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Di-μ-bromo-3:3′κ^4*Br*-bis[μ-(2-phenyl-3-phenylamino-3-sulfido-2-azoniaprop-2-en-1-yl-3κ*S*:8κ*C*^{1})-1,2-dicarba-3-rhoda-*closo*-dodecaborane], a Novel Dimeric Metallacarborane Containing a Rh_2Br_2 Bridging Section and the {–SC(NHPh)–N(Ph)CH_2–} Ligand

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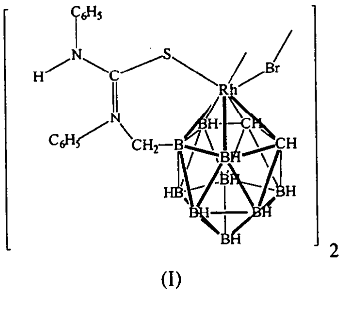
Abstract

The title compound, $[Rh_2Br_2(C_{16}H_{23}B_9N_2S)_2]$, has crystallographic inversion symmetry with two *closo* twelve-vertex {3,1,2-RhC_2B_9}-cages bridged through the Rh atoms by two Br atoms. Each Rh atom is bonded to the S atom of an {—SC(NHPh)—N(Ph)CH_2—} ligand whose methylene C atom in turn is bonded to a B atom of the RhC_2B_9 cage, thereby forming a six-membered RhSCNCB *exo*-cage ring. Principal distances include Rh—Br 2.5903 (7), 2.6702 (7) and Rh—S 2.3471 (10) Å. The distances within the RhSCNCB ring are (in sequence) S—C 1.725 (4), C—N 1.331 (5), N—C 1.473 (5), C—B 1.586 (6) Å.

Comment

Reactions of the rhodacarborane *closo*-[3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$] with excess PhNCS in bromine-containing solvents affords several unusual products, including the title compound {3-[η^1-SC(NHPh)N(Ph)-CH_2]-3-Br-3,1,2-$RhC_2B_9H_{10}$}$_2$, (1).



(I)

A view of (1) is shown in Fig. 1 with the numbering scheme. The structure contains two features which are novel in rhodacarborane chemistry. First is the bridged Rh_2Br_2 central section of (1) where two Rh—Br distances are observed, Rh—Br1 2.5903 (7) and Rh—Br1′ 2.6702 (7) Å. A search of the October 1994 release of the Cambridge Structural Database (Allen, Kennard & Taylor, 1983) showed no previous reports of dimeric rhodaheteroboranes or rhodaboranes which contained two bridging Br atoms. The recently reported anion [(μ-Br)(2-PPh_3-1-NH_2-2,1-$RhCB_{10}H_{10}$)$_2$]$^-$, (2) (Chizhevsky *et al.*, 1993), contains one Br and two NH_2 bridges. The Rh—Br—Rh part of (2) was found to be symmetric with dimensions 2.584 (3), 2.590 (3) Å and 88.0 (1)°. In contrast to the asymmetric bridges in (1), the Rh_2Br_2 moiety in the two independent molecules in crystals of [RhBr(η^5-C_5Me_5)]$_2$(μ-Br)$_2$, (3) (Churchill & Julis, 1978), are almost symmetrical [Rh—Br 2.577 (1) and 2.587 (1) Å in one of the molecules, and 2.566 (1) and 2.575 (1) Å in the other].

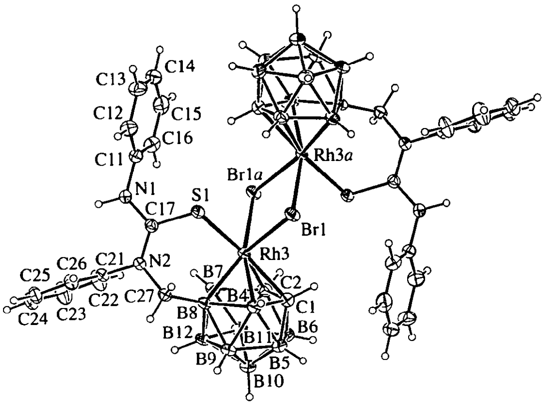


Fig. 1. A view of (1) with the numbering scheme. The non-H atoms are shown as displacement ellipsoids drawn at the 30% probability level. For clarity, H atoms are drawn as small spheres of an arbitrary size.

