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THE CRYSTAL AND MOLECULAR STRUCTURE OF HEPTA-μ-CARBONYLTETRACARBONYL-*tetrahedro*-TETRARHODATE(2—) IN ITS BIS(TRIPHENYLPHOSPHINE)IMINIUM SALT

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Summary

The solid state structure of the cluster complex undecacarbonyltetrarhodate-(2—) has been determined in the salt $(PPh_3NPPh_3)_2[Rh_4(CO)_{11}]$, which crystallizes in the space group $P\bar{1}$ with cell constants a 22.394(3), b 14.351(2), c 11.937(2) Å, α 93.05(2)°, β 96.25(2)°, γ 88.38(2)°, $Z = 2$. The structure was refined by least-squares to a conventional discrepancy factor R of 0.060, based on 3884 reflection intensities collected by counter methods. The metal atom cluster is a distorted tetrahedron to which the ligands are bound four terminally and seven edge bridging; the idealized symmetry of the anion is C_{2v}. The Rh—Rh distances range from 2.662(2) to 2.986(2) Å, and are discussed in terms of ligand topology and the localized character of the anionic charge.

Introduction

The undecacarbonyltetrarhodate dianion which was made recently [1] is of great stereochemical interest, since there are no reports of structures in which eleven carbonyl ligands are bound to a tetrahedral cluster of metal atoms. The solid state structure obtained by diffraction methods provides a fundamental guide to the nature of this and related species. Spectroscopic data, in contrast, are often an ambiguous source of structural information for cluster compounds, as evidenced by the long debate about the structure of $Co_4(CO)_{12}$ [2], and furthermore the ligands are often fluxional in solution, and several different structural isomers may be present in equilibrium.

TABLE 1

POSITIONAL AND THERMAL PARAMETERS OF THE NON-GROUP ATOMS [a-c]

Atom	x	y	z	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
Anisotropic atoms									
Rh(1)	1894(1)	1600(1)	773(1)	23(1)	0(1)	27(1)	54(1)	17(1)	90(1)
Rh(2)	2390(1)	1449(1)	−1157(1)	21(1)	0(1)	7(1)	61(1)	−14(1)	73(1)
Rh(3)	3122(1)	1481(1)	833(1)	24(1)	33(1)	7(1)	85(1)	23(1)	80(1)
Rh(4)	2405(1)	3154(1)	48(1)	44(1)	15(1)	68(1)	45(1)	33(1)	115(1)
P(1)	−360(1)	2567(2)	4031(3)	18(1)	−9(2)	11(2)	24(2)	0(4)	58(3)
P(2)	−815(1)	3267(2)	1816(3)	20(1)	−4(2)	2(3)	46(2)	5(4)	50(3)
P(3)	3922(2)	6881(3)	3862(4)	18(1)	−5(2)	21(3)	42(2)	−29(6)	133(4)
P(4)	4743(2)	7168(3)	2124(4)	18(1)	1(3)	17(3)	60(2)	−50(6)	114(4)

Atom	x	y	z	B (Å^2)	Atom	x	y	z	B (Å^2)
Isotropic atoms									
C(1)	1300(7)	1142(11)	1514(14)	5.4(4)	C(7)	2652(7)	1590(11)	2142(13)	5.2(3)
O(1)	901(5)	824(9)	1938(10)	7.6(3)	O(7)	2659(5)	1682(8)	3143(9)	6.5(3)
C(2)	2401(9)	1001(14)	−2615(17)	7.7(5)	C(8)	3350(7)	1336(12)	−718(14)	5.7(4)
O(2)	2444(7)	730(11)	−3549(13)	10.3(4)	O(8)	3750(5)	1228(8)	−1306(10)	7.1(3)
C(3)	3753(7)	899(12)	1528(14)	5.9(4)	C(9)	1868(7)	3052(11)	1256(13)	4.7(3)
O(3)	4156(6)	474(10)	2000(13)	10.1(4)	O(9)	1604(5)	3487(8)	1932(9)	6.3(2)
C(4)	2417(7)	4380(12)	124(14)	5.9(4)	C(10)	2603(7)	2914(11)	−1484(13)	5.3(3)
O(4)	2453(5)	5205(9)	258(10)	7.7(3)	O(10)	2780(5)	3220(9)	−2298(10)	7.8(3)
C(5)	1484(7)	1776(11)	−831(13)	5.0(3)	C(11)	3344(14)	2923(22)	884(26)	15.1(9)
O(5)	1009(4)	1914(7)	−1316(9)	5.9(2)	O(11)	3791(9)	3480(15)	1249(18)	16.1(6)
C(6)	2240(10)	362(16)	−207(19)	9.0(6)	N(1)	−377(5)	2749(7)	2739(9)	3.3(2)
O(6)	2245(6)	−447(10)	−153(12)	9.1(3)	N(2)	4192(6)	6818(9)	2708(11)	5.6(3)

