H atoms riding, with C—H and N—H 0.95 Å

Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Cu1—Cl1	2.230 (2)	C5—C6	1.479 (8)
Cu1—Cl4	2.235 (2)	C6—C14	1.319 (8)
Cu1—Cl2	2.257 (2)	C6—C7	1.501 (8)
Cu1—Cl3	2.290 (2)	C10—C13	1.506 (9)
N1—C1	1.343 (8)	C14—C15	1.509 (8)
N1—C5	1.352 (7)	C16—C17	1.509 (9)
N2—C16	1.487 (7)	C17—C18	1.467 (10)
N2—C15	1.489 (7)	C18—C19	1.526 (9)
N2—C19	1.499 (7)		
Cl1—Cu1—Cl4	101.40 (8)	C14—C6—C5	120.3 (6)
Cl1—Cu1—Cl2	99.04 (7)	C14—C6—C7	121.4 (6)
Cl4—Cu1—Cl2	136.83 (8)	C5—C6—C7	118.3 (5)
Cl1—Cu1—Cl3	129.83 (9)	C6—C14—C15	124.1 (6)
Cl4—Cu1—Cl3	95.80 (8)	N2—C15—C14	111.4 (5)
Cl2—Cu1—Cl3	99.59 (8)	N2—C16—C17	105.2 (6)
C1—N1—C5	123.3 (6)	C18—C17—C16	108.7 (6)
C16—N2—C15	115.7 (5)	C17—C18—C19	105.2 (6)
C16—N2—C19	105.9 (5)	N2—C19—C18	103.4 (5)
C15—N2—C19	112.2 (5)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···Cl2	0.95	2.31	3.110 (6)	154
N2—H2···Cl3	0.95	2.18	3.080 (6)	161

The space group $P2_1/n$ was determined uniquely from the systematic absences of $h0l$, $h + l = 2n + 1$, and $0k0$, $k = 2n + 1$.

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 structure: *SAPI*91 (Fan, 1991). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). 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: FG1262). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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trans-[2,3-Bis(methylthio)hexane-*S*,*S*′]dichlorozinc(II), *trans*-[1,2-Bis(methylthio)cyclohexane-*S*,*S*′]dichlorozinc(II) and *cis*-[5,6-Bis(methylthio)-1,3-cycloheptadiene-*S*,*S*′]dichlorozinc(II)

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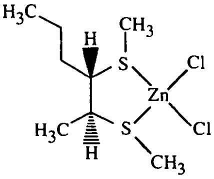
Abstract

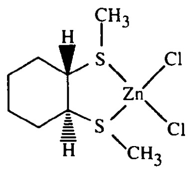
The crystal structures of *trans*-[2,3-bis(methylthio)hexane-*S*,*S*′]dichlorozinc(II), $[ZnCl_2(C_8H_{18}S_2)]$, *trans*-[1,2-bis(methylthio)cyclohexane-*S*,*S*′]dichlorozinc(II), $[ZnCl_2(C_8H_{16}S_2)]$, and *cis*-[5,6-bis(methylthio)-1,3-cycloheptadiene-*S*,*S*′]dichlorozinc(II), $[ZnCl_2(C_9H_{14}S_2)]$, contain distorted tetrahedral Zn atoms coordinated to two Cl and two S atoms, with Zn—Cl and Zn—S distances in the ranges 2.190 (2)–2.222 (2) and 2.369 (2)–2.475 (1) Å, respectively. The Cl—Zn—Cl and S—Zn—S angles in the three compounds are in the ranges 117.35 (4)–122.63 (4) and 88.11 (5)–91.12 (6)°, respectively.

