−6 084(9)
H(8)	3 746(5)	1 248(7)	−7 506(9)
H(9)	4 280(5)	3 217(7)	−7 089(9)
H(10)	5 079(5)	4 136(7)	−5 250(9)
H(11)	3 968(4)	3 765(6)	−3 290(8)
H(12)	3 353(4)	5 161(6)	−2 014(8)
H(13)	4 176(4)	6 614(6)	−500(8)
H(14)	5 613(4)	6 672(6)	−260(8)
H(15)	6 227(4)	5 276(6)	−1 536(8)
H(16)	7 674(5)	1 755(5)	−4 091(9)
H(17)	7 431(5)	−71(5)	−5 409(9)
H(18)	6 710(5)	−434(5)	−7 335(9)
H(19)	6 232(5)	1 030(5)	−7 941(9)
H(20)	6 475(5)	2 857(5)	−6 623(9)
H(21)	7 408(4)	4 415(7)	−1 793(11)
H(22)	8 559(4)	4 691(7)	−427(11)
H(23)	9 852(4)	4 354(7)	−1 228(11)
H(24)	9 994(4)	3 741(7)	−3 394(11)
H(25)	8 843(4)	3 465(7)	−4 759(11)
H(26)	6 822(4)	5 788(5)	−4 124(8)
H(27)	7 252(4)	7 224(5)	−5 219(8)
H(28)	8 136(4)	6 942(5)	−6 928(8)
H(29)	8 590(4)	5 224(5)	−7 540(8)
H(30)	8 160(4)	3 788(5)	−6 445(8)

showed bands at 2 040(sh), 2 020s, 1 975(sh), 1 875w, 1 840m, and 1 815w cm^{-1}.

Crystallography.—Crystal data. $C_{98}H_{60}N_2O_{24}P_4Rh_{12}$, M = 2 008.3, Triclinic, a = 17.190(4), b = 13.049(4), c = 11.581(3) Å, α = 103.24(1), β = 88.69(1), γ = 102.24(1)°, U = 2 470.3 Å^3, D_m = 2.05, Z = 1, D_c = 2.02 g cm^{-3}, $F(000)$ = 1 454, space group $P\bar{1}$ (no. 2), Mo-K_α radiation, λ= 0.7107 Å, μ(Mo-K_α) = 18.93 cm^{-1}.

Intensity measurements. A crystal fragment with average dimension 0.25 mm was mounted on a Philips PW 1100 diffractometer. Diffraction intensities were measured on half of the reciprocal lattice in the range $2 < \theta < 30°$ by the ω-scan method, with scan interval 1.6° and speed 2.7° min^{-1}. The background was measured at both sides of the reflections for a total time equal to the peak scanning time. 8 604 Diffraction intensities were collected, 3 421 of which having $F_o > 5\sigma(F_o)$ were used for the structure solution and refinement. The integrated intensities were reduced to F_o values and an experimental correction for absorption was applied.

Determination of the structure. For all the computations the SHELX package of crystallographic programs was used.[14] The structure was solved by application of direct methods, but the rationalization of the geometry of the metal-atom polyhedron was not straightforward because multiple images were found in the Fourier map and we had no previous information on the cluster complexity. Troubles arose not only from the high symmetry of the metal-atom polyhedron but also from some degree of disorder. After various attempts a Rh_{12} polyhedron was recognized situated around a crystallographic inversion centre. The polyhedron consisted of two outer squares in eclipsed configuration and a central layer con-

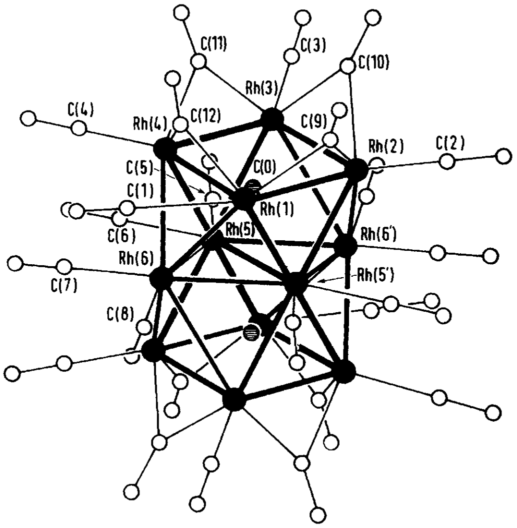

Figure 1. The anion $[Rh_{12}C_2(CO)_{24}]^{2-}$ showing the atom labelling. The oxygen atoms of the CO ligands, not labelled, bear the same numbers as the corresponding carbons