[a] The estimated standard deviation in the last significant figure is given in parentheses here and in the succeeding Tables. [b] All the parameters × 10^4, except for the isotropic B factors. [c] The anisotropic temperature factors are given by $\exp - (h^2 b_{11} + k^2 b_{22} + l^2 b_{33} + hkb_{12} + hlb_{13} + klb_{23})$.

Experimental

Crystal data. $C_{83}H_{60}N_2O_{11}P_4Rh_4$, mol.wt. 1796.9, triclinic, a 22.394(3), b 14.351(2), c 11.937(2) Å, α 93.05(2), β 96.25(2), γ 88.38(2)°, U 3807.1 Å^3, D_m 1.52(2), Z 2, D_c 1.54 g cm^{-3}, $F(000) = 1800$. Space group $P\bar{1}$ (No. 2). Mo — K_α radiation, $\lambda = 0.7107$ Å, $\mu(\text{Mo} - K_\alpha) = 9.7$ cm^{-1}.

Intensity measurements. A small crystal of the compound was mounted on a Philips PW 1100, computer controlled, four-circle diffractometer. Lattice parameters and diffraction intensities were measured using graphite monochromatized Mo — K_α radiation. Reflections were collected in the range $4° < 2\theta < 40°$ by the ω-scan method with a scan width of 0.8° and a speed of 0.05°/sec. Background intensities were measured on both sides of each reflection for half the peak scanning time. Of the 7124 reflections measured, 3884 had intensities significantly above background ($I > 4\sigma(I)$) and were used in the structure determination and refinement. Corrections were made for Lorentz and polarization effects but not for absorption. The intensities of three standard reflections, measured every 60 minutes, showed a decay of 5% during the whole data collection and a compensating correction was applied to all the intensities during the data reduction step.

Determination and refinement of the structure. The structure was solved by the three-dimensional Patterson synthesis, which showed the metal atom positions, and by a difference Fourier map that revealed the carbonyl ligands and the cations. The whole structure was refined by the least-squares method in the block-diagonal approximation. The thermal motion was refined anisotropically for the rhodium and phosphorus atoms and isotropically for the remaining ones. The phenyl rings were treated as rigid groups with idealized symmetry (C—C 1.392 Å, angle C—C—C 120°) and with one mean temperature factor for each group. The hydrogen atoms were located in their ideal positions (C—H 1.08 Å) and their contribution was kept into account in the structure factors calculations. The observations were weighted according to the formula $w = 1/(A + BF_0 + CF_0^2)$; the values of A, B and C, 22.8, —0.06 and 7 × 10^{-4}, respectively, were chosen on the basis of an analysis of $\Sigma w(F_0 - k|F_c|)^2$. Atomic scattering factors were taken from ref. 3 for hydrogen and from ref. 4 for the other species; the rhodium factor was corrected for anomalous dispersion effects [5].

The function $\Sigma w(F_0 - k|F_c|)^2$ was minimized until all shifts became less than 0.25 σ. The final reliability indices were $R = 0.060$ and $R' = 0.069$, $R' = [\Sigma w(F_0 - k|F_c|)^2/\Sigma wF_0^2]^{1/2}$.

