C20	0.27849 (8)	0.2610 (7)	0.6310 (2)	0.0628 (9)
C21	0.25673 (8)	0.4226 (6)	0.6593 (2)	0.0609 (9)
C22	0.22212 (7)	0.3898 (5)	0.6490 (2)	0.0494 (7)
N1	0.11362 (5)	0.1400 (3)	0.58165 (12)	0.0303 (5)
N2	0.20882 (5)	0.2036 (4)	0.61384 (14)	0.0392 (5)
O1	0.16338 (4)	0.4178 (3)	0.52301 (11)	0.0409 (4)
S1	0.16238 (2)	−0.10773 (12)	0.68413 (4)	0.0445 (2)
Ni1	0.16055 (8)	0.17385 (5)	0.59674 (2)	0.0343 (2)

Table 2. *Selected geometric parameters (Å, °)*

C1—O1	1.299 (3)	C18—N2	1.341 (3)
C1—C10	1.405 (3)	C22—N2	1.333 (4)
C9—C10	1.456 (3)	N1—Ni1	1.862 (2)
C11—N1	1.313 (3)	N2—Ni1	1.914 (2)
C12—N1	1.439 (3)	O1—Ni1	1.843 (2)
C17—S1	1.732 (3)	S1—Ni1	2.141 (2)
C16—C17—S1	122.7 (2)	O1—Ni1—N1	95.45 (8)
C12—C17—S1	118.2 (2)	O1—Ni1—N2	85.71 (8)
C22—N2—Ni1	120.2 (2)	N1—Ni1—N2	178.84 (9)
C18—N2—Ni1	122.0 (2)	O1—Ni1—S1	174.59 (5)
C1—O1—Ni1	128.4 (2)	N1—Ni1—S1	89.96 (6)
C17—S1—Ni1	98.27 (9)	N2—Ni1—S1	88.88 (7)

Table 3. *Comparison of bond lengths (Å) in some similar nickel(II) complexes*

	Ni—S	Ni—N1	Ni—N2	Ni—O	S—C	C—O	C═N
(I)	2.141 (1)	1.862 (2)	1.914 (2)	1.843 (2)	1.732 (3)	1.299 (3)	1.313 (1)
(II)		1.848 (4)	1.947 (4)	1.817 (1)		1.315 (2)	1.292 (5)
(III)		1.849 (3)	1.955 (4)	1.831 (3)		1.322 (5)	1.303 (5)
(IV)		1.912 (3)		1.832 (2)		1.305 (4)	1.297 (4)
(V)		1.854 (4)	1.970 (4)	1.828 (4)		1.335 (8)	1.263 (5)
(VI)		1.898 (4)	1.936 (5)	1.848 (8)		1.322 (2)	1.285 (4)
(VII)	2.138 (2)	1.881 (2)	1.956 (2)	1.856 (3)	1.743 (3)	1.306 (4)	1.312 (5)
(VIII)	2.139 (2)	1.856 (4)	1.888 (4)	1.844 (4)	1.728 (5)	1.293 (6)	1.290 (7)
(IX)	2.142 (1)	1.890 (2)	1.950 (2)	1.850 (1)	1.748 (2)	1.322 (2)	1.289 (2)

Complexes: (I) [*N*-(2-mercaptophenyl)-2-hydroxynaphthaldiminato]-(pyridine)nickel(II) (present work); (II) [1-(2-hydroxyphenyliminomethyl)-2-naphtholato-*N*,*O*,*O*′](piperidine)nickel(II) (Elerman, Paulus & Fuess, 1991; CSD refcode: KIFYIH); (III) (diethylamino)[1-(2-hydroxyphenyliminomethyl)-2-naphtholato-*N*,*O*,*O*′]nickel(II) (Elerman, Fuess & Paulus, 1992; CSD refcode: VOKNOY); (IV) bis{*N*-[(1,3-dioxolan-2-yl)methyl]-2-hydroxy-1-naphthaldiminato}nickel(II) (Fernandez-G, Rosales-Hoz, Rubio-Arroyo, Salcedo, Toscano & Vela, 1987; CSD refcode: FEBWAK); (V) [*N*-(2-hydroxyphenyl)salicylaldiminato](ammine)nickel(II) (Elerman, Svoboda & Fuess, 1992; CSD refcode: VOPCIM); (VI) *N*-(2-hydroxyphenyl)salicylaldiminato-(diethylamine)nickel(II) (Elerman, Paulus & Svoboda, 1992; CSD refcode: VOPHUD); (VII) [*N*-(2-mercaptophenyl)salicylaldiminato]-(piperidine)nickel(II) (Kabak, Elerman & Ozbey, 1995); (VIII) ammine-(salicylaldehyde thiosemicarbazonato)nickel(II) (Gyepes & Glowiak, 1989; CSD refcode: AMSCNI11); (IX) [*N*-(2-mercaptophenyl)salicylaldiminato](diethylamino)nickel(II) (Elerman, Kabak & Svoboda, 1996).