Comment

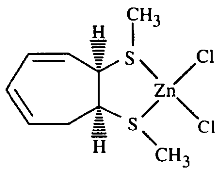
The addition of dimethyl disulfide to an alkene using a Lewis acid catalyst such as BF_3 is a well known process (Caserio, Fisher & Kim, 1985). The mechanism is thought to proceed *via* a thiiranium ion intermediate which undergoes a ring opening by the incoming thiomethyl anion to give *anti* addition across the double bond. Our interest in montmorillonite clays prompted us to investigate this reaction using K-10 montmorillonite impregnated with ZnCl$_2$. Reaction of 2-hexene, dimethyl disulfide and K-10/ZnCl$_2$ yielded a white solid. Treatment of cyclohexene under these conditions also yielded a white solid. These results were unexpected as 2,3-bis(thiomethyl)hexane and 1,2-bis(thiomethyl)cyclohexane are oils. Since coordination of ZnCl$_2$ to the dimethylthio products was suspected in these reactions, X-ray analyses were performed to elucidate the mode of coordination and stereochemistry of the disulfide addition which unequivocally established the structures of the 2-hexene and cyclohexene addition products as (1) and (2), respectively.



(1)



(2)



(3)

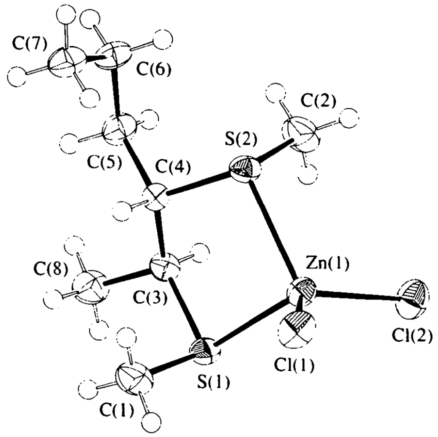
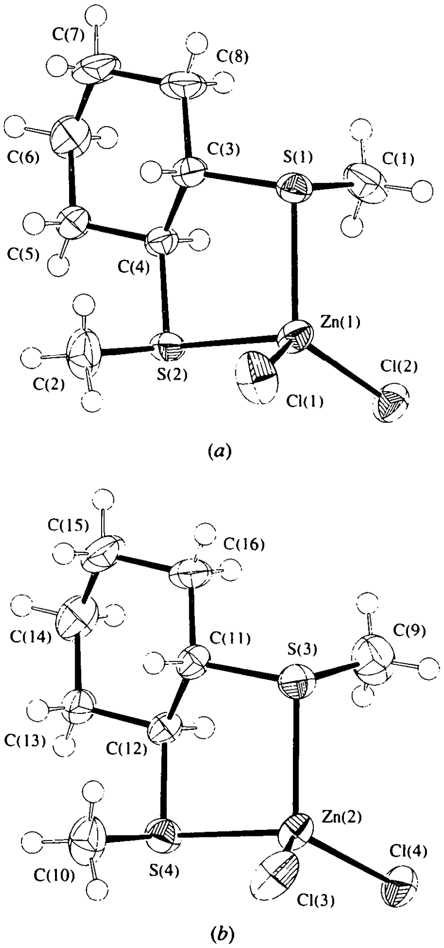


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of (1) with the atomic numbering scheme. Displacement ellipsoids are plotted at the 50% probability level and H atoms have been assigned arbitrary radii.



(*a*)

(*b*)

Fig. 2. *ORTEP*II (Johnson, 1976) drawings of (*a*) 89.3% occupancy and (*b*) 77.1% occupancy sites of the two molecules of (2) in the asymmetric unit with the atomic numbering scheme; the thiocyclohexyl groups representing the minor fractions in each have been excluded. Displacement ellipsoids are plotted at the 50% probability level and H atoms have been assigned arbitrary radii.

Furthermore, dimethyl disulfide is known to add *anti* across a double bond to afford *trans*-bis(thiomethyl) alkanes in the presence of Lewis acids such as BF$_3$ (Caserio, Fisher & Kim, 1985). Recently, we have shown that montmorillonite clays doped with metal salts such as ZnCl$_2$ and FeCl$_3$ are active catalysts for the addition of alkyl disulfides across the double bonds of unconjugated alkenes resulting in the formation of *trans* products (Clark, Mesher & Parvez, 1997). This methodology has been extended to conjugated dienes and trienes and in the case of cycloheptatriene yields yellow crystals on reaction with dimethyl disulfide over a K-10 montmorillonite clay doped with ZnCl$_2$. Initial spectroscopic analysis indicated both 1,2-*cis* addition and coordination to ZnCl$_2$. X-ray analysis of the product, (3), was performed to confirm what is believed to be the first example of *cis* addition of a disulfide to a double bond.

