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

Br(1)—C(2)	1.888 (6)	B(4)—B(9)	1.758 (12)
C(1)—C(2)	1.692 (8)	B(5)—B(6)	1.764 (10)
C(1)—B(3)	1.735 (9)	B(5)—B(9)	1.780 (12)
C(1)—B(4)	1.728 (9)	B(5)—B(10)	1.773 (11)
C(1)—B(5)	1.714 (9)	B(6)—B(10)	1.755 (11)
C(1)—B(6)	1.737 (9)	B(6)—B(11)	1.780 (11)
C(1)—C(11)	1.494 (7)	B(7)—B(8)	1.770 (12)
C(2)—B(3)	1.701 (9)	B(7)—B(11)	1.804 (12)
C(2)—B(6)	1.721 (9)	B(7)—B(12)	1.790 (12)
C(2)—B(7)	1.693 (10)	B(8)—B(9)	1.772 (12)
C(2)—B(11)	1.725 (10)	B(8)—B(12)	1.800 (12)
B(3)—B(4)	1.763 (11)	B(9)—B(10)	1.766 (12)
B(3)—B(7)	1.769 (11)	B(9)—B(12)	1.744 (13)
B(3)—B(8)	1.735 (11)	B(10)—B(11)	1.741 (12)
B(4)—B(5)	1.792 (11)	B(10)—B(12)	1.755 (12)
B(4)—B(8)	1.755 (11)	B(11)—B(12)	1.755 (12)
C(2)—C(1)—B(3)	59.5 (4)	C(1)—B(6)—B(5)	58.6 (4)
C(2)—C(1)—B(6)	60.3 (4)	C(2)—B(6)—B(11)	59.0 (4)
C(2)—C(1)—C(11)	121.1 (4)	B(5)—B(6)—B(10)	60.5 (4)
B(3)—C(1)—B(4)	61.2 (4)	B(10)—B(6)—B(11)	59.0 (5)
B(3)—C(1)—C(11)	118.0 (4)	C(2)—B(7)—B(3)	58.8 (4)
B(4)—C(1)—B(5)	62.8 (4)	C(2)—B(7)—B(11)	59.0 (4)
B(4)—C(1)—C(11)	120.9 (4)	B(3)—B(7)—B(8)	58.7 (4)
B(5)—C(1)—B(6)	61.5 (4)	B(8)—B(7)—B(12)	60.7 (5)
B(5)—C(1)—C(11)	121.7 (4)	B(11)—B(7)—B(12)	58.5 (5)
B(6)—C(1)—C(11)	119.5 (4)	B(3)—B(8)—B(4)	60.7 (4)
Br(1)—C(2)—C(1)	116.7 (4)	B(3)—B(8)—B(7)	60.6 (5)
Br(1)—C(2)—B(3)	117.7 (4)	B(4)—B(8)—B(9)	59.8 (5)
Br(1)—C(2)—B(6)	115.9 (4)	B(7)—B(8)—B(12)	60.2 (5)
Br(1)—C(2)—B(7)	120.8 (4)	B(9)—B(8)—B(12)	58.4 (5)
Br(1)—C(2)—B(11)	120.5 (4)	B(4)—B(9)—B(5)	60.9 (5)
C(1)—C(2)—B(3)	61.5 (4)	B(4)—B(9)—B(8)	59.6 (5)
C(1)—C(2)—B(6)	61.2 (4)	B(5)—B(9)—B(10)	60.0 (5)
B(3)—C(2)—B(7)	62.8 (4)	B(8)—B(9)—B(12)	61.6 (5)
B(6)—C(2)—B(11)	62.2 (4)	B(10)—B(9)—B(12)	60.0 (5)
B(7)—C(2)—B(11)	63.7 (4)	B(5)—B(10)—B(6)	60.0 (4)
C(1)—B(3)—C(2)	59.0 (4)	B(5)—B(10)—B(9)	60.4 (5)
C(1)—B(3)—B(4)	59.2 (4)	B(6)—B(10)—B(11)	61.2 (5)
C(2)—B(3)—B(7)	58.4 (4)	B(9)—B(10)—B(12)	59.4 (5)
B(4)—B(3)—B(8)	60.2 (4)	B(11)—B(10)—B(12)	60.3 (5)
B(7)—B(3)—B(8)	60.7 (5)	C(2)—B(11)—B(6)	58.8 (4)
C(1)—B(4)—B(3)	59.6 (4)	C(2)—B(11)—B(7)	57.3 (4)
C(1)—B(4)—B(5)	58.2 (4)	B(6)—B(11)—B(10)	59.8 (5)
B(3)—B(4)—B(8)	59.1 (4)	B(7)—B(11)—B(12)	60.4 (5)
B(5)—B(4)—B(9)	60.2 (4)	B(10)—B(11)—B(12)	60.3 (5)
B(8)—B(4)—B(9)	60.6 (5)	B(7)—B(12)—B(8)	59.1 (5)
C(1)—B(5)—B(4)	59.0 (4)	B(7)—B(12)—B(11)	61.2 (5)
C(1)—B(5)—B(6)	59.9 (4)	B(8)—B(12)—B(9)	60.0 (5)
B(4)—B(5)—B(9)	59.0 (4)	B(10)—B(12)—B(11)	59.5 (5)
B(6)—B(5)—B(10)	59.5 (4)	C(1)—C(11)—C(12)	119.8 (4)
B(9)—B(5)—B(10)	59.6 (5)	C(1)—C(11)—C(16)	120.1 (4)
C(1)—B(6)—C(2)	58.6 (4)		

