High Nuclearity Carbonyl Clusters of Rhodium. Part 1. Crystallographic Characterization of Dodeca-μ-carbonyl-dodecacarbonyldihydrido-*polyhedro*-tridecarhodate(3−) in its Benzyltriphenylphosphonium Salt

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The title complex crystallizes in the monoclinic space group $P2_1/n$ with unit-cell dimensions a = 14.334 (2), b = 29.231(4), c = 24.626(3) Å, β = 94.61(3)°, and Z = 4. The structure has been determined by conventional methods from *X*-ray single-crystal counter data and refined by least-squares calculations to R 0.061 for 7 286 significant diffraction intensities. The $[Rh_{13}H_2(CO)_{24}]^{3-}$ anion contains a polyhedron of rhodium atoms consisting of a fragment of hexagonal close packing (D_{3h} symmetry). The mean Rh–Rh distance is 2.794 Å. Twelve of the CO ligands are terminally bonded and 12 symmetrically edge bridging on half of the polyhedron edges; the idealized overall molecular symmetry is C_s. On the basis of the Rh–Rh distances and of the holes left by the ligands on the cluster surface, the hydride atoms have been located in two semi-octahedral cavities of the cluster.

Two new cluster species, $[Rh_{13}H_3(CO)_{24}]^{2-}$ and $[Rh_{13}H_2(CO)_{24}]^{3-}$, have been recently prepared [1] and the structure of the dianion has been ascertained by a crystallographic study.[1] The metal atoms in this complex are arranged in a polyhedron which is a fragment of hexagonal close packing. The carbonyl ligands are co-ordinated on the cluster surface, 12 terminally and 12 edge-bridging. An unambiguous location of the hydrogen atoms was not possible. Although interstitial locations inside the metal atom polyhedron were suggested by an analysis of the Rh–Rh distances, we preferred to obtain more information prior to proposing a complete structural model.

The structure of $[Rh_{13}H_2(CO)_{24}]^{3-}$ was assumed to be essentially similar to that of the dianion because the i.r. spectra of the two complexes show very similar patterns and the complexes are easily interconverted [equation (1)]. The characterization of the anions has been

$$[Rh_{13}H_3(CO)_{24}]^{2-} \underset{H^+}{\overset{[OH]^-}{\rightleftharpoons}} [Rh_{13}H_2(CO)_{24}]^{3-} \qquad (1)$$

improved by a n.m.r. study [2] which has demonstrated the fluxionality of the carbonyl groups and of the hydrogen atoms in both complexes. The n.m.r. spectrum of the hydrogens at room temperature has been explained in terms of rapid migration of these atoms inside the metal atom cluster.

We have undertaken a complete structural analysis of the trianion $[Rh_{13}H_2(CO)_{24}]^{3-}$ in its benzyltriphenylphosphonium salt in order to gain a precise knowledge of at least one structure. Our major ambition was to assess unequivocally the hydrogen locations through a comparison of the Rh–Rh distances in the two clusters.

EXPERIMENTAL

Crystal Data.—$C_{99}H_{68}O_{24}P_3Rh_{13}$, M = 3 072.3, Monoclinic, a = 14.334(2), b = 29.231(4), c = 24.626(3) Å, β = 94.61(3)°, U = 10 284.8 Å^3, D_m = 1.96(2) (by flotation), Z = 4, D_c = 1.98 g cm^{-3}, $F(000)$ = 5 936, space group $P2_1/n$ (no. 14), Mo-K_α radiation (λ = 0.710 7 Å), μ(Mo-K_α) = 20.8 cm^{-1}.

Intensity Measurements.—A crystal with dimensions 0.39 × 0.55 × 0.62 mm was mounted on a Philips PW 1100 diffractometer. Diffraction intensities were collected in the range $3 < \theta < 23°$ by the θ—2θ scan method, with scan width 1.4° and speed 0.06° s^{-1}. The background was measured on both sides of each reflection for half of the peak-scanning time. 13 960 Reflections were measured, 7 286 of which were significantly above background [$\sigma(I)/I < 0.3$] and were used in the structure determination and refinement. Three standard intensities were measured at periodic intervals, a 15% decay being detected. Integrated intensities were reduced to F_o values by correction for Lorentz, polarization, and decay effects. The absorption correction was computed and the transmission factors were in the range 0.49—0.67.

