7,8-Diphenyl-9-dimethylsulfido-10,11-μ-hydro-7,8-dicarba-*nido*-undecaborane(9)[1]

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In the title compound, $C_{16}H_{25}B_9S$, there are two crystallographically independent molecules, and the conformations of the phenyl and SMe_2 substituents indicate some intramolecular steric crowding. The bridging H atom is asymmetrically disposed. The title compound is a precursor to a crowded vertex-labelled *nido* carborane ligand important in establishing the mechanism of isomerization of icosahedral heteroboranes.

Comment

We have demonstrated recently that deliberately overcrowding dicarbametallaboranes can lead to two interesting consequences (Welch, 1999). Metallation of [7,8-Ph_2-7,8-*nido*-$C_2B_9H_9$]$^{2-}$ with an {$M(\eta$-L)} fragment ($L = \eta$-bonded polyene) affords pseudo-*closo* carbametallaboranes in which the cage C—C connectivity is prized open by Ph···Ph crowding (Brain *et al.*, 1996). In contrast, metallation with {$M(PR_3)_2$} fragments (M = Pt, Ni) or with an {Mo(η-C_3H_5)(CO)$_2$} fragment yields, at low temperatures, C atom isomerizations of either the 1,2→1,7 (Baghurst *et al.*, 1993) or 1,2→1,2 type (Garrioch *et al.*, 1999), including, in the former case, the isolation of an isomerization intermediate (Dunn *et al.*, 1997).
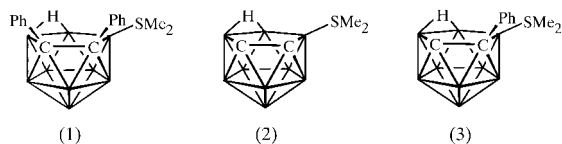
With regard to isomerizations, analogous chemistry using vertex-labelled carborane ligands should lead to a reliable experimental mapping of the isomerization mechanism. Thus we have recently described the consequences of metallation/isomerization of [7,8-Ph_2-10-SMe_2-7,8-*nido*-$C_2B_9H_8$]$^-$ (Dunn *et al.*, 1999) and have begun to prepare other vertex-labelled carboranes (*e.g.* McGrath *et al.*, 2000). We report herein the molecular structure of 7,8-Ph_2-9-SMe_2-7,8-*nido*-$C_2B_9H_9$

[super^{2}carb'H, (1)], a vertex-labelled carborane we first described a few years ago (Rosair *et al.*, 1997) and which we have previously metallated with an {Ru(η-C_5Me_5)} cap (Rosair *et al.*, 1998). Super^{2}carb'H is an analogue of carb'H [(2); Cowie *et al.*, 1994] and 11-supercarb'H [(3); Rosair *et al.*, 1997], both of which have been structurally characterized.

Compound (1) crystallizes with two independent molecules in the asymmetric fraction of the unit cell, and a perspective view of one molecule, together with the atomic numbering scheme, is shown in Fig. 1. In the second independent molecule, corresponding atom labels are primed, except for H10A which becomes H10B.

The carborane cage has the expected *nido*-icosahedral geometry, with Ph substituents at C7 and C8 and an SMe_2 function attached to B9. B10—B11 is bridged asymmetrically by hydrogen [unprimed molecule H10A—B10 1.19 (3) and H10A—B11 1.35 (3) Å; primed molecule H10B—B10′ 1.17 (3) and H10B—B11′ 1.30 (3) Å]. The weighted r.m.s.d. of the {C_2B_9} portion of the unprimed and primed molecules is only 0.007 Å, and only 0.024 Å if atoms C71, C81 and S9 are included.

The conformations of the substituents on the cage are best described by the angles θ and τ. Angle θ is the twist angle of the phenyl substituents, defined (Cowie *et al.*, 1994) as the modulus of the average C_{cage}—C_{cage}—C_{ipso}—C angle, and τ is the C8—B9—S9—S(lone pair) torsion angle (Hamilton & Welch, 1991), calculated from the measurable C8—B9—S9—C(Me) angles. In the unprimed molecule, θ_{ring7}, θ_{ring8} and τ are 3.9 (3), 18.2 (3) and 27.6 (3)°, respectively. In the primed molecule, the corresponding values are 5.6 (3), 13.6 (3) and 18.7 (3)°. These data, taken together with the key molecular parameters in Table 1, provide evidence of intramolecular steric crowding in (1) between the three sequential substituents. The low τ values result from the Me groups on S9 positioning themselves far from the Ph substituent on C8. The deviations of τ and θ_{ring8} from 0° are conrotatory (and anti-clockwise in the sense of Fig. 1) and there is a further geared, although smaller, rotation of ring 7. In (1), the (hydrogen-bridged) facial B10—B11 distance [average 1.864 (6) Å] is, as expected, significantly longer than the (unbridged) B9—B10
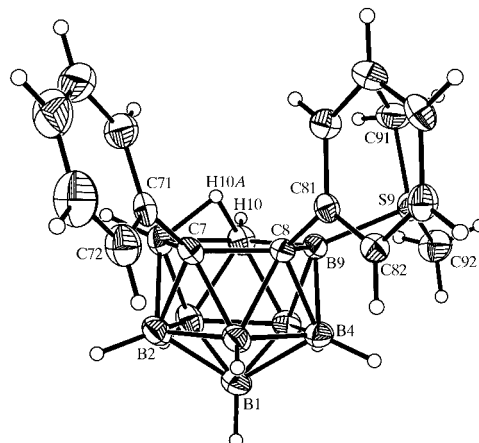

Figure 1
Perspective view of (1) with displacement ellipsoids shown at the 50% probability level for non-H atoms. H atoms are drawn as small circles of arbitrary radii.