A final difference Fourier synthesis revealed residual fluctuations in the range ±0.8 e/Å^3. Final structure parameters are reported in Tables 1 and 2; bond distances and angles in Tables 3 and 4. The list of observed and computed structure factors can be obtained on application to the Authors.

Computations. All computations were performed on a UNIVAC 1106 computer. Counter data reduction and statistical analysis for weighting schemes were based upon Fortran programmes written in our laboratory. In addition, local versions of entries Nos. 7528, 7531, 7532, 7535 in the 1966 International World List of Crystallographic Programs were used for Fourier analysis, structure factors, and least-squares calculations. A programme by Domenicano and Vaciago was used for computation of the molecular parameters.

TABLE 2

PARAMETERS OF PHENYL GROUP ATOMS [a,b]

Atom	x	y	z	Atom	x	y	z
C(111)	395(3)	2704(8)	4675(7)	C(311)	3582(6)	5788(7)	4035(8)
C(112)	861(4)	2550(5)	4000(5)	C(312)	3304(6)	5321(6)	3072(7)
C(113)	1456(3)	2605(6)	4477(7)	C(313)	3025(5)	4480(6)	3157(8)
C(114)	1584(3)	2816(8)	5628(7)	C(314)	3024(6)	4100(7)	4205(8)
C(115)	1118(4)	2970(5)	6303(5)	C(315)	3301(6)	4563(6)	5168(7)
C(116)	524(3)	2915(6)	5826(7)	C(316)	3580(5)	5407(6)	5083(8)
C(121)	−571(6)	1409(6)	4227(8)	C(321)	3358(6)	7784(8)	3943(8)
C(122)	−777(4)	842(6)	3290(6)	C(322)	3318(4)	8464(9)	3147(8)
C(123)	−972(4)	−51(6)	3432(7)	C(323)	2900(5)	9197(7)	3205(9)
C(124)	−961(6)	−378(6)	4512(8)	C(324)	2522(6)	9250(8)	4059(8)
C(125)	−755(4)	188(6)	5448(6)	C(325)	2562(4)	8571(9)	4855(8)
C(126)	−561(4)	1082(6)	5306(7)	C(326)	2980(5)	7838(7)	4797(9)
C(131)	−830(4)	3354(6)	4785(8)	C(331)	4468(5)	7035(11)	5045(10)
C(132)	−695(3)	4297(6)	4825(8)	C(332)	4928(6)	6369(8)	5221(11)
C(133)	−1054(4)	4951(4)	5359(8)	C(333)	5377(5)	6500(9)	6113(13)
C(134)	−1548(4)	4661(6)	5852(8)	C(334)	5367(5)	7298(11)	6828(10)
C(135)	−1683(3)	3719(6)	5811(8)	C(335)	4907(6)	7964(8)	6651(11)
C(136)	−1324(4)	3065(4)	5278(8)	C(336)	4458(5)	7833(9)	5759(13)
C(211)	−863(6)	2569(7)	527(8)	C(411)	5241(6)	7934(9)	2980(10)
C(212)	−423(4)	1890(8)	350(8)	C(412)	5070(4)	8864(10)	3168(11)
C(213)	−453(5)	1359(7)	−663(10)	C(413)	5436(6)	9451(7)	3893(12)
C(214)	−925(6)	1506(7)	−1500(8)	C(414)	5974(6)	9107(9)	4430(10)
C(215)	−1365(4)	2185(8)	−1322(8)	C(415)	6145(4)	8176(10)	4242(11)
C(216)	−1335(5)	2717(7)	−309(10)	C(416)	5779(6)	7590(7)	3517(12)
C(221)	−1570(4)	3417(9)	2150(10)	C(421)	5168(7)	6173(9)	1670(12)
C(222)	−1922(5)	2630(6)	2111(10)	C(422)	4975(5)	5286(12)	1854(12)
C(223)	−2512(5)	2714(7)	2374(10)	C(423)	5306(8)	4500(8)	1531(13)
C(224)	−2750(4)	3587(9)	2677(10)	C(424)	5830(7)	4601(9)	1024(12)
C(225)	−2398(5)	4374(6)	2716(10)	C(425)	6023(5)	5488(12)	839(12)
C(226)	−1808(5)	4289(7)	2452(10)	C(426)	5692(8)	6274(8)	1162(13)
C(231)	−520(4)	4371(5)	1561(8)	C(431)	4445(7)	7786(10)	910(10)
C(232)	37(4)	4625(5)	2104(7)	C(432)	3833(6)	7740(9)	558(13)
C(233)	265(3)	5494(7)	1943(8)	C(433)	3581(5)	8273(11)	−321(13)
C(234)	−63(4)	6110(5)	1239(8)	C(434)	3940(7)	8852(10)	−847(10)
C(235)	−621(4)	5855(5)	696(7)	C(435)	4552(6)	8898(9)	−494(13)
C(236)	−849(3)	4986(7)	857(8)	C(436)	4805(5)	8365(11)	384(13)
H(112)[c]	762	2386	3104	H(312)	3306	5620	2256
H(113)	1819	2485	3952	H(313)	2809	4119	2407
H(114)	2047	2859	6000	H(314)	2807	3443	4272
H(115)	1219	3134	7200	H(315)	3301	4267	5985
H(116)	161	3036	6352	H(316)	3797	5768	5834
H(122)	−785	1097	2450	H(322)	3613	8423	2482
H(123)	−1131	−493	2703	H(323)	2869	9727	2585
H(124)	−1112	−1074	4623	H(324)	2197	9821	4104
H(125)	−746	−65	6289	H(325)	2268	8613	5520
H(126)	−400	1525	6036	H(326)	3011	7309	5417
H(132)	−310	4522	4442	H(332)	4936	5748	4665
H(133)	−948	5685	5391	H(333)	5736	5982	6251
H(134)	−1827	5171	6268	H(334)	5718	7401	7522
H(135)	−2068	3494	6196	H(335)	4900	8586	7208
H(136)	−1429	2331	5246	H(336)	4100	8352	5622
H(212)	−55	1776	1002	H(412)	4651	9133	2751
H(213)	−110	830	−800	H(413)	5303	10175	4040
H(214)	−948	1093	−2289	H(414)	6260	9563	4994
H(215)	−1732	2301	−1973	H(415)	6565	7909	4660
H(216)	−1678	3246	−170	H(416)	5913	6866	3371
H(222)	−1737	1951	1875	H(422)	4568	5207	2250