Determination of the Structure.—The structure was solved by deconvolution of the Patterson map and, after a preliminary refinement of the rhodium atom parameters, a difference-Fourier synthesis showed the locations of all the non-hydrogen atoms. The structure was refined by block-diagonal least squares (9 × 9 and 4 × 4 blocks) to R = 0.061 and R' = 0.081. A difference-Fourier synthesis, computed after refinement, revealed only interference peaks in the range ±1.3 e Å^{-3}. During the refinements, weights 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 202.4, −2.36, and 0.013 and were chosen on the basis of an analysis of $\Sigma w\Delta^2$. Atomic scattering factors were taken from ref. 3, the real and imaginary part of the anomalous dispersion for Rh and P being taken into account.[4] The phenyl rings of the cations were treated as rigid groups of idealized D_{6h} symmetry (C–C distance 1.392 Å); the hydrogen atoms were omitted.

Final atom positions are reported in Table 1 and bond distances and angles in Table 2. Observed and computed structure factors and thermal parameters are given in Supplementary Publication No. SUP 22435 (29 pp.).† All computations were carried out on a UNIVAC 1108 computer at the computing centre of Milan University, using local programs.

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† For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

TABLE 1

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

Atom	x	y	z
Rh(1)	2 938(1)	1 312(1)	3 071(1)
Rh(2)	2 030(1)	2 130(1)	3 257(1)
Rh(3)	2 338(1)	1 907(1)	2 192(1)
Rh(4)	1 333(1)	1 146(1)	1 677(1)
Rh(5)	1 894(1)	572(1)	2 547(1)
Rh(6)	1 643(1)	831(1)	3 611(1)
Rh(7)	717(1)	1 642(1)	3 794(1)
Rh(8)	151(1)	2 234(1)	2 903(1)
Rh(9)	464(1)	1 979(1)	1 835(1)
Rh(10)	−464(1)	1 152(1)	2 023(1)
Rh(11)	107(1)	612(1)	2 901(1)
Rh(12)	−816(1)	1 424(1)	3 073(1)
Rh(13)	1 051(1)	1 413(1)	2 745(1)
P(1)	275(3)	3 795(1)	451(2)
P(2)	3 044(5)	337(3)	−486(3)
P(3)	774(4)	1 650(1)	−2 340(2)
C(1)	4 099(13)	1 154(6)	2 910(7)
C(2)	2 137(18)	2 601(9)	3 731(11)
C(3)	3 387(15)	1 901(7)	1 813(9)
C(4)	1 713(13)	1 316(6)	1 031(8)
C(5)	2 925(13)	209(6)	2 675(7)
C(6)	1 648(14)	288(7)	3 956(8)
C(7)	677(16)	2 069(8)	4 321(10)
C(8)	154(18)	2 789(9)	3 228(11)
C(9)	−160(14)	2 042(7)	1 182(8)
C(10)	−1 554(14)	1 301(7)	1 633(8)
C(11)	−448(14)	260(7)	3 385(8)
C(12)	−2 020(13)	1 193(6)	3 013(8)
C(13)	2 614(14)	2 452(7)	2 671(8)
C(14)	3 266(14)	1 866(7)	3 521(8)
C(15)	1 628(12)	2 297(6)	1 646(7)
C(16)	3 030(13)	916(6)	3 731(8)
C(17)	−204(12)	2 501(6)	2 156(7)
C(18)	1 302(14)	1 173(7)	4 280(8)
C(19)	1 909(13)	540(6)	1 737(8)
C(23)	−1 166(13)	2 091(6)	3 083(8)
C(21)	−555(17)	1 358(8)	3 868(10)
C(22)	125(12)	904(6)	1 367(7)
C(23)	919(11)	103(5)	2 634(6)
C(24)	−882(13)	547(6)	2 304(7)
C(25)	77(13)	4 363(6)	174(8)
C(26)	3 396(26)	24(13)	180(15)
C(27)	−295(12)	1 405(6)	−2 683(7)
O(1)	4 842(11)	1 022(5)	2 823(6)
O(2)	2 242(14)	2 901(7)	4 038(8)
O(3)	4 060(12)	1 889(6)	1 564(7)
O(4)	1 968(11)	1 455(5)	608(6)
O(5)	3 581(10)	−21(5)	2 768(6)