The second novel feature in (1) is the {η^1-SC(NHPh)N(Ph)CH_2—} ligand, the structure of which can be related to the thiourea PhHNC(S)NPhMe. The location of the single H atom on N1 together with analysis of the dimensions at N1, C17 and N2 clearly indicate that these atoms adopt sp^2-hybridization schemes; the location of the two H atoms on C27 and consideration of the dimensions at C27 and S1 require that these atoms be sp^3 hybridized. The C27—N2, N2—C17 and N1—C17 distances are in agreement with those reported for similar interactions which are listed in the compendium by Orpen *et al.* (1994); the C17—S1 distance, 1.725 (4) Å, is slightly shorter than the typical C(sp^2)—S(sp^3) distance (1.751 Å) but much longer than expected for a C(sp^2)=S double bond (1.681 Å).

The C27—B8 distance of 1.586 (6) Å is normal for a B(cage)—C(*exo*-cage) single bond. The equiva-

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lent C—B distance in $[2\text{-}(PPh_3)\text{-}H\text{-}2\text{-}(Ph_2PC_6H_4)\text{-}2,1\text{-}RhTeB_{10}H_9]$ was found to be 1.582 (6) Å (Ferguson, Faridoon & Spalding, 1988). The Rh3—S1 distance in (1) is 2.3471 (10) Å, which is longer than a typical Rh—S distance in dithiolates (2.308 Å) but shorter than Rh—S in dialkyl thioether complexes (2.430 Å; Orpen *et al.*, 1994).

In the crystal structure, the dimeric molecules are linked to form infinite one-dimensional chains by N—H···π-arene hydrogen bonding. Pairs of C_6H_5—N(H)— moieties pack face-to-face about inversion centres, as shown in Fig. 2, with an interplanar separation of 3.467 (8) Å between phenyl rings. The H atom on N1 is directed towards C14 of the adjacent ring with H···C 2.64 Å and N1—H···C14 147°.

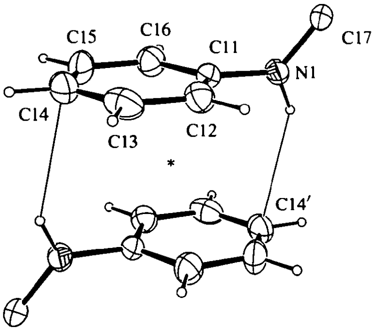

Fig. 2. A view of the N—H···π-arene interactions between two C_6H_5—N(H)— moieties related by an inversion centre (indicated by *). Displacement ellipsoid are drawn at the 30% probability level. The coordinates of the symmetry-related ring are obtained from those in Table 1 by the symmetry transformation 2 − *x*, 2 − *y*, 1 − *z*.

Experimental

The title compound (1) was synthesized in 60% yield from the reaction of CH_2Br_2 with 3-(2-phenyl-3-phenylimino-3-sulfido-2-azoniaprop-1-en-1-yl-*S*,*C*′)-3-(triphenylphosphine)-1,2-dicarba-3-rhodadodecarborane, (2), at 340 K for 2 d. The rhodacarborane reagent (2) had been synthesized previously in 5% yield in the reaction of PhNCS with *closo*-$[3,3\text{-}(PPh_3)_2\text{-}3,1,2\text{-}RhC_2B_9H_{11}]$ (O'Connell, 1994).

Crystal data

$[Rh_2Br_2(C_{16}H_{23}B_9N_2S)_2]$
$M_r = 1111.05$
Triclinic
$P\bar{1}$
$a = 8.2971 (11)$ Å
$b = 10.0909 (13)$ Å
$c = 13.863 (4)$ Å
$\alpha = 78.330 (14)°$
$\beta = 86.203 (14)°$
$\gamma = 87.326 (8)°$
$V = 1133.5 (4)$ Å^3
$Z = 1$
$D_x = 1.628$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 18.0–23.5°$
$\mu = 2.58$ mm^{-1}
$T = 293$ K
Plate
0.375 × 0.153 × 0.056 mm
Orange

Data collection

Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ-scans at 4° steps (North, Phillips & Mathews, 1968)
$T_{min} = 0.778$, $T_{max} = 0.996$
4905 measured reflections
4905 independent reflections