continued

TABLE 2 (continued)

Atom	x	y	z	Atom	x	y	z
H(223)	—2786	2102	2345	H(423)	5156	3809	1675
H(224)	—3209	3653	2883	H(424)	6088	3990	773
H(225)	—2583	5054	2952	H(425)	6431	5568	444
H(226)	—1533	4903	2483	H(426)	5843	6965	1019
H(232)	294	4146	2653	H(432)	3553	7289	968
H(233)	700	5693	2366	H(433)	3104	8237	—595
H(234)	114	6787	1114	H(434)	3744	9268	—1531
H(235)	—878	6335	149	H(435)	4833	9350	—903
H(236)	—1283	4789	435	H(436)	5282	8401	660

[a] $x, y, z \times 10^4$. [b] The isotropic mean thermal parameters of the twelve phenyl groups are: 3.8(1), 4.8(1), 4.1(1), 6.1(1), 6.6(2), 4.5(1), 6.4(2), 6.5(2), 8.3(2), 7.8(2), 9.2(2), 8.9(2) Å^2. [c] The hydrogen atoms have the same labels and thermal factors of the carbon atoms to which they are linked.

Crystal and molecular structure and discussion

The crystal contains discrete $[Rh_4(CO)_{11}]^{2-}$ anions and $(Ph_3PNPPh_3)^+$ cations, packed as shown in Fig. 1. The rhodium atoms in the anion (Fig. 2) are located at the vertices of a distorted tetrahedron with C_{2v} idealized symmetry. The distortions comprise the presence of one edge shorter (2.66 Å) and another longer