O(6)	1 653(11)	−68(5)	4 184(7)
O(7)	610(13)	2 354(7)	4 645(8)
O(8)	201(15)	3 155(7)	3 409(9)
O(9)	−535(12)	2 060(5)	727(7)
O(10)	−2 254(12)	1 374(6)	1 390(7)
O(11)	−830(11)	41(5)	3 694(6)
O(12)	−2 752(10)	1 043(5)	2 957(6)
O(13)	3 003(9)	2 816(4)	2 607(5)
O(14)	3 934(11)	1 995(5)	3 788(6)
O(15)	1 818(10)	2 575(5)	1 312(6)
O(16)	3 618(10)	785(5)	4 062(6)
O(17)	−679(10)	2 817(5)	1 999(6)
O(18)	1 475(11)	1 105(5)	4 762(6)
O(19)	2 128(12)	242(6)	1 417(7)
O(20)	−1 836(11)	2 312(5)	3 153(6)
O(21)	−1 001(12)	1 235(6)	4 249(7)
O(22)	−160(10)	715(5)	955(6)
O(23)	806(8)	−297(4)	2 556(5)
O(24)	−1 485(9)	291(4)	2 165(5)
C(111)	971(8)	3 820(5)	1 085(4)
C(112)	1 796(9)	4 073(4)	1 105(4)
C(113)	2 370(8)	4 098(4)	1 588(5)
C(114)	2 119(8)	3 871(5)	2 050(4)
C(115)	1 295(9)	3 618(4)	2 031(4)
C(116)	721(8)	3 592(4)	1 548(5)
C(121)	900(13)	3 486(6)	−21(6)
C(122)	813(11)	3 592(5)	−574(7)
C(123)	1 323(10)	3 349(5)	−935(5)
C(124)	1 920(12)	2 998(6)	−744(6)
C(125)	2 007(11)	2 892(5)	−191(7)
C(126)	1 497(10)	3 136(5)	169(5)
C(131)	−824(8)	3 518(5)	526(5)
C(132)	−1 127(7)	3 157(5)	188(5)
C(133)	−2 012(9)	2 969(4)	227(5)
C(134)	−2 593(8)	3 142(5)	604(5)
C(135)	−2 290(7)	3 503(5)	942(5)
C(136)	−1 405(9)	3 691(4)	903(5)
C(141)	−556(10)	4 656(5)	514(5)
C(142)	−1 494(10)	4 693(4)	324(4)
C(143)	−2 100(7)	4 960(5)	606(6)
C(144)	−1 767(10)	5 189(5)	1 077(5)
C(145)	−829(10)	5 153(4)	1 267(4)
C(146)	−223(7)	4 886(5)	986(6)
C(211)	1 841(9)	400(8)	−632(7)
C(212)	1 273(11)	487(5)	−211(5)
C(213)	313(11)	543(6)	−324(6)
C(214)	−78(9)	512(8)	−858(7)
C(215)	488(11)	425(5)	−1 279(5)
C(216)	1 448(11)	369(6)	−1 166(6)
C(221)	3 723(19)	158(10)	−1 053(9)
C(222)	4 600(21)	331(7)	−1 147(11)
C(223)	5 164(15)	98(10)	−1 490(11)
C(224)	4 849(19)	−306(10)	−1 739(9)
C(225)	3 972(21)	−478(7)	−1 645(11)
C(226)	3 409(15)	−246(10)	−1 302(11)
C(231)	3 587(23)	877(8)	−266(12)
C(232)	3 591(15)	1 205(11)	−676(8)
C(233)	3 887(17)	1 649(9)	−550(11)
C(234)	4 179(23)	1 764(8)	−15(12)
C(235)	4 176(15)	1 436(11)	394(8)
C(236)	3 880(17)	992(9)	268(11)
C(241)	3 100(27)	−455(7)	14(11)
C(242)	3 804(15)	−784(13)	37(11)
C(243)	3 573(22)	−1 247(11)	15(11)
C(244)	2 638(27)	−1 380(7)	−30(11)
C(245)	1 934(15)	−1 051(13)	−54(11)
C(246)	2 165(22)	−589(11)	−32(11)
C(311)	966(14)	2 214(4)	−2 575(5)
C(312)	1 325(12)	2 268(4)	−3 080(6)
C(313)	1 471(10)	2 705(5)	−3 281(4)
C(314)	1 258(14)	3 088(4)	−2 979(5)
C(315)	899(12)	3 034(4)	−2 474(6)
C(316)	753(10)	2 597(5)	−2 272(4)
C(321)	618(12)	1 683(6)	−1 626(4)
C(322)	1 401(9)	1 641(6)	−1 257(7)
C(323)	1 315(9)	1 699(5)	−702(6)
C(324)	446(12)	1 798(6)	−516(4)
C(325)	−336(9)	1 840(6)	−885(7)
C(326)	−250(9)	1 783(5)	−1 440(6)
C(331)	1 789(7)	1 311(4)	−2 450(5)
C(332)	1 706(7)	845(4)	−2 557(5)
C(333)	2 499(9)	586(3)	−2 634(5)
C(334)	3 376(7)	793(4)	−2 604(5)
C(335)	3 459(7)	1 259(4)	−2 497(5)
C(336)	2 665(9)	1 519(3)	−2 420(5)
C(341)	−360(12)	1 450(6)	−3 293(5)
C(342)	−829(11)	1 829(5)	−3 524(6)
C(343)	−921(11)	1 881(5)	−4 087(7)
C(344)	−545(12)	1 555(6)	−4 420(5)
C(345)	−77(11)	1 177(5)	−4 188(6)
C(346)	15(11)	1 124(5)	−3 625(7)