The crystal structures of the three compounds contain discrete monomeric molecules (Figs. 1–3) separated by normal van der Waals distances. There are two independent molecules in the asymmetric unit of (2) with disordered thiocyclohexyl moieties. An S atom in compound (3) is also disordered. The metal atoms in all the structures show distorted tetrahedral geometry and are bonded to two Cl atoms and two S atoms of bis(methylthio) hydrocarbon ligands. In all the struc-

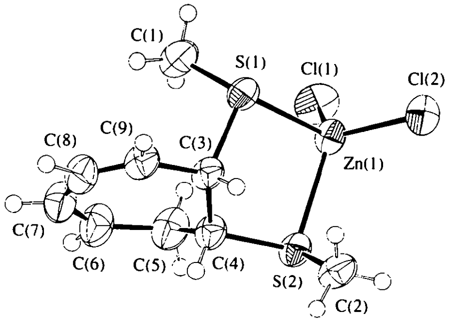


Fig. 3. *ORTEP*II (Johnson, 1976) drawing of (3) with the atomic numbering scheme; S(1*A*) represents only 6.6% occupancy and has been omitted. Displacement ellipsoids are plotted at the 50% probability level and H atoms have been assigned arbitrary radii.

tures, the Zn—Cl distances lie within a narrow range, 2.190 (2)–2.222 (2) Å, while the Zn—S distances span a rather larger range, *i.e.* 2.399 (1) and 2.409 (1) Å in (1), 2.369 (1)–2.475 (1) Å in (2) ignoring the 2.44 (2) and 2.506 (9) Å distances involving the smaller occupancy sites of S(1*A*) and S(3*A*), respectively, and 2.414 (2) and 2.443 (2) Å in (3). A similar distorted tetrahedral geometry around zinc has been reported for the structure of (*N*,*N*′-dimethyldithiooxamide)dichlorozinc(II) (Antolini *et al.*, 1987).

The S—C distances in (1) and (3) involving terminal methyl groups are significantly shorter [1.800 (4) and 1.809 (4) Å in (1), and 1.793 (6) and 1.802 (6) Å in (3)] than those involving the hydrocarbons [1.827 (4) and 1.830 (4) Å in (1), and 1.841 (6) and 1.831 (5) Å in (3)]. The S—C distances in (2) lie in a broad range, 1.794 (4)–1.848 (5) Å, which may be due to disorder in the two molecules.

The five-membered ZnS_2C_2 ring in (1) adopts a half-chair conformation with the displacement of C atoms from the ZnS_2 plane being C(3) −0.413 (3) and C(4) 0.307 (3) Å. The corresponding rings in the two molecules of (2) also adopt C(3)- and C(12)-envelope conformations, with the C(3) and C(12) atoms 0.591 (5) and 0.635 (5) Å, respectively, out of the plane of the remaining ZnS_2 atoms, involving the major fractions of the disordered atoms. The ZnS_2C_2 ring in (3) has a C(4)-envelope conformation, with C(4) out of the plane of the remaining atoms of the ring by 0.673 (5) Å. The hydrocarbon moieties in (1) and (2) are *trans*-fused to the bis(methylthio)dichlorozinc(II) moiety and exhibit a non-extended conformation of hexane in (1) and a classic chair conformation of cyclohexane in both molecules of (2); the minor fractions of the disordered cyclohexanes were constrained as regular chairs. The cycloheptadiene ring is *cis*-fused to bis(methylthio)dichlorozinc(II) in (3) and adopts a sofa conformation, with C(4) 0.631 (8) Å out of the plane of the rest of the ring C atoms which are planar to within 0.024 (5) Å. The bond distances and angles in the hydrocarbon moieties of the three structures lie within expected values.