Data collection: *SDP* (Frenz, 1985). Cell refinement: *SDP*. Data reduction: *SDP*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1375). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Chloro(2,3,7,8,12,13,17,18-octaethylporphinato)gallium(III)

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(Received 11 April 1996; accepted 18 June 1996)

Abstract

The crystal structure of [Ga($C_{36}H_{44}N_4$)Cl].1.45CH_2Cl_2 has been determined. Examination of the crystal established a two-molecule triclinic unit cell with space group $P\bar{1}$. The asymmetric unit contains one porphyrin molecule and two solvate molecules, one as an approximate half molecule with required inversion symmetry. All measurements were made at 127 (2) K. The average Ga—N distance is 2.035 (4) Å and the axial Ga—Cl distance 2.240 (1) Å. The displacement of the Ga atom from the N_4 porphyrin plane is 0.40 Å.

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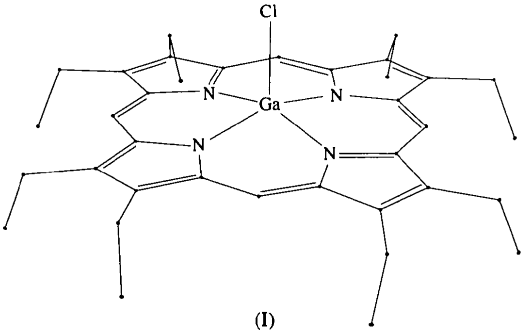
Comment

Upon exposure to light, a methylene chloride solution of μ-hydroxo-bis[(octaethylporphinato)gallium(III)] yields a decomposition product, namely the title porphinate, neutral [Ga(OEP)Cl], (I).



(I)

An *ORTEP*II (Johnson, 1976) diagram of the molecule with the atomic labeling scheme is shown in Fig. 1. Average values for the unique chemical classes of distances and angles in the porphinato core are given in Fig. 2. The Ga atom is five-coordinate with Cl as the axial ligand. The coordination geometry is square pyramidal, with an average Ga—N_p bond length of 2.035 (4) Å (N_p denotes a pyrrole N atom), an axial Ga—Cl bond length of 2.240 (1) Å and an average value of the four N_p—Ga—Cl angles of 101.3 (6)°. These Ga—N_p bond lengths are shorter than those observed in $[Ga(TPP)(CH_2Cp)]$ [average 2.100 (7) Å; TPP is tetraphenylporphinate and Cp is cyclopentadienyl; Balch, Hart & Parkin, 1993], but are comparable to those found for other five-coordinate gallium(III) porphyrinates, *e.g.* 2.034 (3) Å in $[Ga(OEP)(N_3)]$ (Coutsolelos, Guilard, Boukhris & Lecomte, 1986), 2.021 (2) Å in [Ga(TPP)Cl] (Coutsolelos, Guilard, Bayeul & Lecomte, 1986), 2.013 (2) Å in $[Ga(OEP)(SO_3CH_3)]$ (Boukhris, Lecomte, Coutsolelos & Guilard, 1986) and 2.047 (2) Å in $[Ga(TPP)(CC^{n}Pr)]$ (Balch, Latos-Grazynski, Noll & Phillips, 1993). The Ga—Cl distance [2.240 (1) Å] is similar to both the distance of 2.217 (1) Å found for a chloro(phthalocyanato)gallium(III) derivative (Wynne, 1984) and the axial bond length of 2.196 (2) Å in [Ga(TPP)Cl] (Coutsolelos, Guilard, Bayeul & Lecomte, 1986).