TABLE 3

BOND DISTANCES (Å) AND ANGLES (DEG.) IN THE ANION

Rh(1)—Rh(2)	2.662(2)	C(3)—O(3)	1.18(2)
Rh(1)—Rh(3)	2.744(2)	C(4)—O(4)	1.19(2)
Rh(1)—Rh(4)	2.756(2)	C(5)—O(5)	1.17(2)
Rh(2)—Rh(3)	2.735(2)	C(6)—O(6)	1.17(2)
Rh(2)—Rh(4)	2.772(2)	C(7)—O(7)	1.19(2)
Rh(3)—Rh(4)	2.986(2)	C(8)—O(8)	1.20(2)
Rh(1)—C(1)	1.83(2)	C(9)—O(9)	1.19(2)
Rh(2)—C(2)	1.83(2)	C(10)—O(10)	1.20(2)
Rh(3)—C(3)	1.77(2)	C(11)—O(11)	1.32(4)
Rh(4)—C(4)	1.76(2)		
Rh(1)—C(5)	2.06(2)	Rh(1)—C(1)—O(1)	176(1)
Rh(2)—C(5)	2.14(2)	Rh(2)—C(2)—O(2)	176(2)
Rh(1)—C(6)	2.24(2)	Rh(3)—C(3)—O(3)	177(2)
Rh(2)—C(6)	2.03(2)	Rh(4)—C(4)—O(4)	175(2)
Rh(1)—C(7)	2.23(2)	Rh(1)—C(5)—O(5)	141(1)
Rh(3)—C(7)	1.97(2)	Rh(2)—C(5)—O(5)	140(1)
Rh(2)—C(8)	2.16(2)	Rh(1)—C(6)—O(6)	137(2)
Rh(3)—C(8)	1.97(2)	Rh(2)—C(6)—O(6)	146(2)
Rh(1)—C(9)	2.13(2)	Rh(1)—C(7)—O(7)	131(1)
Rh(4)—C(9)	1.99(2)	Rh(3)—C(7)—O(7)	147(1)
Rh(2)—C(10)	2.23(2)	Rh(2)—C(8)—O(8)	131(1)
Rh(4)—C(10)	1.94(2)	Rh(3)—C(8)—O(8)	147(1)
Rh(3)—C(11)	2.14(2)	Rh(1)—C(9)—O(9)	132(1)
Rh(4)—C(11)	2.25(2)	Rh(4)—C(9)—O(9)	144(1)
C(1)—O(1)	1.19(2)	Rh(2)—C(10)—O(10)	130(1)
C(2)—O(2)	1.17(2)	Rh(4)—C(10)—O(10)	147(1)
		Rh(3)—C(11)—O(11)	140(2)
		Rh(4)—C(11)—O(11)	134(2)

TABLE 4

BOND DISTANCES (Å) AND ANGLES (deg.) IN THE CATIONS

N(1)—P(1)	1.57(1)	N(1)—P(2)—C(211)	108.6(6)
N(1)—P(2)	1.59(1)	N(1)—P(2)—C(221)	114.4(6)
N(2)—P(3)	1.56(1)	N(1)—P(2)—C(231)	110.3(6)
N(2)—P(4)	1.59(2)	N(2)—P(3)—C(311)	108.1(7)
P(1)—C(111)	1.79(1)	N(2)—P(3)—C(321)	112.9(7)
P(1)—C(121)	1.78(1)	N(2)—P(3)—C(331)	113.7(7)
P(1)—C(131)	1.80(1)	N(2)—P(4)—C(411)	115.7(7)
P(2)—C(211)	1.79(1)	N(2)—P(4)—C(421)	108.6(8)
P(2)—C(221)	1.78(1)	N(2)—P(4)—C(431)	107.8(4)
P(2)—C(231)	1.79(1)	C(111)—P(1)—C(121)	107.7(6)
P(3)—C(311)	1.79(1)	C(111)—P(1)—C(131)	107.2(6)
P(3)—C(321)	1.79(1)	C(121)—P(1)—C(131)	108.2(6)
P(3)—C(331)	1.77(1)	C(211)—P(2)—C(221)	105.2(6)
P(4)—C(411)	1.79(1)	C(211)—P(2)—C(231)	108.1(5)
P(4)—C(421)	1.79(1)	C(221)—P(2)—C(231)	109.9(6)
P(4)—C(431)	1.79(1)	C(311)—P(3)—C(321)	108.0(7)
		C(311)—P(3)—C(331)	105.4(7)
P(1)—N(1)—P(2)	136.8(8)	C(321)—P(3)—C(331)	108.4(6)
P(3)—N(2)—P(4)	141.1(9)	C(411)—P(4)—C(421)	108.4(7)
N(1)—P(1)—C(111)	108.4(6)	C(411)—P(4)—C(431)	107.3(7)
N(1)—P(1)—C(121)	110.9(6)	C(421)—P(4)—C(431)	108.9(7)
N(1)—P(1)—C(131)	114.2(5)		