Experimental

For the preparation of alkenes (1) and (2), K-10/$ZnCl_2$ (25 g) (Clark, Cullen, Barlow & Bastock, 1994) was suspended in a solution of 1,2-dichloroethane (60 ml) and dimethyl disulfide (2.82 g, 30 mmol) at room temperature. A solution of an alkene (25 mmol) and 1,2-dichloroethane (10 ml) was added dropwise to this mixture. After 3 h the mixture was filtered and the catalyst washed with CH_2Cl_2 (3 × 25 ml). The solution was then evaporated under reduced pressure to yield a clear oil which was triturated with hexane to afford a white solid. Recrystallization was achieved by slow evaporation of ethanol. For the preparation of diene (3), K-10/$ZnCl_2$ (25 g) (Clark, Cullen, Barlow & Bastock, 1994) was suspended in a solution of 1,2-dichloroethane (60 ml) and dimethyl disulfide (2.82 g, 30 mmol) at 243 K. A solution of the diene (25 mmol) and 1,2-dichloroethane (10 ml) was added dropwise to this mixture. After 4 h, the mixture was allowed to warm to room temperature and stirred for an additional 4 h. The mixture was filtered and the catalyst washed with CH_2Cl_2 (3 × 25 ml). The solution was then evaporated under reduced pressure to yield a yellow oil, which was triturated with hexane to afford a yellow solid. Recrystallization was achieved with ethyl acetate/ether to afford pale yellow crystals.

Compound (1)

Crystal data

$[ZnCl_2(C_8H_{18}S_2)]$
$M_r = 314.64$
Monoclinic
$P2_1/n$
$a = 9.170 (3)$ Å
$b = 15.540 (7)$ Å
$c = 9.339 (2)$ Å
$\beta = 99.14 (2)°$
$V = 1313.9 (7)$ Å^3
$Z = 4$
$D_x = 1.590$ Mg m$^{-3$}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 10.0–15.0°$
$\mu = 2.552$ mm^{-1}
$T = 200$ K
Prism
0.40 × 0.35 × 0.21 mm
Colourless

Data collection

Rigaku AFC-6*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical (North, Phillips & Mathews, 1968)
$T_{\min} = 0.433$, $T_{\max} = 0.585$
2582 measured reflections
2428 independent reflections

1597 reflections with $I > 3\sigma(I)$
$R_{\rm int} = 0.041$
$\theta_{\max} = 25.0°$
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 18$
$l = -11 \rightarrow 10$
3 standard reflections every 200 reflections intensity decay: 0.25%

Refinement

Refinement on F
$R = 0.027$
$wR = 0.022$
$S = 1.403$
1597 reflections
119 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o) + 0.008(F_o^2)]$

$(\Delta/\sigma)_{\max} = 0.006$
$\Delta\rho_{\max} = 0.28$ e Å^{-3}
$\Delta\rho_{\min} = -0.31$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °) for (1)*

Zn(1)—Cl(1)	2.192 (1)	S(1)—C(1)	1.800 (4)
Zn(1)—Cl(2)	2.209 (1)	S(1)—C(3)	1.827 (4)
Zn(1)—S(1)	2.399 (1)	S(2)—C(2)	1.809 (4)
Zn(1)—S(2)	2.409 (1)	S(2)—C(4)	1.830 (3)
Cl(1)—Zn(1)—Cl(2)	117.35 (4)	C(1)—S(1)—C(3)	104.3 (2)
Cl(1)—Zn(1)—S(1)	111.49 (4)	Zn(1)—S(2)—C(2)	102.2 (1)
Cl(1)—Zn(1)—S(2)	114.80 (4)	Zn(1)—S(2)—C(4)	101.0 (1)
Cl(2)—Zn(1)—S(1)	110.50 (4)	C(2)—S(2)—C(4)	103.4 (2)
Cl(2)—Zn(1)—S(2)	109.56 (4)	S(1)—C(3)—C(4)	114.5 (2)
S(1)—Zn(1)—S(2)	89.84 (3)	S(1)—C(3)—C(8)	110.1 (2)
Zn(1)—S(1)—C(1)	103.8 (1)	S(2)—C(4)—C(3)	112.5 (2)
Zn(1)—S(1)—C(3)	99.7 (1)	S(2)—C(4)—C(5)	111.1 (2)

Compound (2)