[Ga(OEP)Cl] has modest doming of the porphyrin core. Quantitative aspects of the domed-core conformation can be seen in Fig. 2, which displays the perpendicular displacements of each atom from the mean plane of the 24-atom core. The Ga and porphinato N atoms are above the mean plane, while the C*b* atoms are 'saucered away' below the mean plane, one *trans* pair by much more than the other. The porphyrin molecules are well separated in the lattice.

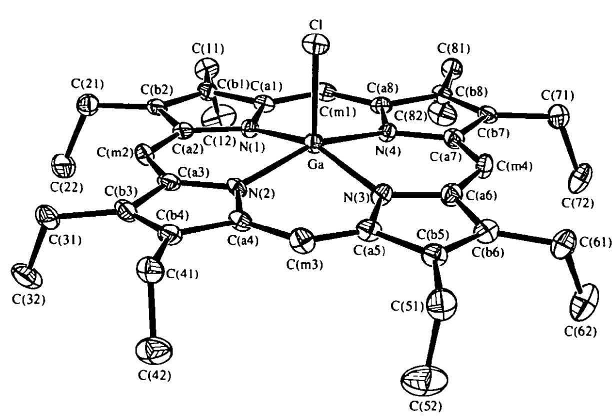


Fig. 1. An *ORTEP*II (Johnson, 1976) diagram of [Ga(OEP)Cl] with the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level and porphyrin H atoms atoms have been omitted for clarity.

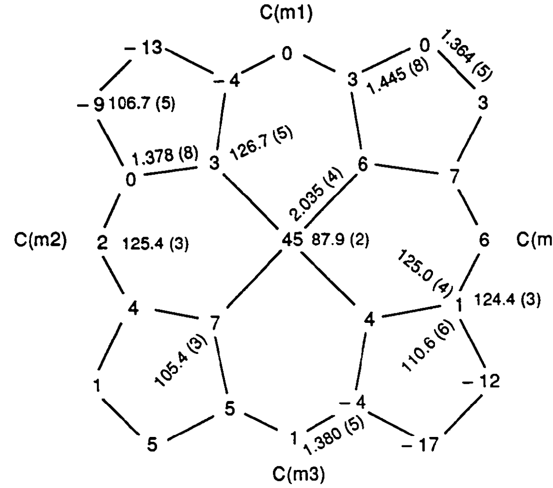


Fig. 2. A formal diagram of the porphinato core of [Ga(OEP)Cl] displaying the average values for the bond parameters. The numbers in parentheses are the e.s.d.'s calculated on the assumption that the average values were all drawn from the same population. Also displayed are the perpendicular displacements, in units of 0.01 Å, of each atom from the 24-atom mean plane of the core.

Five-coordinate gallium derivatives can be divided into two classes depending on the perpendicular displacement of the Ga atom from the N_4 plane. In the title compound, Ga is displaced out of the N_4 plane by 0.40 Å, which falls in the region of the two derivatives of Coutsolelos *et al.* {0.36 Å in $[Ga(OEP)(N_3)]$ (Coutsolelos, Guilard, Boukhris & Lecomte, 1986) and 0.38 Å in [Ga(TPP)Cl] (Coutsolelos, Guilard, Bayeul & Lecomte, 1986)}, a sulfonato derivative {0.32 Å in $[Ga(OEP)(SO_3CH_3)]$ (Boukhris, Lecomte, Coutsolelos, & Guilard, 1986)} and a phthalocyanato derivative reported by Wynne (1984) (0.44 Å). A second group, with larger displacements, is exemplified by Balch *et al.* for two alkyl derivatives {0.60 Å in $[Ga(TPP)(CC^{n}Pr)]$ (Balch, Latos-Grazynski, Noll & Phillips, 1993) and 0.58 Å in $[Ga(TPP)(CH_2Cp)]$ (Balch, Hart & Parkin, 1993)}.

Experimental

The title compound was obtained as a decomposition product in the course of synthetic work on μ-hydroxo-bis[(octaethylporphinato)gallium(III)] complexes and recrystallized by vapor diffusion of hexanes into dichloromethane.