DISCUSSION

The stereochemistry of the non-hydrogen atoms of the anion $[Rh_{13}H_2(CO)_{24}]^{3-}$ is illustrated in Figure 1; it is very similar to that of $[Rh_{13}H_3(CO)_{24}]^{2-}$.[1] The metal atom cluster (Figure 2) consists of a closed polyhedron, of D_{3h} idealized symmetry, representing a fragment of hexagonal close packing. The 13 atoms are disposed in three layers, two outer triangles with the same orientation and a central centred hexagon. The central atom exhibits a true metallic 12-co-ordination, while the surface atoms have five metal–metal connections. The polyhedron contains both triangular (eight) and square (six) faces. The rhodium–rhodium distances are in the range 2.746—2.887(3) Å; these values are not very scattered and can be considered as normal.

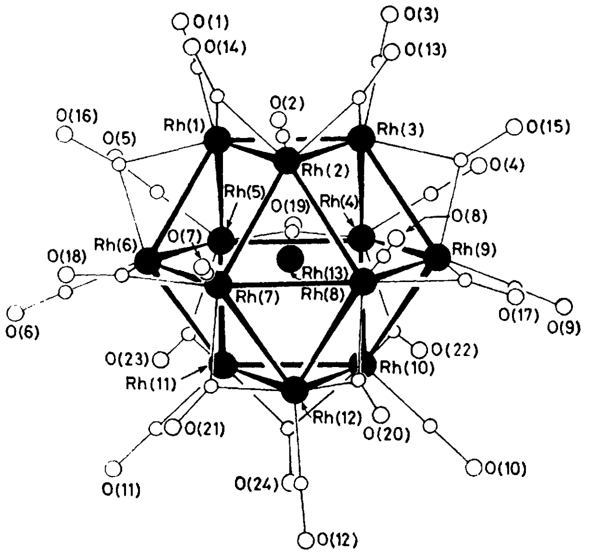

FIGURE 1 Structure of the anion $[Rh_{13}H_2(CO)_{24}]^{3-}$

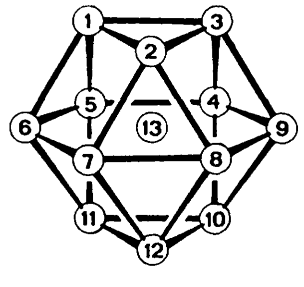

FIGURE 2 A view of the Rh_{13} cluster

Twelve of the carbonyl ligands are terminally bound, one per surface rhodium atom, and twelve symmetrically bridging on half of the polyhedron edges in such a way as to give three Rh–C connections per metal atom. In this way, bridged edges in the upper part of the molecule correspond to unbridged ones in the lower part and *vice versa*. The average Rh–C and C–O distances for the terminal and bridging groups are 1.81, 1.17 and 2.00, 1.20 Å, respectively.

TABLE 2

Bond distances and angles within the salt $[P(CH_2Ph)Ph_3]_3[Rh_{13}H_2(CO)_{24}]$

Distances (Å)

(*a*) Anion

Rh(1)–Rh(2)	2.777(3)	Rh(1)–C(14)	1.99(2)
Rh(1)–Rh(3)	2.856(3)	Rh(1)–C(16)	1.99(2)
Rh(1)–Rh(5)	2.878(3)	Rh(2)–C(13)	1.96(2)
Rh(1)–Rh(6)	2.753(3)	Rh(2)–C(14)	1.99(2)
Rh(2)–Rh(3)	2.770(3)	Rh(3)–C(13)	2.00(2)