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[1] *Steric effects in heteroboranes*. Part 26. For Part 25, see Garrioch *et al.* (2000).

organic compounds

distance [average 1.780 (6) Å]. Less well understood is the fact that C7—B11 is longer than C8—B9, although the same feature has previously been noted in both (2) and (3). In moving from compound (2) to compound (3) (addition of one Ph substituent), both the C8—B9 and C7—C8 distances increase (*ca* 1.58→1.61 and 1.53→1.56 Å, respectively), whilst in moving from (3) to (1) (addition of second Ph substituent), only C7—C8 shows a further increase (*ca* 1.56→1.59 Å).

Deprotonation of (1) followed by addition of an {Ru(η-C₅Me₅)⁺} fragment leads (Rosair *et al.*, 1998) to a pseudo-*closo* carbametallaborane which, although deformed from an icosahedral geometry, has not isomerized. Future contributions (Ellis *et al.*, 2000) will report further metallations of (deprotonated) (1), which result in low-temperature isomerizations and in which the SMe₂ group is used as a marker for the movement of B9 in these rearrangements.

Experimental

The title compound was prepared as described previously (Rosair *et al.*, 1997) and the purity was checked by microanalysis, and ¹H and ¹¹B NMR spectroscopies. Crystals suitable for diffraction were grown from a solution of (1) in CH₂Cl₂, layered with 60–80 petroleum ether.

Crystal data

$C_{16}H_{25}B_9S$	$D_x = 1.139$ Mg m⁻³
$M_r = 346.71$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 45
$a = 13.039$ (2) Å	reflections
$b = 15.2610$ (16) Å	$\theta = 2.66–16.24°$
$c = 21.319$ (5) Å	$\mu = 0.156$ mm⁻¹
$\beta = 107.581$ (14)°	$T = 160$ (2) K
$V = 4044.2$ (13) Å³	Plate, colourless
$Z = 8$	$0.62 \times 0.44 \times 0.21$ mm

Data collection

Bruker $P4$ diffractometer	$R_{int} = 0.033$
ω scans	$\theta_{max} = 25°$
Absorption correction: ψ scan	$h = -15 \rightarrow 1$
(North *et al.*, 1968)	$k = -18 \rightarrow 1$
$T_{min} = 0.924$, $T_{max} = 0.968$	$l = -24 \rightarrow 25$
8786 measured reflections	3 standard reflections
7111 independent reflections	every 97 reflections
5279 reflections with $I > 2\sigma(I)$	intensity decay: 1.7%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0523P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.050$	$+ 1.8495P]$
$wR(F^2) = 0.129$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.037$	$(\Delta/\sigma)_{max} = 0.001$
7111 reflections	$\Delta\rho_{max} = 0.40$ e Å⁻³
523 parameters	$\Delta\rho_{min} = -0.22$ e Å⁻³
H atoms treated by a mixture of	
independent and constrained	
refinement	

Phenyl H atoms were set riding with C—H = 0.95 Å and with isotropic displacement parameters equal to $1.2U_{eq}$ of the corresponding C atom. Cluster H atoms were allowed free positional refinement, but were assigned isotropic displacement parameters equal to $1.2U_{eq}$ of the corresponding B atom.

Data collection: *XSCANS* (Bruker, 1997); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Sheldrick, 1999); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Table 1
Selected geometric parameters (Å, °).

C7—C8	1.585 (3)	C7′—C8′	1.585 (3)
C7—B11	1.654 (3)	C7′—B11′	1.651 (3)
C7—C71	1.508 (3)	C7′—C71′	1.507 (3)
C8—B9	1.612 (3)	C8′—B9′	1.617 (3)
C8—C81	1.507 (3)	C8′—C81′	1.509 (3)
B9—S9	1.889 (3)	B9′—S9′	1.888 (3)
B9—B10	1.782 (4)	B9′—B10′	1.778 (4)
B10—B11	1.862 (4)	B10′—B11′	1.863 (4)
B10—H10A	1.19 (3)	B10′—H10B	1.17 (3)
B11—H10A	1.35 (3)	B11′—H10B	1.30 (3)
S9—C91	1.796 (3)	S9′—C91′	1.804 (3)
S9—C92	1.792 (3)	S9′—C92′	1.797 (3)
C71—C7—C8	118.83 (18)	C71′—C7′—C8′	120.43 (17)
C81—C8—C7	117.32 (18)	C81′—C8′—C7′	116.92 (18)
C92—S9—C91	99.89 (13)	C92′—S9′—C91′	100.89 (19)
C92—S9—B9	103.29 (12)	C92′—S9′—B9′	104.49 (13)
C91—S9—B9	105.16 (12)	C91′—S9′—B9′	104.08 (13)
C8—C7—C71—C76	94.3 (3)	C8′—C7′—C71′—C72′	98.0 (3)
C8—C7—C71—C72	−86.5 (3)	C8′—C7′—C71′—C76′	−86.9 (3)
C7—C8—C81—C82	109.2 (2)	C7′—C8′—C81′—C82′	−104.6 (3)
C7—C8—C81—C86	−72.8 (3)	C7′—C8′—C81′—C86′	77.4 (3)
C8—B9—S9—C92	155.50 (18)	C8′—B9′—S9′—C92′	−146.0 (2)
B10—B9—S9—C92	−58.0 (2)	B10′—B9′—S9′—C92′	69.1 (3)
C8—B9—S9—C91	−100.21 (19)	C8′—B9′—S9′—C91′	108.6 (2)
B10—B9—S9—C91	46.3 (2)	B10′—B9′—S9′—C91′	−36.4 (3)

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