Crystal data

$[Ga(C_{36}H_{44}N_4)Cl].1.45CH_2Cl_2$
$M_r = 760.36$
Triclinic
$P\bar{1}$
$a = 10.0660\,(7)$ Å
$b = 13.7530\,(14)$ Å
$c = 14.729\,(2)$ Å
$\alpha = 66.52\,(2)°$
$\beta = 80.500\,(12)°$
$\gamma = 75.870\,(14)°$
$V = 1808.4\,(4)$ Å^3
$Z = 2$
$D_x = 1.396$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 250 reflections
$\theta = -20.5–20.5°$
$\mu = 1.080$ mm^{-1}
$T = 127\,(2)$ K
Broken plate
0.19 × 0.10 × 0.07 mm
Dark purple

Data collection

Enraf–Nonius FAST area-detector diffractometer
Ellipsoid-mask fitting
Absorption correction: none
17 565 measured reflections
9170 independent reflections

5714 observed reflections $[I > 2\sigma(I)]$
$R_{\rm int} = 0.0875$
$\theta_{\rm max} = 29.89°$
$h = -11 \rightarrow 13$
$k = -13 \rightarrow 19$
$l = -17 \rightarrow 20$
No measurable crystal decay

Refinement

Refinement on F^2
$R(F) = 0.0767$
$wR(F^2) = 0.1501$
$S = 1.047$
9168 reflections
450 parameters
H atoms idealized with riding model
$w = 1/[\sigma^2(F_o^2) + (0.0641P)^2 + 2.7218P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = -0.001$
$\Delta\rho_{\rm max} = 0.798$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.797$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Ga	0.24043 (6)	0.12171 (4)	0.17811 (4)	0.01520 (14)
Cl	0.40912 (12)	0.21629 (10)	0.12336 (10)	0.0210 (3)
N(1)	0.1958 (4)	0.1149 (3)	0.0513 (3)	0.0140 (8)
N(2)	0.0727 (4)	0.2424 (3)	0.1635 (3)	0.0150 (8)
N(3)	0.2233 (4)	0.0931 (3)	0.3260 (3)	0.0168 (8)
N(4)	0.3510 (4)	−0.0319 (3)	0.2110 (3)	0.0148 (8)
C(*a*1)	0.2622 (5)	0.0413 (4)	0.0081 (4)	0.0140 (9)
C(*a*2)	0.1122 (5)	0.1937 (4)	−0.0184 (4)	0.0171 (10)
C(*a*3)	0.0053 (5)	0.3048 (4)	0.0797 (4)	0.0178 (10)
C(*a*4)	0.0205 (5)	0.2933 (4)	0.2303 (4)	0.0171 (10)
C(*a*5)	0.1456 (5)	0.1606 (4)	0.3723 (4)	0.0191 (10)
C(*a*6)	0.3021 (5)	0.0124 (4)	0.3971 (4)	0.0194 (10)
C(*a*7)	0.4165 (5)	−0.0943 (4)	0.2968 (4)	0.0185 (10)
C(*a*8)	0.3999 (5)	−0.0849 (4)	0.1463 (4)	0.0173 (10)
C(*m*1)	0.3594 (5)	−0.0501 (4)	0.0522 (4)	0.0170 (10)
C(*m*)	0.0242 (5)	0.2825 (4)	−0.0058 (4)	0.0167 (9)
C(*m*3)	0.0549 (5)	0.2550 (4)	0.3270 (4)	0.0212 (10)
C(*m*4)	0.3955 (5)	−0.0733 (4)	0.3823 (4)	0.0198 (10)
C(*b*1)	0.2176 (5)	0.0736 (4)	−0.0896 (4)	0.0166 (10)
C(*b*2)	0.1251 (5)	0.1687 (4)	−0.1072 (4)	0.0159 (9)
C(*b*3)	−0.0902 (5)	0.3961 (4)	0.0924 (4)	0.0198 (10)
C(*b*4)	−0.0796 (5)	0.3907 (4)	0.1852 (4)	0.0200 (10)
C(*b*5)	0.1746 (5)	0.1185 (4)	0.4751 (4)	0.0206 (10)
C(*b*6)	0.2737 (5)	0.0265 (4)	0.4907 (4)	0.0208 (10)
C(*b*7)	0.5079 (5)	−0.1888 (4)	0.2846 (4)	0.0176 (10)
C(*b*8)	0.4967 (5)	−0.1825 (4)	0.1913 (4)	0.0163 (10)
C(11)	0.2638 (5)	0.0101 (4)	−0.1551 (4)	0.0208 (10)
C(12)	0.1868 (7)	−0.0826 (5)	−0.1261 (5)	0.0360 (15)
C(21)	0.0449 (5)	0.2337 (4)	−0.1960 (4)	0.0207 (10)
C(22)	−0.0984 (6)	0.2092 (5)	−0.1819 (4)	0.0297 (13)
C(31)	−0.1878 (5)	0.4760 (4)	0.0186 (4)	0.0242 (11)
C(32)	−0.3155 (5)	0.4331 (5)	0.0220 (5)	0.0328 (14)
C(41)	−0.1538 (5)	0.4681 (4)	0.2334 (4)	0.0232 (11)
C(42)	−0.2782 (6)	0.4338 (5)	0.3015 (5)	0.0353 (15)
C(51)	0.1007 (6)	0.1647 (5)	0.5500 (4)	0.0315 (13)
C(52)	−0.0397 (8)	0.1339 (7)	0.5864 (6)	0.051 (2)
C(61)	0.3363 (6)	−0.0497 (4)	0.5857 (4)	0.0261 (12)
C(62)	0.2654 (8)	−0.1453 (5)	0.6385 (5)	0.038 (2)
C(71)	0.5903 (6)	−0.2765 (4)	0.3642 (4)	0.0258 (12)
C(72)	0.5062 (7)	−0.3593 (5)	0.4348 (5)	0.0367 (15)
C(81)	0.5684 (5)	−0.2605 (4)	0.1433 (4)	0.0194 (10)
C(82)	0.4793 (6)	−0.3360 (4)	0.1444 (5)	0.0287 (13)
C(*s*1)	0.3337 (7)	0.3939 (5)	0.2528 (5)	0.0376 (15)
Cl(*s*1)	0.2006 (2)	0.50380 (14)	0.2520 (2)	0.0496 (5)
Cl(*s*2)	0.3870 (2)	0.3160 (2)	0.3712 (2)	0.0617 (6)
C(*s*2)†	0.079 (2)	−0.5400 (16)	0.515 (2)	0.068 (8)
Cl(*s*3)†	0.1405 (6)	−0.4248 (5)	0.4843 (4)	0.065 (2)
Cl(*s*4)†	−0.0877 (6)	−0.5104 (7)	0.4720 (5)	0.076 (2)