taining two interpenetrating rhombi in staggered configuration, which clearly indicated a rotational disorder. The rotational symmetry along the stacking direction was two-fold, but the molecular hindrance was evidently dominated by the four-fold symmetry of the outer squares causing randomization of the central rhomb in two orthogonal orientations. A least-squares refinement of the metal-atom positions showed that the disorder was partial and gave an occupancy factor of 0.774 for the stronger image of the central layer.

A difference-Fourier map showed most of the light atoms; as expected some lack of resolution was found in the region of the carbonyl ligands bonded to the central layer. Further refinement of the whole structure model did not give separate images of the two sets of equatorial ligands because partial atom superimposition occurred. Therefore only one set of carbonyl ligands was refined with unit weights. Only the metal atoms were allowed to vibrate anisotropically and the phenyl groups in the cations were treated as rigid groups. The final agreement indices were $R = 0.050$ and $R' = 0.055$. A difference-Fourier map computed after the refinement showed residual peaks lower than 1.0 e Å^{-3} in the vicinity of the CO ligands in the equatorial plane.

The atomic co-ordinates are reported in Table 1, bond distances and relevant angles in Table 2. The label P refers to the weaker image of the disorder.

Results and Discussion

The crystal comprises discrete anions $[Rh_{12}C_2(CO)_{24}]^{2-}$ (Figure 1) and cations $[N(PPh_3)_2]^+$. The cations occupy general positions; the anions have crystallographic symmetry C_i-$\bar{1}$ and idealized D_{2h}-*mmm* symmetry. The metal-atom polyhedron may be described in terms of a square–rhomb–square sequence of layers, resulting in the formation of two prismatic cavities in which two isolated carbon atoms are allocated [Figure 2(*a*)]. An alternative description is in terms of two trigonal prisms sharing one inter-basal edge plus two extra atoms capping pairs of rectangular faces facing each other [Figure 2(*b*)]. The metal–metal connections are four for the atoms in the outer squares, six for the atoms defining the long diagonal of the central rhomb, and seven for those defining the short diagonal. Most Rh–Rh distances are found in the narrow range 2.754(2)—2.834(2), average 2.773 Å. Only the interlayer interactions of the atoms defining the long diagonal of the central rhomb, Rh(6) and Rh(6′), show a significantly longer mean value of 2.915 Å. Minor deviations from the average values conform to the idealized molecular symmetry.

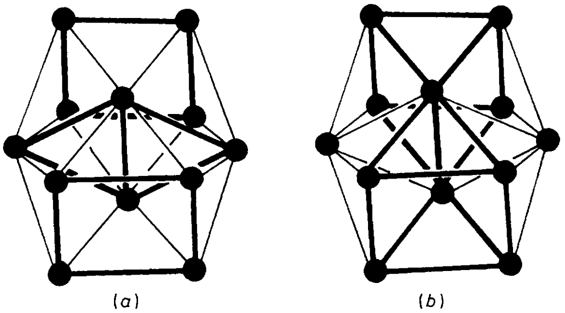

Figure 2. The Rh_{12} polyhedron viewed as a sequence of layers (*a*) and as two prisms sharing an edge plus two capping atoms (*b*)

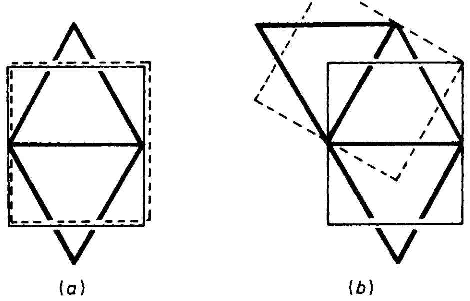

Figure 3. Comparsion of the packing of the metal-atom layers in $[Rh_{12}C_2(CO)_{24}]^{2-}$ and $[Co_{13}C_2(CO)_{24}]^{4-}$. Thick lines define the central layers, thin and broken lines define upper and lower layers, respectively

Eight of the CO ligands bridge all the edges of the outer squares and 16 are terminal, two per metal atom in the central rhomb and one for each of the other atoms. In this way the metal atoms in the outer layers with fewer metal–metal connections have three metal–ligand bonds and those in the central layer only two. In spite of the different connectivities all the metal atoms formally receive four electrons from the outer ligands. The Rh–C and C–O interactions have the following average values: 1.89, 1.10 Å for the terminal groups and 2.04, 1.17 Å for the bridging groups. The Rh–C(carbide) distances average 2.12 Å, in very good agreement with the value (2.13 Å) found in $[Rh_6C(CO)_{15}]^{2-}$.[1] The apparent radius of carbon has the expected value 0.73 Å.

