The systematic absences of $h0l$, $h + l = 2n + 1$ and $0k0$, $k = 2n + 1$ uniquely determined the space group to be $P2_1/n$ for (1). Based on statistical analyses of intensity distributions and successful solution and refinement of the structures, the space group $P\bar{1}$ was assigned to (2) and (3). The structures were solved by direct methods and refined by full-matrix least-squares calculations. The non-H atoms were allowed anisotropic displacement parameters. The H atoms were included at geometrically idealized positions with a C—H distance of 0.95 Å. The thiocyclohexyl moieties in (2) were disordered, with atoms S(1), C(3)–C(8) and S(3), C(11)–C(16) representing the major fractions in the two molecules; the cyclohexyl rings of the minor thiocyclohexyl moieties [S(1*A*), C(3*A*)–C(8*A*) and S(3*A*), C(11*A*)–C(16*A*)] were constrained to be regular chairs. One of the S atoms in compound (3) is also disordered over two sites S(1) and S(1*A*); S(1*A*) was allowed an isotropic displacement parameter during the refinement.

For all compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1994); program(s) used to solve structures: *SAPI91* (Fan, 1991). Program(s) used to refine structures: *TEXSAN* for (1); *SHELXL93* (Sheldrick, 1993) for (2) and (3). For all compounds, software used to prepare material for publication: *TEXSAN*.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: FG1260). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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9,12-Dibromo-3,3-bis(triphenylphosphine-*P*)-1,2-dicarba-3-hydrido-3-rhoda-*closo*-dodecaborane–Dichloromethane (1/1)

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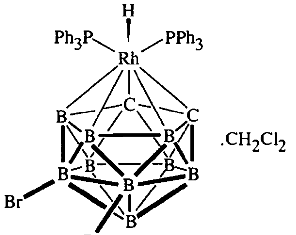
Abstract

In the title complex, $[RhH(C_2B_9H_9Br_2)(C_{18}H_{15}P)_2].CH_2Cl_2$, the rhodacarborane molecule adopts a closed icosahedral RhC_2B_9-cage geometry with adjacent Rh and C atoms. Principal distances include Rh—P 2.345 (2) and 2.276 (2), Rh—C 2.289 (8) and 2.241 (8), and B—Br 1.974 (9) and 1.980 (9) Å.

Comment

Few metallaheteroborane ligands containing boron–halide bonds have been structurally characterized. However, the halogenated carborane metal sandwich anions [3,3′-*commo*-bis(8-chlorodecahydro-1,2-dicarba-3-ferrous-*closo*-dodecaborate)]$^-$, (1) (Kirillova *et al.*, 1989), and [3,3′-*commo*-bis(8,9,12-tribromooctahydro-1,2-dicarba-3-cobalta-*closo*-dodecaborate)]$^-$, (2) (Sivý *et al.*, 1986), have previously been studied using X-ray crystallography.

The title compound, [3,3-$(PPh_3)_2$-3-H-9,12-$(Br)_2$-3,1,2-*closo*-$RhC_2B_9H_9$], (3), is the first rhodacarborane system with a halogenated cage to be structurally characterized (Fig. 1). The two Br atoms are bonded to B9 and B12 in the carborane cage, *i.e.* the boron positions directly opposite the C atoms. The B—Br distances in (3) are essentially the same [B9—Br 1.974 (9) and B12—Br 1.980 (9) Å] and are comparable to those in $[Co(C_2B_9H_8Br_3)_2]^-$, (2) [1.960 (12), 1.968 (14) and 1.940 (11) Å], or those in the silver(I) and caesium salts of the *closo*-$[12\text{-Br-}CB_{11}H_{11}]^-$ anion, (4) [1.995 (3) and 1.998 (9) Å, respectively; Jelinek, Baldwin, Scheidt & Reed, 1993]. The distances and angles within the RhC_2B_9 cage do not differ substantially from those in either *closo*-[3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$], (5) (Hardy, Callahan, Strouse & Hawthorne, 1976), or *closo*-[3,3-$(PPh_3)_2$-3-Cl-3,1,2-$RhC_2B_9H_{11}$], (6) (Ferguson, Spalding & McEneaney, 1996). The C—C distance in (3) is 1.631 (11) Å, while that in (6) is 1.606 (9) Å. The C—B and B—B distances are in the ranges 1.636 (11)–1.734 (13) and 1.734 (14)–1.844 (12) Å, respectively, in (3) and 1.670 (11)–1.717 (10) and 1.727 (12)–1.827 (10) Å, respectively, in (6). The B9—B12 distances in (3) and (6) are essentially the same [1.779 (13) and 1.788 (12) Å, respectively].