† Site occupancy = 0.449 (5).

Table 2. *Selected geometric parameters (Å, °)*

Ga—N(2)	2.030 (4)	Ga—N(3)	2.038 (4)
Ga—N(1)	2.033 (4)	Ga—Cl	2.2397 (13)
Ga—N(4)	2.037 (4)		
N(2)—Ga—N(1)	87.6 (2)	N(4)—Ga—N(3)	87.9 (2)
N(2)—Ga—N(4)	158.3 (2)	N(2)—Ga—Cl	100.9 (1)
N(1)—Ga—N(4)	87.6 (2)	N(1)—Ga—Cl	102.2 (1)
N(2)—Ga—N(3)	88.1 (2)	N(4)—Ga—Cl	100.8 (1)
N(1)—Ga—N(3)	156.6 (2)	N(3)—Ga—Cl	101.3 (1)

Detailed methods and procedures for small molecule X-ray data collection with the FAST system have been described previously (Scheidt & Turowska-Tyrk, 1994). *MADNES* (Messerschmitt & Pflugrath, 1987) was used for data collection, cell refinement and data reduction. The structure was solved using *SHELXS*86 (Sheldrick, 1990) and refined using *SHELXL*93 (Sheldrick, 1993). The structure determination revealed one porphyrin molecule and two dichloromethane solvent regions, including approximately half a molecule of dichloromethane per asymmetric unit; the remainder was related by an inversion center. All porphyrin H atoms were idealized with standard *SHELXL*93 idealization methods and included in the least-squares process as fixed contributors.