(2.99 Å) than the mean value of the other four (2.75 Å). The agreement of the latter value with the mean Rh—Rh distance in $Rh_4(CO)_{12}$ (2.73 Å) [2] shows that the two singular interactions in the anion are truly anomalous, and an interpretation of this is discussed below.

The eleven CO ligands are located on the cluster surface, four terminally, one per metal atom, and seven edge bridging. All but one of the tetrahedron edges contain one bridging ligand, while the remaining edge is associated with two such ligands. In this way two metal atoms, Rh(1) and Rh(2), are penta-connected to the ligands, and the other two are tetra-connected. The overall ligand stereochemistry conforms to the idealized C_{2v} cluster symmetry. The polyhedron of non-bonded contacts described by the carbon atoms is shown in Fig. 3, in which the full lines indicate contacts in the range 2.7—3.3 Å; two longer contacts, ca. 3.8 Å, are shown by dotted lines. The figure is not a simple one and can be rationalized in terms of fused polyhedra. A central trigonal prism (atoms C(i), i from 5 to 10) is capped on the rectangular faces [capping atoms C(1), C(2), C(11)] generating three square pyramides; the remaining atoms [C(3) and C(4)] cap two opposite faces of one of the pyramides. This figure shows that the cluster surface is not overcrowded, especially in the zones around Rh(3) and Rh(4), and suggests possible directions of chemical attack on the cluster.

The ligand stereochemistry can be considered to be the result of various contending factors, especially the tendency of the metal atoms towards the noble gas electronic configuration and that of the ligands towards the minimization of the non-bonded contacts. For an explanation of the ligand distribution between terminal and bridging geometries another factor should be taken into account, i.e. the higher π-acidity of the bridging CO groups compared with that of the