(3)

The (PPh_3)$_2$RhH unit in (3) is orientated asymmetrically with respect to the C_2B_3 face of the carborane cage (Fig. 2 in supplementary material). This is similar to what was reported for the (PPh_3)$_2$RhH unit in the parent rhodacarborane [3,3-(PPh_3)$_2$-3-H-3,1,2-*closo*-$RhC_2B_9H_{11}$], (5) (Hardy *et al.*, 1976). The two Rh—P bond lengths in (3) [2.345 (2) and 2.276 (2) Å] are significantly different, even more so than in (5) [2.357 (3) and 2.301 (1) Å]. The Rh—P distance of 2.276 (2) Å in (3) is unusually short for an Rh^{III}–phosphine heteroborane. In (3), the phosphines in the (PPh_3)$_2$RhH unit are positioned such that the longer Rh3—P1 bond vector is orientated almost directly above the C—C vector and the shorter Rh3—P2 bond is positioned almost opposite the C2 atom.

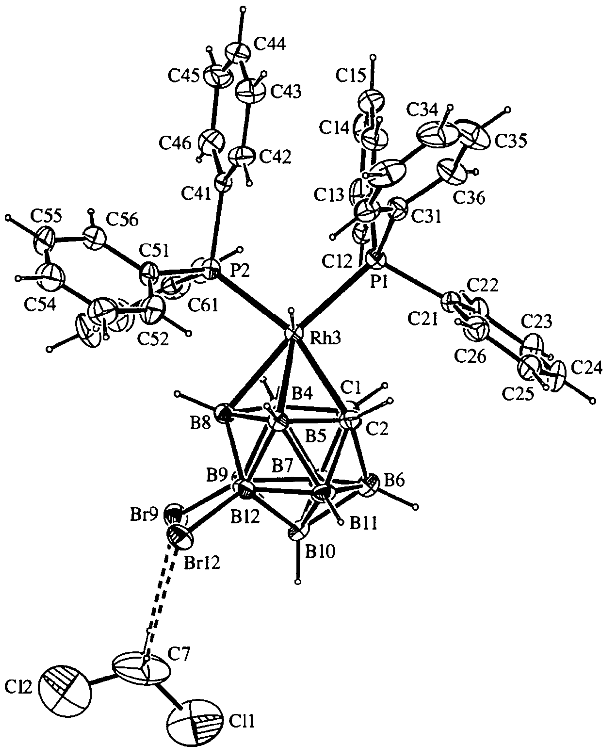


Fig. 1. A view of (3) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

The dichloromethane solvent molecule present in the crystal lattice of (3) is linked *via* C—H···Br hydrogen-bonds to the Br atoms of (3); details are given in Table 2. The solvent molecule fills what would otherwise have been a void in the asymmetric unit. Examination of the structure with *PLATON* (Spek, 1996*a*) showed that there were no other solvent-accessible voids in the crystal lattice.

Experimental

Reaction of [$Rh(PPh_3)_3Cl$] with Cs[5,6-Br_2-7,8-*nido*-$C_2B_9H_{10}$] (Zakharkin & Kalinin, 1967) in ethanol at 323 K for 30 min afforded a yellow precipitate of *closo*-[3,3-(PPh_3)$_2$-3-H-9,12-(Br)$_2$-3,1,2–$RhC_2B_9H_9$] (3) in 20% yield. The compound was purified by preparative thin-layer chromatography (60:40 dichloromethane/hexane) and crystals suitable for X-ray analysis were grown by slow diffusion of a layer of heptane into a dichloromethane solution.