The authors thank the National Institutes of Health for support of this research under grant GM-38401. Funds for the purchase of the FAST area-detector diffractometer were provided through NIH grant RR-06709.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1254). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 2710–2713

3-Chloro-3,3-bis(triphenylphosphine-*P*)-1,2-dicarba-3-rhoda-*closo*-dodecaborane–Dichloromethane (1/1.1)

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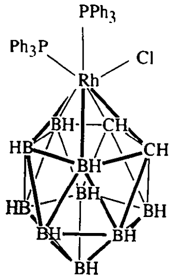
(*Received 26 June 1996; accepted 16 July 1996*)

Abstract

The title compound, [3,3-$(PPh_3)_2$-3-Cl-3,1,2-$RhC_2B_9H_{11}$] or [$RhCl(C_2H_{11}B_9)(C_{18}H_{15}P)_2$].1.1$CH_2Cl_2$, contains a triangulated icosahedral *closo*-RhC_2B_9 cage. Principal bond distances are Rh—Cl 2.423 (2), Rh—P 2.373 (2) and 2.383 (2), Rh—C 2.190 (6) and 2.191 (6), and Rh—B 2.203 (8)–2.289 (8) Å. The conformation of the $Rh(PPh_3)_2Cl$ group above the C_2B_3 face of the dicarbaborane ligand is such that the Rh—Cl bond is located above the cage C—C vector.

Comment

Rhodium chloride-containing rhodacarbaborane complexes of the type [{$Rh(PR_3)_nCl$}$C_2B_9H_{11}$] have been identified as products from a variety of reactions involving [{$Rh(PR_3)_2H$}$C_2B_9H_{11}$] reagents. The compounds [3,3-$(PR_3)_2$-3-Cl-3,1,2-$RhC_2B_9H_{11}$], with R_3 = Ph_3 (Baker *et al.*, 1984) or $MePh_2$ (Ferguson *et al.*, 1996), were obtained from the reactions between [3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$], (1), and aqueous HCl in $CHCl_3$ (R_3 = Ph_3, 73%), or from [3-{η^2-SC(H)NPh}-3-(PPh_3)-3,1,2-$RhC_2B_9H_{11}$] and $PMePh_2$ in CH_2Cl_2 (R_3 = $MePh_2$, 96%), respectively (Ferguson *et al.*, 1996). The 16-electron species [2-(PPh_3)-2-Cl-2,1,7-$RhC_2B_9H_{11}$], (2), was the unexpected product from the reaction between the 2,1,7-isomer of (1) and aqueous HCl in $CHCl_3$ (Baker *et al.*, 1984). We now report an alternative route to [3,3-$(PPh_3)_2$-3-Cl-3,1,2-$RhC_2B_9H_{11}$], (3), and the structural characterization of (3) using X-ray crystallography.



(3)

The overall form of the rhodadicarbaborane cage structure in (3) is, as expected, a *closo* 12-atom species (Fig. 1). Considering the bonding to the *exo*-cage ligands first, the Rh—Cl distance [2.423 (2) Å] is very similar to that found in [3,3-$(PMePh_2)_2$-3-Cl-3,1,2-$RhC_2B_9H_{11}$] [(4); 2.4205 (8) Å; Ferguson *et al.*, 1996], but the Rh—P distances show some differences between the two structures. The Rh—P distances in (3) are not significantly different from their mean value [2.378 (5) Å], whereas the equivalent bonds in compound (4) are significantly different [Rh—P1 2.3500 (9) and Rh—P2 2.3414 (9) Å]. The Rh—P [2.329 (1) Å] and Rh—Cl [2.299 (1) Å] distances in the 16-electron species [2-(PPh_3)-2-Cl-2,1,7-$RhC_2B_9H_{11}$] [(2); Baker *et al.*, 1984] are significantly shorter than those in the 18-electron compounds (3) and (4), suggesting stronger *exo*-cage bonding in compound (2).

The Rh3—C1 and Rh3—C2 distances in compound (3) (Table 2) are essentially identical and the equivalent distances in (4) [2.208 (3) and 2.205 (3) Å, respectively] are very similar. In contrast, the Rh—C distances in (2) are distinctly different [2.215 (4) and 2.165 (4) Å]. Since the C1 atom in (2) is *trans* with respect to the phosphine ligand, with a P—Rh—C1 angle of 175.2 (1)°, and the

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