Crystal data

[$ZnCl_2(C_8H_{16}S_2)$]
$M_r = 312.62$
Triclinic
$P\bar{1}$
$a = 12.325\ (2)$ Å
$b = 13.196\ (2)$ Å
$c = 8.535\ (1)$ Å
$\alpha = 107.69\ (1)°$
$\beta = 92.31\ (1)°$
$\gamma = 98.63\ (1)°$
$V = 1302.1\ (4)$ Å^3
$Z = 4$
$D_x = 1.595$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 10.0–17.5°$
$\mu = 2.575$ mm^{-1}
$T = 200$ K
Prismatic
0.60 × 0.55 × 0.48 mm
Colourless

Data collection

Rigaku AFC-6*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical (North, Phillips & Mathews, 1968)
$T_{\min} = 0.269$, $T_{\max} = 0.291$
6289 measured reflections
5997 independent reflections

3887 reflections with $F > 4\sigma(F)$
$R_{\rm int} = 0.027$
$\theta_{\max} = 27.5°$
$h = 0 \rightarrow 16$
$k = -17 \rightarrow 16$
$l = -11 \rightarrow 11$
3 standard reflections every 200 reflections intensity decay: 0.42%

Refinement

Refinement on F^2
$R(F) = 0.029$
$wR(F^2) = 0.060$
$S = 0.998$
5950 reflections
288 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0139P)^2 + 1.9227P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.36$ e Å^{-3}
$\Delta\rho_{\min} = -0.45$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

Zn(1)—Cl(1)	2.201 (1)	Zn(2)—Cl(4)	2.200 (1)
Zn(1)—Cl(2)	2.206 (1)	Zn(2)—Cl(3)	2.210 (1)
Zn(1)—S(1)	2.385 (2)	Zn(2)—S(3)	2.369 (2)
Zn(1)—S(2)	2.475 (1)	Zn(2)—S(4)	2.414 (1)
S(2)—C(2)	1.794 (4)	S(4)—C(10)	1.807 (4)
S(2)—C(4)	1.807 (3)	S(4)—C(12)	1.810 (4)
C(1)—S(1)	1.836 (4)	C(9)—S(3)	1.848 (5)
S(1)—C(3)	1.823 (4)	S(3)—C(11)	1.834 (4)
Cl(1)—Zn(1)—Cl(2)	122.63 (4)	Cl(4)—Zn(2)—Cl(3)	119.52 (4)
Cl(1)—Zn(1)—S(1)	116.85 (6)	Cl(4)—Zn(2)—S(3)	111.72 (6)
Cl(2)—Zn(1)—S(1)	112.77 (6)	Cl(3)—Zn(2)—S(3)	109.86 (6)
Cl(1)—Zn(1)—S(2)	105.42 (4)	Cl(4)—Zn(2)—S(4)	112.47 (4)
Cl(2)—Zn(1)—S(2)	103.11 (4)	Cl(3)—Zn(2)—S(4)	108.51 (4)
S(1)—Zn(1)—S(2)	88.11 (5)	S(3)—Zn(2)—S(4)	91.12 (6)
C(2)—S(2)—C(4)	106.0 (2)	C(10)—S(4)—C(12)	108.3 (2)
C(2)—S(2)—Zn(1)	103.42 (15)	C(10)—S(4)—Zn(2)	102.72 (13)
C(4)—S(2)—Zn(1)	101.05 (12)	C(12)—S(4)—Zn(2)	97.88 (14)
C(3)—S(1)—C(1)	105.1 (2)	C(11)—S(3)—C(9)	105.1 (2)
C(3)—S(1)—Zn(1)	101.94 (14)	C(11)—S(3)—Zn(2)	100.0 (2)
C(1)—S(1)—Zn(1)	99.93 (14)	C(9)—S(3)—Zn(2)	102.5 (2)

Compound (3)