Rh(2)–Rh(7)	2.781(3)	Rh(3)–C(15)	1.98(2)
Rh(2)–Rh(8)	2.780(3)	Rh(4)–C(19)	1.96(2)
Rh(3)–Rh(4)	2.887(3)	Rh(4)–C(22)	1.97(2)
Rh(3)–Rh(9)	2.767(3)	Rh(5)–C(19)	2.00(2)
Rh(4)–Rh(5)	2.790(3)	Rh(5)–C(23)	1.98(2)
Rh(4)–Rh(9)	2.776(3)	Rh(6)–C(16)	2.00(2)
Rh(4)–Rh(10)	2.779(3)	Rh(6)–C(18)	2.02(2)
Rh(5)–Rh(6)	2.780(3)	Rh(7)–C(18)	1.96(2)
Rh(5)–Rh(11)	2.774(3)	Rh(7)–C(21)	2.03(2)
Rh(6)–Rh(7)	2.770(3)	Rh(8)–C(17)	2.02(2)
Rh(6)–Rh(11)	2.775(3)	Rh(8)–C(20)	2.02(2)
Rh(7)–Rh(8)	2.862(3)	Rh(9)–C(15)	2.00(2)
Rh(7)–Rh(12)	2.786(3)	Rh(9)–C(17)	2.00(2)
Rh(8)–Rh(9)	2.804(3)	Rh(10)–C(22)	2.02(2)
Rh(8)–Rh(12)	2.793(3)	Rh(10)–C(24)	2.01(2)
Rh(9)–Rh(10)	2.817(3)	Rh(11)–C(23)	2.03(2)
Rh(10)–Rh(11)	2.748(3)	Rh(11)–C(24)	1.97(2)
Rh(10)–Rh(12)	2.791(3)	Rh(12)–C(20)	2.01(2)
Rh(11)–Rh(12)	2.767(3)	Rh(12)–C(21)	1.97(2)
Rh(13)–Rh(1)	2.775(3)	C(1)–O(1)	1.17(2)
Rh(13)–Rh(2)	2.769(3)	C(2)–O(2)	1.16(3)
Rh(13)–Rh(3)	2.784(3)	C(3)–O(3)	1.18(3)
Rh(13)–Rh(4)	2.803(3)	C(4)–O(4)	1.20(3)
Rh(13)–Rh(5)	2.800(3)	C(5)–O(5)	1.16(2)
Rh(13)–Rh(6)	2.806(3)	C(6)–O(6)	1.19(3)
Rh(13)–Rh(7)	2.749(3)	C(7)–O(7)	1.16(3)
Rh(13)–Rh(8)	2.767(3)	C(8)–O(8)	1.16(3)
Rh(13)–Rh(9)	2.858(3)	C(9)–O(9)	1.20(3)
Rh(13)–Rh(10)	2.800(3)	C(10)–O(10)	1.15(3)
Rh(13)–Rh(11)	2.746(3)	C(11)–O(11)	1.16(3)
Rh(13)–Rh(12)	2.859(3)	C(12)–O(12)	1.14(2)
Rh(1)–C(1)	1.80(2)	C(13)–C(13)	1.22(3)
Rh(2)–C(2)	1.80(2)	C(14)–O(14)	1.18(3)
Rh(3)–C(3)	1.83(2)	C(15)–O(15)	1.20(3)
Rh(4)–C(4)	1.79(2)	C(16)–O(16)	1.19(2)
Rh(5)–C(5)	1.83(2)	C(17)–O(17)	1.20(2)
Rh(6)–C(6)	1.80(2)	C(18)–O(18)	1.21(3)
Rh(7)–C(7)	1.81(2)	C(19)–O(19)	1.23(3)
Rh(8)–C(8)	1.81(3)	C(20)–O(20)	1.18(3)
Rh(9)–C(9)	1.79(2)	C(21)–O(21)	1.23(3)
Rh(10)–C(10)	1.82(2)	C(22)–O(22)	1.20(2)
Rh(11)–C(11)	1.81(2)	C(23)–O(23)	1.20(2)
Rh(12)–C(12)	1.85(2)	C(24)–O(14)	1.17(2)