3318 observed reflections $[I > 3.0\sigma(I)]$
$\theta_{max} = 26.88°$
$h = -10 \rightarrow 10$
$k = 0 \rightarrow 12$
$l = -16 \rightarrow 17$
3 standard reflections
frequency: 120 min
intensity decay: none, variation 1.0%

Refinement

Refinement on F
$R = 0.027$
$wR = 0.033$
$S = 0.97$
3318 reflections
271 parameters
H atoms included as riding atoms, C—H and B—H in $C_2H_{11}B_9$ 1.04 Å; other C—H, N—H 0.95 Å

$w = 1/[\sigma^2(F) + 0.0005F^2]$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.45$ e Å^{-3}
$\Delta\rho_{min} = -0.32$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

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

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

	x	y	z	U_{eq}
Rh3	0.50939 (4)	0.48183 (3)	0.64116 (2)	0.02951 (15)
Br1	0.28825 (5)	0.53550 (4)	0.51413 (3)	0.0407 (2)
C1	0.3989 (5)	0.2914 (4)	0.7058 (3)	0.041 (2)
C2	0.5914 (5)	0.2765 (4)	0.6981 (3)	0.040 (2)
B4	0.3332 (6)	0.4306 (5)	0.7597 (3)	0.039 (3)
B5	0.3262 (7)	0.2547 (5)	0.8229 (4)	0.049 (3)
B6	0.4875 (7)	0.1580 (5)	0.7828 (4)	0.050 (3)
B7	0.6852 (6)	0.4009 (4)	0.7464 (3)	0.037 (2)
B8	0.5169 (5)	0.4982 (4)	0.7939 (3)	0.034 (2)
B9	0.4010 (6)	0.3762 (5)	0.8820 (3)	0.042 (3)
B10	0.4978 (7)	0.2132 (5)	0.8942 (4)	0.051 (3)
B11	0.6685 (6)	0.2264 (5)	0.8099 (4)	0.046 (3)
B12	0.6164 (6)	0.3589 (5)	0.8738 (3)	0.042 (2)
S1	0.53903 (13)	0.71674 (10)	0.59497 (7)	0.0378 (5)
N1	0.7936 (4)	0.8468 (3)	0.6252 (2)	0.0462 (19)
N2	0.6713 (4)	0.7190 (3)	0.7657 (2)	0.0351 (16)
C11	0.8294 (5)	0.8826 (4)	0.5209 (3)	0.041 (2)
C12	0.7724 (6)	1.0041 (4)	0.4691 (3)	0.053 (3)
C13	0.8127 (7)	1.0394 (5)	0.3686 (4)	0.064 (3)
C14	0.9049 (6)	0.9553 (6)	0.3218 (3)	0.060 (3)
C15	0.9613 (6)	0.8330 (6)	0.3735 (4)	0.063 (3)
C16	0.9242 (5)	0.7967 (4)	0.4742 (3)	0.050 (3)
C17	0.6792 (5)	0.7613 (4)	0.6682 (3)	0.035 (2)
C21	0.7989 (5)	0.7458 (4)	0.8248 (3)	0.037 (2)
C22	0.9359 (6)	0.6646 (5)	0.8340 (4)	0.061 (3)
C23	1.0523 (6)	0.6862 (6)	0.8943 (4)	0.071 (3)
C24	1.0321 (6)	0.7909 (5)	0.9449 (4)	0.060 (3)
C25	0.8954 (6)	0.8720 (4)	0.9352 (3)	0.051 (3)
C26	0.7776 (5)	0.8500 (4)	0.8749 (3)	0.043 (2)
C27	0.5310 (5)	0.6450 (4)	0.8165 (3)	0.037 (2)

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

Rh3—Br1	2.5903 (7)	B8—C27	1.586 (6)
Rh3—Br1^i	2.6702 (7)	S1—C17	1.725 (4)
Rh3—C1	2.167 (4)	N1—C11	1.432 (5)
Rh3—C2	2.158 (4)	N1—C17	1.340 (5)