Crystal data

[$ZnCl_2(C_9H_{14}S_2)$]
$M_r = 322.62$
Triclinic
$P\bar{1}$
$a = 7.513\ (6)$ Å
$b = 12.044\ (7)$ Å
$c = 7.470\ (4)$ Å
$\alpha = 95.15\ (2)°$
$\beta = 93.67\ (3)°$
$\gamma = 103.66\ (4)°$
$V = 651.6\ (7)$ Å^3
$Z = 2$
$D_x = 1.644$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 15 reflections
$\theta = 10.0–15.0°$
$\mu = 2.576$ mm^{-1}
$T = 200$ K
Prismatic
0.45 × 0.30 × 0.20 mm
Pale yellow

Data collection

Rigaku AFC-6*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical (North, Phillips & Mathews, 1968)
$T_{\min} = 0.449$, $T_{\max} = 0.597$
2485 measured reflections
2296 independent reflections

1531 reflections with $F > 4\sigma(F)$
$R_{\rm int} = 0.026$
$\theta_{\max} = 25.0°$
$h = 0 \rightarrow 8$
$k = -14 \rightarrow 13$
$l = -8 \rightarrow 8$
3 standard reflections every 200 reflections intensity decay: 1.35%

Refinement

Refinement on F^2
$R(F) = 0.038$
$wR(F^2) = 0.090$
$S = 1.085$
2294 reflections
145 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0404P)^2 + 1.1957P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.003$
$\Delta\rho_{\max} = 0.66$ e Å^{-3}
$\Delta\rho_{\min} = -0.45$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 3. *Selected geometric parameters (Å, °) for (3)*

Zn(1)—Cl(1)	2.190 (2)	S(1)—C(1)	1.793 (6)
Zn(1)—Cl(2)	2.222 (2)	S(1)—C(3)	1.841 (6)
Zn(1)—S(2)	2.414 (2)	S(2)—C(2)	1.802 (6)
Zn(1)—S(1)	2.443 (2)	S(2)—C(4)	1.831 (5)
Cl(1)—Zn(1)—Cl(2)	121.49 (8)	C(1)—S(1)—C(3)	103.8 (3)
Cl(1)—Zn(1)—S(2)	115.45 (7)	C(1)—S(1)—Zn(1)	109.6 (2)
Cl(2)—Zn(1)—S(2)	109.55 (7)	C(3)—S(1)—Zn(1)	98.4 (2)
Cl(1)—Zn(1)—S(1)	111.20 (8)	C(2)—S(2)—C(4)	103.2 (3)
Cl(2)—Zn(1)—S(1)	103.54 (7)	C(2)—S(2)—Zn(1)	104.2 (2)
S(2)—Zn(1)—S(1)	90.55 (6)	C(4)—S(2)—Zn(1)	98.7 (2)

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: *SAPI*91 (Fan, 1991). Program(s) used to refine structures: *TEXSAN* for (1); *SHELXL*93 (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, $[\mathrm{RhH}(\mathrm{C_2B_9H_9Br_2})(\mathrm{C_{18}H_{15}P})_2]$.$\mathrm{CH_2Cl_2}$, the rhodacarborane molecule adopts a closed icosahedral $\mathrm{RhC_2B_9}$-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-$(\mathrm{PPh_3})_2$-3-H-9,12-$(\mathrm{Br})_2$-3,1,2-*closo*-$\mathrm{RhC_2B_9H_9}$], (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 $[\mathrm{Co}(\mathrm{C_2B_9H_8Br_3})_2]^-$, (2) [1.960 (12), 1.968 (14) and 1.940 (11) Å], or those in the silver(I) and caesium salts of the *closo*-$[12\text{-Br-CB}_{11}\mathrm{H}_{11}]^-$ anion, (4) [1.995 (3) and 1.998 (9) Å, respectively; Jelinek, Baldwin, Scheidt & Reed, 1993]. The distances and angles within the $\mathrm{RhC_2B_9}$ cage do not differ substantially from those in either *closo*-[3,3-$(\mathrm{PPh_3})_2$-3-H-3,1,2-$\mathrm{RhC_2B_9H_{11}}$], (5) (Hardy, Callahan, Strouse & Hawthorne, 1976), or *closo*-[3,3-$(\mathrm{PPh_3})_2$-3-Cl-3,1,2-$\mathrm{RhC_2B_9H_{11}}$], (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)

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