(*b*) Cations

P(1)–C(111)	1.79(1)	P(2)–C(26)	1.91(4)
P(1)–C(121)	1.77(2)	C(26)–C(241)	1.51(4)
P(1)–C(131)	1.80(1)	P(3)–C(311)	1.78(1)
P(1)–C(25)	1.81(2)	P(3)–C(321)	1.79(1)
C(25)–C(141)	1.54(3)	P(3)–C(331)	1.80(1)
P(2)–C(211)	1.74(2)	P(3)–C(27)	1.84(2)
P(2)–C(221)	1.84(3)	C(27)–C(341)	1.50(2)
P(2)–C(231)	1.82(3)		

Angles (°)

Rh(1)–C(1)–O(1)	175(2)	Rh(1)–C(16)–O(16)	138(2)
Rh(2)–C(2)–O(2)	177(2)	Rh(6)–C(16)–O(16)	135(2)
Rh(3)–C(3)–O(3)	179(2)	Rh(8)–C(17)–O(17)	133(2)
Rh(4)–C(4)–O(4)	176(2)	Rh(9)–C(17)–O(17)	138(2)
Rh(5)–C(5)–O(5)	179(2)	Rh(6)–C(18)–O(18)	132(2)
Rh(6)–C(6)–O(6)	180(2)	Rh(7)–C(18)–O(18)	139(2)
Rh(7)–C(7)–O(7)	176(2)	Rh(4)–C(19)–O(19)	136(2)
Rh(8)–C(8)–O(8)	175(2)	Rh(5)–C(19)–O(19)	134(2)
Rh(9)–C(9)–O(9)	175(2)	Rh(8)–C(20)–O(20)	135(2)
Rh(10)–C(10)–O(10)	177(2)	Rh(12)–C(20)–O(20)	138(2)
Rh(11)–C(11)–O(11)	178(2)	Rh(7)–C(21)–O(21)	136(2)
Rh(12)–C(12)–O(12)	177(2)	Rh(12)–C(21)–O(21)	136(2)
Rh(2)–C(13)–O(13)	138(2)	Rh(4)–C(22)–O(22)	136(2)
Rh(3)–C(13)–O(13)	134(2)	Rh(10)–C(22)–O(22)	135(2)
Rh(1)–C(14)–O(14)	136(2)	Rh(5)–C(23)–O(23)	138(1)
Rh(2)–C(14)–O(14)	136(2)	Rh(11)–C(23)–O(23)	134(1)
Rh(3)–C(15)–O(15)	136(2)	Rh(10)–C(24)–O(24)	134(2)
Rh(9)–C(15)–O(15)	135(1)	Rh(11)–C(24)–O(24)	138(2)