The C atoms of the phenyl ring were constrained to form a regular hexagon (C—C = 1.395 Å); cage H atoms were allowed positional refinement subject to a common B—H distance of 1.11 (5) Å; phenyl H atoms were set in idealized positions. All H atoms were refined with a single group displacement parameter [0.060 (49) Å² at convergence].

Data reduction and corrections for Lorentz and polarization effects were performed using *CADABS* (Gould & Smith, 1986). *SHELX*76 (Sheldrick, 1976) was used to solve (Patterson synthesis for Br atom, difference Fourier syntheses for C, B and cage H atoms) and refine the structure. Fig. 1 was drawn using *SHELXTL/PC* (Sheldrick, 1990). Molecular geometry calculations were made using *CALC* (Gould & Taylor, 1986).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1111). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Steric Effects in Heteroboranes. V. 1-Ph-2-Me₃Si-1,2-*closo*-C₂B₁₀H₁₀

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Abstract

The structure of 1-phenyl-2-trimethylsilyl-1,2-dicarba-*closo*-dodecaborane(12), $C_{11}H_{24}B_{10}Si$, has been determined crystallographically. The C_{cage}—C_{cage} distance is 1.708 (4) Å, only slightly longer than in the 2-methyl analogue. However, in contrast to the 2-methyl and 2-bromo analogues, relief from steric congestion is afforded by a mutual 'bend back' of both the phenyl and trimethylsilyl groups, the latter involving deformation of valency angles both at Si and the C_{cage} atom to which it is attached.

Comment

In the two preceding papers in the series (McGrath & Welch, 1995a,b) we described the molecular struc-

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tures of 1-Ph-2-Me-1,2-*closo*-$C_2B_{10}H_{10}$ and 1-Ph-2-Br-1,2-*closo*-$C_2B_{10}H_{10}$, respectively. These were examined as potential reference members of a series of compounds 1-Ph-2-*R*-1,2-*closo*-$C_2B_{10}H_{10}$ with the group *R* varying in steric demand, in the anticipation that the exopolyhedral Me or Br substituent would afford relatively little Ph···*X* congestion, while establishing a reference orientation for the phenyl substituent. In the light of these studies, the bromocarbaborane was chosen as the more suitable reference point for this series. We now present the structure of 1-Ph-2-Me₃Si-1,2-*closo*-$C_2B_{10}H_{10}$, (I), which is liable to exhibit intramolecular crowding of greater significance.
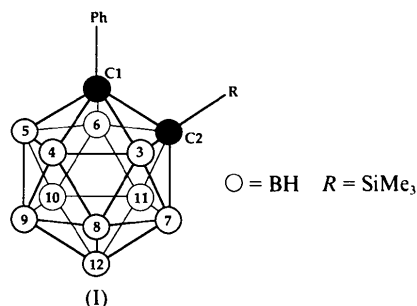

(I)

Fig. 1 shows a perspective view of a single molecule of the title compound and the atomic numbering scheme employed. Note that for consistency we have again chosen to label the C_{cage} atom bearing the aryl moiety as C(1); the crystallographic numbering scheme for the cage atoms differs from conventional chemical numbering, in which B(4ⁱ), B(3ⁱ), B(8ⁱ) and B(7ⁱ) would be B(5), B(6), B(10) and B(11), respectively.