This is the second example of a dicarbide cluster containing two carbon atoms in different prismatic cavities the other being $[Co_{13}C_2(CO)_{24}]^{4-}$.[9] At first sight the two polyhedra seem to be totally different, but if one regards them as stacks of layers a simple relationship becomes apparent, as shown in Figure 3. The differences between the $Rh_{12}C_2$ (*a*) and $Co_{13}C_2$ (*b*) polyhedra arise from the presence of the thirteenth atom in the central layer of the cobalt cluster which forms a third condensed triangle. As a consequence in the Rh_{12} polyhedron the outer squares can be built up only in eclipsed configuration, if prismatic cavities are to be formed. In the Co_{13} species, on the other hand, there are two possibilities, the one found in Rh_{12} and that adopted in the actual structure in which one square layer is aligned to each inner diagonal; therefore the outer layers are displaced with respect to each other.

Table 2. Distances (Å) and relevant angles (°) with estimated standard deviations in parentheses

Rh(1)-Rh(5′)	2.758(2)	Rh(3)-Rh(5P)	2.928(4)	Rh(4)-C(4)	1.90(1)	C(2)-O(2)	1.17(1)
Rh(1)-Rh(2)	2.834(2)	Rh(4)-Rh(5P)	3.009(4)	Rh(5)-C(5)	1.94(2)	C(3)-O(3)	1.10(1)
Rh(1)-Rh(4)	2.772(1)	Rh(5P)-Rh(6P)	2.871(4)	Rh(5)-C(6)	1.94(2)	C(4)-O(4)	1.13(1)
Rh(1)-Rh(6)	2.903(2)	Rh(6P)-Rh(6′P)	2.727(3)	Rh(6)-C(7)	1.87(1)	C(5)-O(5)	1.09(2)
Rh(2)-Rh(5′)	2.759(2)			Rh(6)-C(8)	1.86(1)	C(6)-O(6)	1.11(1)
Rh(2)-Rh(3)	2.778(1)	Rh(1)-C(0)	2.12(1)	Rh(1)-C(9)	2.03(1)	C(7)-O(7)	1.06(1)
Rh(2)-Rh(6′)	2.918(2)	Rh(2)-C(0)	2.12(1)	Rh(2)-C(9)	2.01(1)	C(8)-O(8)	1.06(1)
Rh(3)-Rh(4)	2.814(2)	Rh(3)-C(0)	2.10(1)	Rh(2)-C(10)	2.03(1)	C(9)-O(9)	1.21(2)
Rh(3)-Rh(6′)	2.919(2)	Rh(4)-C(0)	2.09(1)	Rh(3)-C(10)	2.04(1)	C(10)-O(10)	1.17(1)
Rh(4)-Rh(6)	2.921(2)	Rh(5)-C(0)	2.14(1)	Rh(3)-C(11)	2.05(1)	C(11)-O(11)	1.19(1)
Rh(5)-Rh(5′)	2.758(2)	Rh(6) · · · C(0)	2.89(1)	Rh(4)-C(11)	2.02(1)	C(12)-O(12)	1.11(2)
Rh(5)-Rh(3)	2.760(1)			Rh(1)-C(12)	2.09(1)		
Rh(5)-Rh(4)	2.765(2)	Rh(1)-C(1)	1.93(2)	Rh(4)-C(12)	2.08(1)		
Rh(5)-Rh(6)	2.754(2)	Rh(2)-C(2)	1.84(1)				
Rh(5)-Rh(6′)	2.756(2)	Rh(3)-C(3)	1.90(2)	C(1)-O(1)	1.10(2)		
Rh(1)-C(1)-O(1)	179(2)	Rh(5)-C(5)-O(5)	161(2)	Rh(1)-C(9)-O(9)	133(2)	Rh(3)-C(11)-O(11)	134(1)
Rh(2)-C(2)-O(2)	179(2)	Rh(5)-C(6)-O(6)	169(3)	Rh(2)-C(9)-O(9)	138(2)	Rh(4)-C(11)-O(11)	138(1)
Rh(3)-C(3)-O(3)	176(2)	Rh(6)-C(7)-O(7)	178(1)	Rh(2)-C(10)-O(10)	138(2)	Rh(1)-C(12)-O(12)	136(1)
Rh(4)-C(4)-O(4)	176(1)	Rh(6)-C(8)-O(8)	170(1)	Rh(3)-C(10)-O(10)	136(1)	Rh(4)-C(12)-O(12)	138(1)