The rationalization of the ligand stereochemistry demands an analysis of the possible bridging-group arrangements which maintain three-co-ordination for all the metal atoms. If one divides the polyhedron edges into planar and oblique, calling planar the edges contained in the planes of the three metal-atom layers and oblique the interlayer connections, the possible ligand locations are as follows (see Figure 3): on all the planar edges (*a*), on all the oblique edges (*b*), on half of both kinds of edges, (*c*) and (*d*). Structures (*c*) and (*d*) differ only in the occupation of the alternate hexagon edges, which can occur in two ways. We call structure (*d*) that in which the bridged hexagon edges belong to the square faces of the polyhedron; this is the structure found in the crystal. Structures (*a*) and (*b*) do not alter the D_{3h} cluster symmetry, while (*c*) and (*d*) lower the molecular symmetry to C_s. Structure (*d*) seems to yield the best non-bonded contacts on the cluster surface.

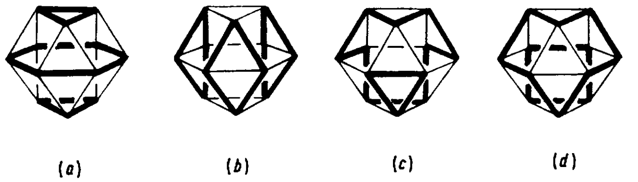

FIGURE 3 Possible geometries for the edge-bridging carbonyl groups (see text). Bold lines indicate bridged edges of the rhodium-atom polyhedron

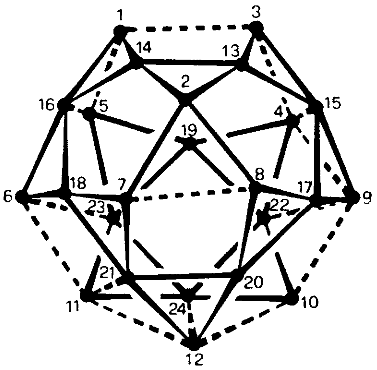

FIGURE 4 Polyhedron described by the carbon atoms on the cluster surface. (Full lines indicate distances <3.10 Å, broken lines those in the range 3.12—3.61 Å.) The largest holes, C(1,3,4,19,5) and C(9,10,12,20,17), correspond to the cluster cavities occupied by hydrogen atoms. The hole C(6,11,12,21,18) is smaller than its symmetry equivalent C(9,10,12,20,17) [*e.g.* C(11)–C(12) is 3.43 Å, while C(10)–C(20) is 4.25 Å]

TABLE 3

Comparison of sets of corresponding Rh–Rh mean distances (Å) in the two Rh_{13} cluster anions