The title compound crystallizes as isolated molecules with no close intermolecular approaches, and with crystallographically imposed C_s molecular symmetry. As a direct consequence of this constraint, any molecular distortion which relieves steric congestion clearly must maintain the mirror symmetry. Thus, both the angle θ describing the conformation of the phenyl ring about C(1)—C(11) (θ is the modulus of the average of the two C_{cage}—C_{cage}—C—C torsion angles), and the torsion angle C(11)—C(1)—C(2)—Si(1), must be exactly zero; hence no relief from crowding may here be achieved by a mutual twisting away of substituents *via* a combination of these modes.

In the present compound the C(1)—C(11) distance is 1.513 (4) Å, essentially the same as in the 2-Me analogue [1.514 (4) Å] but 0.019 (8) Å longer than in the corresponding 2-Br species [1.494 (8) Å]. However, the C(1)—C(2) bond [1.708 (4) Å] is only slightly longer than the corresponding distance in the 2-Me and 2-Br analogues [1.696 (5) and 1.692 (8) Å, respectively]. Although this latter minor elongation may perhaps be attributed in part to the value of θ being as low as is possible, which has been predicted (Lewis & Welch, 1993) to weaken the C_{cage}—C_{cage} bond, it is

nevertheless surprising that the replacement of Me or Br by SiMe₃ apparently causes such a small change in C(1)—C(2). Closer examination of the structure of the title compound affords a rationalization of this anomaly: in brief, both cluster substituents bend measurably away from each other, thus minimizing their mutual steric congestion.

The phenyl ring is essentially planar (r.m.s. deviation ~ 0.02 Å), and does not appear to move away from the adjacent trimethylsilyl moiety [C(2)—C(1)—C(11) is 119.9 (3)°]. However, there is evidence of structural flexibility in the SiMe₃ group, which apparently takes the form of two distinct 'bending back' mechanisms. The first involves bend back at Si, since C(22)—Si(1)—C(2) is greater than C(21)—Si(1)—C(2) by *ca* 5°; the second involves bend back at C(2), since the largest Si(1)—C(2)—*X* angle is that to C(1).

Such bending-back mechanisms are not without precedent. In the uncrowded 1-Me₃Si-1,2-*closo*-$C_2B_{10}H_{11}$ (Kirillova, Klimova, Struchkov & Stanko, 1981) there is no deformation of the SiMe₃ group and this whole group actually bends forward towards the other cage C atom, while in the more congested relative 1-Me-2-Me₃Si-1,2-*closo*-$C_2B_{10}H_{10}$ (Kirillova, Klimova, Struchkov & Stanko, 1979) the trimethylsilyl group behaves in a manner similar to that observed in the present compound, albeit to a slightly lesser extent.

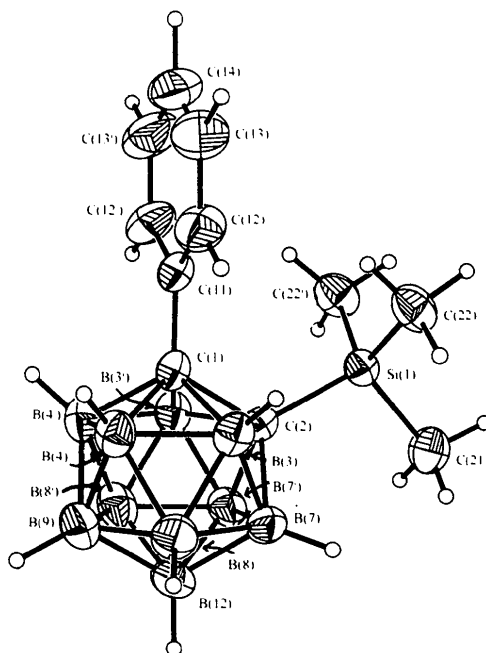In conclusion, this study has revealed further possible modes by which *C*-substituted 1-phenyl-*closo*-1,2-