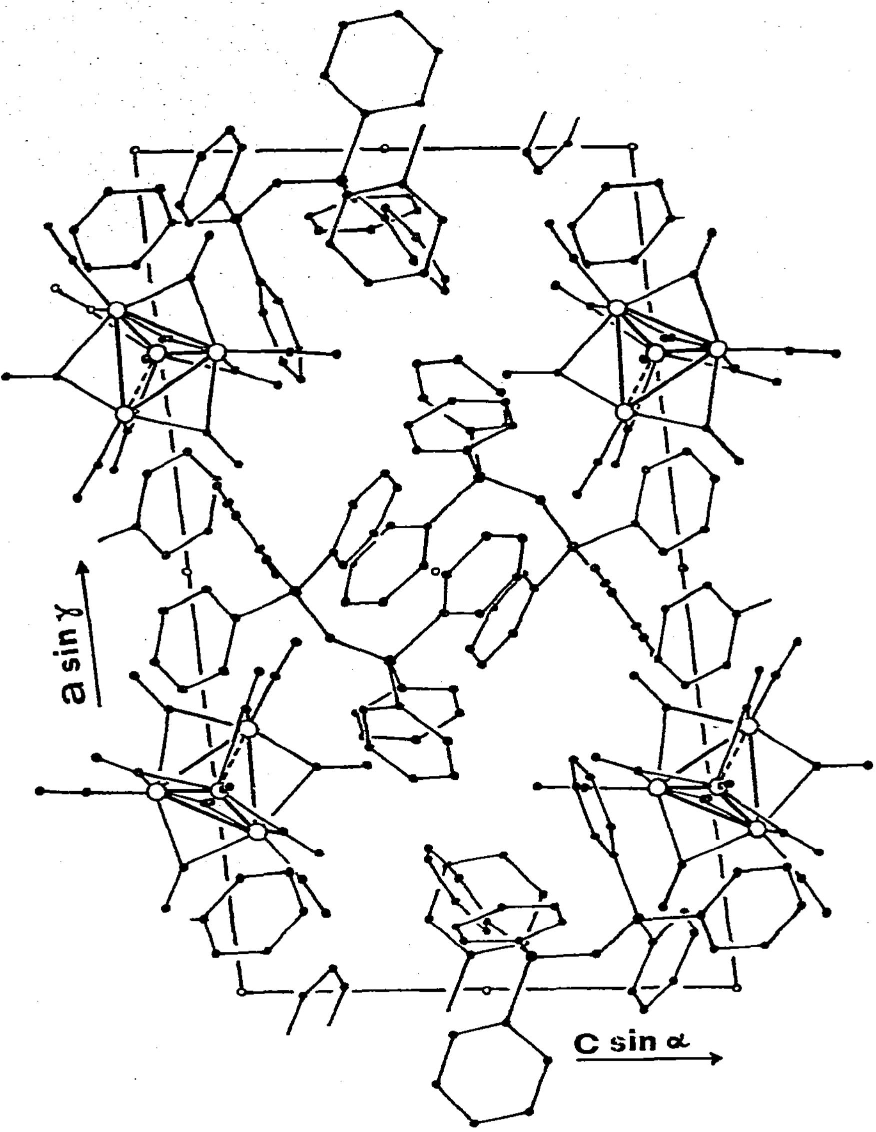

Fig. 1. Unit cell content projected down the *b* axis.

terminal ones [6]; therefore the anionic clusters are more like to contain several bridging groups. In this anion a very high bridging-to-terminal ratio of CO groups has been achieved: viz. 7 : 4.

The factors governing the ligand stereochemistry generally do not conflict with each other, and lead to regular distributions of the ligands, with the highest possible symmetry. Some difficulty in matching topological and electronic requirements rises whenever the ligands can not be evenly distributed among apices, edges, and faces of the metal atom polyhedron. This is the case in the present anion, which possesses an odd number of ligands and, consequently, a low molecular symmetry which leads to a substantial localization of the cluster orbitals.

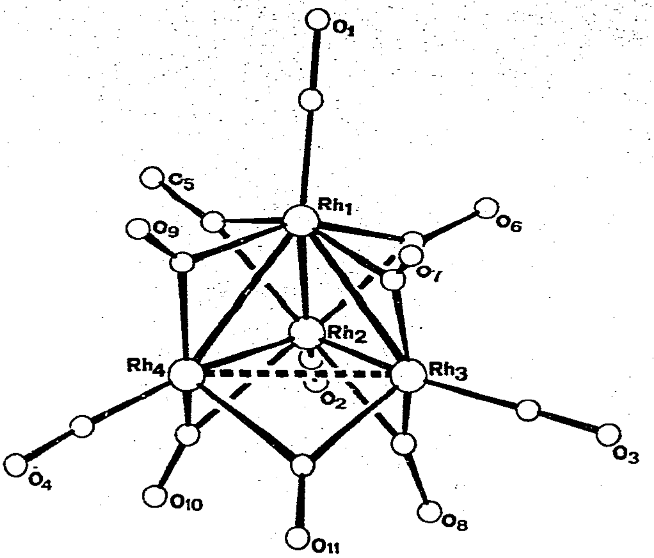

Fig. 2. The structure of $[Rh_4(CO)_{11}]^{2-}$.