Crystal data

[$RhH(C_2B_9H_9Br_2)$-
($C_{18}H_{15}P)_2$].CH_2Cl_2
$M_r = 1003.59$
Monoclinic
$P2_1/c$
$a = 13.811\ (2)$ Å
$b = 14.0419\ (15)$ Å
$c = 22.409\ (3)$ Å
$\beta = 97.391\ (11)°$
$V = 4309.8\ (9)$ Å^3
$Z = 4$
$D_x = 1.547$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 9.80–15.45°$
$\mu = 2.478$ mm^{-1}
$T = 294\ (1)$ K
Lath
0.43 × 0.26 × 0.10 mm
Pale orange

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: numerical by Gaussian integration
$T_{min} = 0.533$, $T_{max} = 0.791$
7849 measured reflections
7601 independent reflections

4105 reflections with $I > 2\sigma(I)$
$R_{int} = 0.034$
$\theta_{max} = 25°$
$h = -16 \rightarrow 16$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 26$
3 standard reflections
frequency: 120 min
intensity variation: 0.7%

Refinement

Refinement on F^2
$R(F) = 0.0656$
$wR(F^2) = 0.1346$
$S = 0.919$
7601 reflections
496 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0515P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.000$
$\Delta\rho_{max} = 0.861$ e Å^{-3}
$\Delta\rho_{min} = -0.481$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected bond lengths (Å)*

Rh3—P1	2.345 (2)	Rh3—B7	2.237 (9)
Rh3—P2	2.276 (2)	Rh3—B8	2.250 (9)
Rh3—C1	2.289 (8)	Br9—B9	1.974 (9)
Rh3—C2	2.241 (8)	Br12—B12	1.980 (9)
Rh3—B4	2.298 (9)	C1—C2	1.631 (11)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C7—H7*A*···Br9	0.97	2.87	3.838 (17)	178
C7—H7*B*···Br12	0.97	2.88	3.537 (14)	126

In a penultimate $\Delta\rho$ map, the top peak in the peak list was 1.24 Å from Rh3 in a position consistent with it being associated with the H atom bonded to Rh3; this is a relatively short distance (the Rh/H covalent radii sum is 1.68 Å). In the final refinement cycles, this H atom was included at the coordinates from the difference map and not refined. Other H atoms were treated as riding atoms with C—H 0.93–1.10 and B—H 1.10 Å.

Data collection: *CAD*-4-*PC Software* (Enraf–Nonius, 1992). Cell refinement: *SET*4 and *CELDIM* in *CAD*-4-*PC Software*. Data reduction: *DATRD*2 in *NRCVAX*96 (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *NRCVAX*96 *via* Patterson heavy-atom method. Program(s) used to refine structure: *NRCVAX*96 and *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *NRCVAX*96, *ORTEP*II (Johnson, 1976), *PLATON* (Spek, 1996*a*) and *PLUTON* (Spek, 1996*b*). Software used to prepare material for publication: *NRCVAX*96, *SHELXL*93 and *WordPerfect* macro *PREPCIF*97 (Ferguson, 1997).

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: AB1472). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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cis- and *trans*-Diisothiocyanato(1,4,8,11-tetraazacyclotetradecane)chromium(III) Perchlorate

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Abstract

The *cis* isomer of the title compound, $[Cr(NCS)_2(C_{10}H_{24}N_4)](ClO_4)$, is a racemate of the Bosnich type V structure; the *trans* complex is a *meso* substance with a Bosnich type III stereochemistry. There is no appreciable change in the structures of the title compound on cooling, even though there are marked color changes. The Cr—N bond lengths are all in the range 1.983 (2)–1.998 (4) Å for the bonds to the isothiocyanate groups and in the range 2.046 (2)–2.088 (3) Å for the bonds to cyclam N atoms.

Comment

As part of our continuing investigations into the effects of temperature, pressure and solvent on the photobehavior and spectroscopy of octahedral-like Cr^{III} amine complexes (Friesen, Lee, Nashiem, Mezyk & Waltz, 1995; Vincze, Friesen, Mezyk & Waltz, 1992), we have examined the UV–visible spectra as a function of temperature of *trans*-$[Cr(cyclam)(NCS)_2](ClO_4)$, (1*a*) and (1*b*), and *cis*-$[Cr(cyclam)(NCS)_2](ClO_4)$, (2*a*) and (2*b*), where cyclam is 1,4,8,11-tetraazacyclotetradecane, and *a* and *b* denote room- and low-temperature studies, respectively.

A notable feature is that, on cooling powders of each complex to liquid nitrogen temperature, their colors change from orange–red (*cis* isomer) or orange–yellow (*trans* isomer) to bright yellow. The color change is reversible on warming to room temperature. Because

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