Fig. 1. A perspective view of 1-Ph-2-Me₃Si-1,2-*closo*-$C_2B_{10}H_{10}$. Displacement ellipsoids are shown at the 50% probability level for non-H atoms and H atoms are represented by spheres with arbitrary radii of 0.1 Å. [Symmetry code: (i) x, $\frac{1}{2} - y$, z.]

carbaboranes may accommodate steric overcrowding; namely, bending back of exopolyhedral substituents and internal distortions of these substituents. These are in addition to previously recognized modes, principally lengthening of the C_{cage}—C_{cage} connectivity and twist of the phenyl group. Other contibutions (e.g. McGrath & Welch, 1995c) will discuss these phenomena further.

Experimental

The title compound was synthesized in very good yield from 1-Ph-1,2-closo-$C_2B_{10}H_{11}$ by an improvement upon the method of Zakharkin, Bregadze & Okhlobytsin (1965). Typically, 1-Ph-1,2-closo-$C_2B_{10}H_{11}$ (0.50 g, 2.27 mmol) (Reid, 1992) was dissolved in benzene (25 ml) and cooled to 273 K. MeLi (2.50 mmol, 1.8 ml of 1.4 M solution in Et_2O) was added dropwise, and the mixture allowed to warm to room temperature. A solution of Me_3SiCl (0.27 g, 2.49 mmol) in benzene (5 ml) was added dropwise; the mixture was stirred for 20 h, and finally warmed to 318 K for 2 h. Removal of volatiles in vacuo yielded a white solid. The product was extracted into CH_2Cl_2 (100 ml) and the extract filtered and evaporated to yield the title compound as a white powder (0.60 g 2.05 mmol, 90%). Found: 45.40% C; 8.51% H. Calculated for $C_{11}H_{24}B_{10}Si$: 45.17% C; 8.27% H. IR (CH_2Cl_2): ν_{CH} = 2980, ν_{BH} = 2570 cm^{-1}. NMR (298 K, $CDCl_3$): $\delta(^1H)$ 7.68–7.27 (5H, C_6H_5), −0.09 p.p.m. [9H, $(CH_3)_3Si$; $^1J_{13_{CH}} \simeq 120$ Hz, $^2J_{29_{SiH}} \simeq 7$ Hz]; $\delta(^{11}B)$ 1.99 (1B), −1.94 (1B), −7.26 (4B), −9.37 (2B), −10.97 (2B) p.p.m. Crystals were obtained by the slow diffusion of water into a methanol solution at 277 K.

Crystal data

$C_{11}H_{24}B_{10}Si$
M_r = 292.51
Monoclinic
$P2_1/m$
a = 8.931 (2) Å
b = 11.303 (6) Å
c = 9.143 (2) Å
β = 103.47 (2)°
V = 897.5 (6) Å^3
Z = 2
D_x = 1.082 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 11–12°
μ = 0.11 mm^{-1}
T = 293 (1) K
Plate
0.4 × 0.25 × 0.15 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
3375 measured reflections
1666 independent reflections
1442 observed reflections [$F \geq 2.0\sigma(F)$]

R_{int} = 0.0128
θ_{max} = 25°
h = −10 → 10
k = −13 → 13
l = 0 → 10
2 standard reflections frequency: 480 min intensity decay: 0.9%

Refinement

Refinement on F
R = 0.0643
wR = 0.0892

$\Delta\rho_{max}$ = 0.43 e Å^{-3} (near Si)
$\Delta\rho_{min}$ = −0.25 e Å^{-3}

S = 1.341
1442 reflections
122 parameters
$w = 1/[\sigma^2(F) + 0.001314F^2]$
$(\Delta/\sigma)_{max}$ = 0.001

Extinction correction: none
Atomic scattering factors from SHELX76 (Sheldrick, 1976)