In fact, an electron count shows that Rh(1) and Rh(2) attain the closed 18 electrons configuration while Rh(3) and Rh(4) result one electron short; thus the anionic charge must be essentially localized on these atoms. This hypothesis offers a convincing explanation of the very long Rh(3)—Rh(4) interaction in terms of bond destabilization induced by electrostatic repulsions. An analysis of the metal—carbonyl interactions confirms that the anionic charge resides on Rh(3) and Rh(4). The terminal groups bound to these atoms exhibit Rh—C distances 0.06 Å shorter than those bound to Rh(1) and Rh(2), as a consequence of the different degree of π metal-to-ligand back-donation, which is higher for negatively charged metal atoms. Even more marked differences are exhibited by the four bridging ligands which interact with one negative [Rh(3), Rh(4)] and one neutral [Rh(1), Rh(2)] metal atom, i.e. Rh(3,4)—C 1.97 Å and Rh(1,2)—C 2.19 Å. In this connection one should note that the two CO groups bridging the

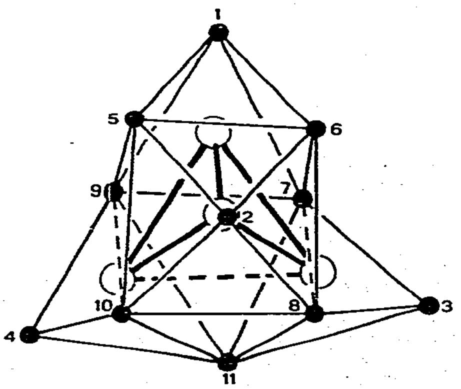

Fig. 3. Polyhedron described by the carbon atoms of the ligands (see text).

Rh(1)—Rh(2) edge are also significantly asymmetric, but their asymmetries are mutually opposite in sense, so that both metal atoms are involved in one long and one short interaction.

The C—O distances are subject to standard deviations which preclude meaningfull comparisons; nevertheless the carbonyl group bridging the negatively charged atoms, C(11)—O(11), exhibits a particularly long interaction, 1.32(4) Å, explicable in terms of the very strong metal-to-ligand back-donation.

Another tetrahedral cluster in which the CO ligands are irregularly distributed among the metal atoms is $Fe_2Rh_2(CO)_8$-π-Cp_2, whose solid state structure has been reported by Churchill and Veidis [7]. In this molecule the two iron atoms are involved in three and four metal—carbonyl interactions, respectively, the eighth carbonyl and the cyclopentadienyl groups being bound to the rhodium atoms. Electron counts formally assign seventeen and nineteen electrons, respectively, to the iron atoms but, if a dative covalent bond is postulated between these atoms, both reach the noble gas configuration. The consequent charge dislocation between the iron atoms is unequivocally confirmed by the mean values of the Fe—C and C—O interactions: viz. 1.69, 1.25 Å for the acceptor iron and 1.79, 1.16 Å for the donor one. It may be noted that the closed electron configuration for the two iron atoms would be more ‘naturally’ achieved by a bridging interiron ligand, but steric factors are probably involved.

These features are fully in keeping with those of our structure, but in the complex $Fe_3Rh(CO)_{11}$-π-Cp [8], in which the same irregularity of ligand distribution occurs, the Fe—C and C—O values are rather scattered, and no significant differences have been detected, probably as a consequence of the ligand overcrowding.

Finally we note that complete delocalization of the cluster orbitals has been found by Dahl and coworkers in a number of paramagnetic clusters [9-12], the only exception being the cation $[Co_3\text{-}\pi\text{-}Cp_3S_2]^+$, in which the metal atom triangle is considerably deformed toward a C_{2v} symmetry.

The stereochemistries of the two independent bis(triphenylphosphine)iminium cations are equal, within experimental errors, to each other and agree with several other independent determinations. The structure of the cation has been discussed from a conformational and electronic standpoint by Handy, Ruff and Dahl [13]. Noteworthy features are the C_2 idealized symmetry, a trigonal hybridization of the nitrogen orbitals, with P—N—P angles of 137 and 141°, respectively, and the orientation of two phosphorous—phenyl bonds approximately in the PNP plane with a *cisoid* conformation that allows a nearly parallel disposition of two phenyl rings separated by about 3.5 Å. This distance is indicative of a phenyl—phenyl interaction comparable with that present in the crystals of aromatic hydrocarbons and in graphite. The particular stability of the molecular conformation is explained by the strength of the phenyl—phenyl interaction which has been observed in several phenyl-rich structures [14-15] and is responsible for various conformational and packing effects.

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