Distance		$[Rh_{13}H_2(CO)_{24}]^{3-}$	$[Rh_{13}H_3(CO)_{24}]^{2-}$
Overall mean (36 values)		2.794	2.81
Surface (24 values)		2.794	2.81
Centre-to-surface (12 values)		2.793	2.81
Cavity [1] Rh(1,3,4,5,13)	Surface	2.853	2.85
	Centre-to-surface	2.791	2.79
	Mean	2.822	2.82
Cavity [2] Rh(1,2,6,7,13)	Surface	2.770	2.79
	Centre-to-surface	2.775	2.80
	Mean	2.773	2.79
Cavity [3] Rh(2,3,8,9,13)	Surface	2.774	2.79
	Centre-to-surface	2.794	2.79
	Mean	2.784	2.79
Cavity [4] Rh(4,5,10,11,13)	Surface	2.773	2.78
	Centre-to-surface	2.787	2.81
	Mean	2.780	2.79
Cavity [5] Rh(6,7,11,12,13)	Surface	2.775	2.82
	Centre-to-surface	2.790	2.84
	Mean	2.783	2.83
Cavity [6] Rh(8,9,10,12,13)	Surface	2.801	2.83
	Centre-to-surface	2.821	2.83
	Mean	2.811	2.83
Surface edges of the ' occupied ' cavities		2.824	2.83
Surface edges of the ' unoccupied ' cavities		2.779	2.78

In order to attempt a location of the hydridic hydrogen atoms we have looked for holes in the ligand distribution and for Rh–Rh bond lengthenings. The polyhedron described by the carbon atoms of the ligands is illustrated in Figure 4. The largest holes on the cluster surface have been found on three square faces defined by atoms Rh (1, 3, 4, 5), Rh (6, 7, 11, 12), and Rh (8, 9, 10, 12). In fact, the bridging ligands located around these faces are one, two, and two, respectively, while the remaining square faces bear three or four bridging groups. The first face is bisected by the idealized symmetry plane; the other two are related by the plane. On the basis of steric arguments, therefore, the hydrogen atoms can be located in the vicinity of the three above faces, either as outer ligands or in semi-interstitial positions.

An analysis (Table 3) of the metal–metal distances in both the Rh_{13} anions has given results in complete agreement with the above geometrical considerations. The data of Table 3 can be summarized as follows. (*i*) the overall Rh–Rh mean distance is slightly shorter in the dihydrido- than in the trihydrido-species. (*ii*) The average edge lengths of the six semi-octahedral cavities fall in two significantly different sets, with mean values 2.823 and 2.786 Å, respectively. Two cavities of the dihydrido-species, [1] and [6], and three of the trihydride, [1], [5], and [6], belong to the former set. These cavities are also associated with the largest holes on the cluster surface; thus it is very likely that they contain the hydride atoms. (*iii*) In both anions the mean surface edges of cavity [1] are longer than the centre-to-surface distances, while in the other occupied cavities, [5] and [6], there are no substantial differences. This may indicate significantly different situations for the hydrogen atoms in non-equivalent cavities, specifically that the hydride ligand in cavity [1] is less interstitial than in the others. (*iv*) Further evidence for the proposed hydrogen location is found in the trihydrido-anion, which contains two singular centre-to-surface distances: one, Rh(13)–Rh(2), not belonging to occupied cavities, and another, Rh(13)–Rh(12), shared between two occupied cavities, [5] and [6]. These distances are, as expected, the shortest and the longest, respectively, among the 12 centre-to-surface interactions.

It seems rather surprising to find an ordered location of the hydrogen atoms in the dihydrido-species but, although some degree of disorder cannot be excluded, the experimental results have led us to accept this evidence. The stereochemistry of the carbonyl ligands in cavity

[6] is somewhat different from that in cavity [5] and a larger hole is present in the former, in spite of the low steric hindrance of the semi-interstitial hydrogen atom. This difference is probably sufficient to cause the ordered packing of the anion.

The crystallographic results are in agreement with those recently obtained from a ^{1}H n.m.r. spectrum in solution of $[Rh_{13}H_3(CO)_{24}]^{2-}$ at -90 °C, which confirms the existence of two kinds of hydrogen atom, one of which, presumably the hydrogen lying on the symmetry plane, in cavity [1], exhibits the expected coupling with all the five rhodium atoms of the interstice.[5]

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