The dianion $[Rh_{12}C_2(CO)_{24}]^{2-}$ is isoelectronic but not isostructural with the already reported $[Rh_{12}C_2(CO)_{25}]$,[4] which contains two bonded carbon atoms. The latter molecule is sterically irregular having no symmetry at all and its existence is due to a particular mechanism of formation. In fact it is a product of partial breakdown of $[Rh_{15}C_2(CO)_{28}]^-$ (ref. 3) that, very probably, cannot find an easy path of rearrangement to the more regular polyhedron found in $[Rh_{12}C_2(CO)_{24}]^{2-}$. This pair of Rh_{12} species is reminiscent of the other isoelectronic pair $[Rh_8C(CO)_{19}]$ [2] and $[Co_8C(CO)_{18}]^{2-}$,[5] in which again the neutral species is sterically irregular and the anionic one is more symmetric. From these findings one can infer that a regular metal-atom polyhedron is more demanding than an irregular one with regard to the number and distribution of the metal–ligand interactions. As a consequence, ligands are accepted on the cluster surface as long as a regular arrangement is possible. If further electron pairs are required to fill up the cluster bonding orbitals they are present as free charges. This is the reason why for some anionic clusters, such as $[Rh_6C(CO)_{15}]^{2-}$,[1] the preparation of the isoelectronic neutral species has proved impossible.

Acknowledgements

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References

1 Part 1, V. G. Albano, M. Sansoni, P. Chini, and S. Martinengo, *J. Chem. Soc., Dalton Trans.*, 1973, 651.

2 Part 2, V. G. Albano, M. Sansoni, P. Chini, S. Martinengo, and D. Strumolo, *J. Chem. Soc., Dalton Trans.*, 1975, 305.

3 Part 3, V. G. Albano, M. Sansoni, P. Chini, S. Martinengo, and D. Strumolo, *J. Chem. Soc., Dalton Trans.*, 1976, 970.

4 Part 4, V. G. Albano, P. Chini, S. Martinengo, M. Sansoni, and D. Strumolo, *J. Chem. Soc., Dalton Trans.*, 1978, 459.

5 Part 5, V. G. Albano, P. Chini, G. Ciani, S. Martinengo, and M. Sansoni, *J. Chem. Soc., Dalton Trans.*, 1978, 468.

6 Part 6, V. G. Albano, P. Chini, G. Ciani, M. Sansoni, and S. Martinengo, *J. Chem. Soc., Dalton Trans.*, 1980, 163.

7 Part 7, V. G. Albano, D. Braga, and S. Martinengo, *J. Chem. Soc., Dalton Trans.*, 1981, 717.

8 Part 8, V. G. Albano, D. Braga, G. Ciani, and S. Martinengo, *J. Organomet. Chem.*, 1981, **213**, 293.

9 Part 9, V. G. Albano, D. Braga, P. Chini, G. Ciani, and S. Martinengo, *J. Chem. Soc., Dalton Trans.*, 1982, 645.

10 B. T. Heaton, L. Strona, S. Martinengo, D. Strumolo, R. J. Goodfellow, and I. H. Sadler, *J. Chem. Soc., Dalton Trans.*, 1982, 1499.

11 P. Chini, *J. Organomet. Chem.*, 1980, **200**, 37 and refs. therein.

12 V. G. Albano, D. Braga, S. Martinengo, and D. Strumolo, unpublished work.

13 S. Martinengo, D. Strumolo, and P. Chini, *Inorg. Synth.*, 1980, **20**, 212.

14 G. M. Sheldrick, SHELX 75 System of Computer Programs, Cambridge, 1975.

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