Rh3—B4	2.125 (5)	N2—C17	1.331 (5)
Rh3—B7	2.147 (4)	N2—C21	1.447 (5)
Rh3—B8	2.163 (4)	N2—C27	1.473 (5)
Rh3—S1	2.3471 (10)		
Br1—Rh3—Br1^{i}	85.31 (2)	Rh3—Br1—Rh3^{i}	94.69 (2)
Br1—Rh3—C1	90.14 (11)	Rh3—B8—C27	117.5 (3)
Br1—Rh3—C2	121.46 (11)	Rh3—S1—C17	107.70 (13)
Br1—Rh3—B4	91.56 (12)	C11—N1—C17	124.4 (3)
Br1—Rh3—B7	169.95 (12)	C17—N2—C21	121.1 (3)
Br1—Rh3—B8	133.53 (11)	C17—N2—C27	120.7 (3)
Br1—Rh3—S1	81.51 (3)	C21—N2—C27	118.3 (3)
Br1^{i}—Rh3—C1	112.75 (11)	S1—C17—N1	118.3 (3)
Br1^{i}—Rh3—C2	84.99 (11)	S1—C17—N2	122.0 (3)
Br1^{i}—Rh3—B4	161.25 (13)	N1—C17—N2	119.7 (3)
Br1^{i}—Rh3—B7	93.66 (12)	B8—C27—N2	114.3 (3)
Br1^{i}—Rh3—B8	139.51 (12)	N1—H1*n*—C14^{ii}	147
Br1^{i}—Rh3—S1	85.93 (3)		

Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $2 - x, 2 - y, 1 - z$.

All H atoms were visible in difference maps; they were positioned geometrically and included as riding atoms in the structure-factor calculations. Section of the difference maps showing the H atoms bonded to N1 and C27 have been deposited. Examination of the structures with *PLATON* (Spek, 1994*a*) showed that there were no solvent-accessible voids in the crystal lattice.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1992). Cell refinement: *SET*4, *CELDIM* (Enraf–Nonius, 1992). Data reduction: *DATRD*2 in *NRCVAX*94 (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *NRCVAX*94 and Patterson heavy-atom method. Program(s) used to refine structure: *NRCVAX*94. Molecular graphics: *ORTEP*II (Johnson, 1976) as implemented in *PLATON* (Spek, 1994*a*), *NRCVAX*94 and *PLUTON* (Spek, 1994*b*). Software used to prepare material for publication: *NRCVAX*94.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1253). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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exo-2-(η^6-Hexamethylbenzene)-*endo*-2-chloro-2-ruthena-*arachno*-tetraborane(8)

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Abstract

The compound *exo*-2-(η^6-hexamethylbenzene)-*endo*-2-chloro-2-ruthena-*arachno*-tetraborane, [RuCl($C_{12}H_{18}$)(B_3H_8)], is based on a four-vertex butterfly structure with an Ru atom occupying a wing-tip position. The Ru atom is coordinated to the [B_3H_8] moiety *via* an Ru—μ-H—B bridge to each of the two B atoms in the hinge positions. Additionally, the Ru atom is ligated by a hexahapto-hexamethylbenzene and a Cl atom. The compound is in a conformation with the Cl atom in the *endo* position and the η^6-arene in the *exo* position.

Comment

Metallaoctahydrotetraboranes that maintain a halogen bound to the metal atom, [(L_n)XMB_3H_8], are of interest in metallaborane synthesis since they may react with borane anions to give larger and novel metallaboranes (Bown, Fontaine, Greenwood, MacKinnon, Kennedy & Thornton-Pett, 1987*a*,*b*; Bown, Greenwood & Kennedy, 1986; Kennedy, 1986). Compounds of this type were first reported several years ago [L_n = η^5-C_5Me_5, X = Cl, M = Ir, Rh (Kennedy, 1986); L_n = η^6-C_6Me_6, X = Cl, M = Ru (Kennedy, 1986; Bown, Greenwood & Kennedy, 1986; Bown, Fontaine, Greenwood, MacKinnon, Kennedy & Thornton-Pett, 1987*a*,*b*), M = Os (Bown, Greenwood & Kennedy, 1986); L_n = *p*-$MeC_6H_4{}^iPr$, X = Cl, M = Os (Bown, 1987)]. More recently, [(CO)(PPh_3)$_2XRuB_3H_8$] (X = Cl, Br, I) (Alcock, Burns, Claire & Hill, 1992; Burns, Hill, Thompsett, Alcock & Claire, 1992) was reported. The structure determination of the title compound was undertaken to establish which one of the two possible confor-