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}
C(1)	−0.3575 (4)	1/4	−0.0839 (4)	0.035 (2)
C(2)	−0.1623 (4)	1/4	−0.0630 (4)	0.033 (2)
B(3)	−0.2542 (4)	0.3758 (3)	−0.0224 (4)	0.0418 (18)
B(4)	−0.4067 (4)	0.3288 (3)	0.0575 (4)	0.048 (2)
B(7)	−0.0790 (4)	0.3288 (3)	0.0948 (4)	0.046 (2)
B(8)	−0.2312 (4)	0.3772 (4)	0.1753 (4)	0.056 (2)
B(9)	−0.3232 (6)	1/4	0.2270 (6)	0.061 (4)
B(12)	−0.1216 (7)	1/4	0.2481 (6)	0.061 (4)
C(11)	−0.4626 (4)	1/4	−0.2398 (5)	0.041 (2)
C(12)	−0.5158 (4)	0.3560 (3)	−0.3099 (4)	0.060 (2)
C(13)	−0.6163 (4)	0.3560 (5)	−0.4495 (5)	0.084 (3)
C(14)	−0.6660 (6)	1/4	−0.5207 (7)	0.100 (5)
Si(1)	−0.06582 (12)	1/4	−0.23160 (12)	0.0380 (7)
C(21)	0.1443 (5)	1/4	−0.1478 (6)	0.070 (3)
C(22)	−0.1222 (4)	0.3846 (3)	−0.3476 (3)	0.057 (2)

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

C(1)—C(2)	1.708 (4)	B(4)—B(4^i)	1.781 (5)
C(1)—B(3)	1.717 (4)	B(7)—B(8)	1.776 (5)
C(1)—B(4)	1.710 (5)	B(7)—B(12)	1.775 (6)
C(1)—C(11)	1.513 (4)	B(7)—B(7^i)	1.780 (5)
C(2)—B(3)	1.725 (4)	B(8)—B(9)	1.774 (6)
C(2)—B(7)	1.711 (5)	B(8)—B(12)	1.779 (6)
C(2)—Si(1)	1.934 (3)	B(9)—B(12)	1.765 (7)
B(3)—B(4)	1.770 (5)	C(11)—C(12)	1.389 (5)
B(3)—B(7)	1.760 (5)	C(12)—C(13)	1.379 (6)
B(3)—B(8)	1.771 (5)	C(13)—C(14)	1.386 (7)
B(4)—B(8)	1.770 (5)	Si(1)—C(21)	1.855 (4)
B(4)—B(9)	1.792 (6)	Si(1)—C(22)	1.856 (4)
C(2)—C(1)—B(3)	60.49 (18)	B(3)—B(7)—B(8)	60.1 (2)
C(2)—C(1)—C(11)	119.9 (3)	B(8)—B(7)—B(12)	60.1 (2)
C(3)—C(1)—B(4)	62.2 (2)	B(12)—B(7)—B(7^i)	59.9 (2)
B(3)—C(1)—C(11)	118.5 (3)	B(3)—B(8)—B(4)	60.0 (2)
B(4)—C(1)—C(11)	120.0 (3)	B(3)—B(8)—B(7)	59.5 (2)
B(4)—C(1)—B(4^i)	62.8 (2)	B(4)—B(8)—B(9)	60.8 (2)
C(1)—C(2)—B(3)	60.02 (18)	B(7)—B(8)—B(12)	59.9 (2)
C(1)—C(2)—Si(1)	122.9 (2)	B(9)—B(8)—B(12)	59.6 (2)
B(3)—C(2)—B(7)	61.64 (19)	B(4)—B(9)—B(8)	59.5 (2)
B(3)—C(2)—Si(1)	119.6 (2)	B(4)—B(9)—B(4^i)	60.0 (2)
B(7)—C(2)—Si(1)	119.0 (2)	B(8)—B(9)—B(12)	60.4 (3)
B(7)—C(2)—B(7^i)	62.70 (19)	B(7)—B(12)—B(8)	60.0 (2)
C(1)—B(3)—C(2)	59.49 (18)	B(7)—B(12)—B(7^i)	60.2 (2)
C(1)—B(3)—B(4)	58.69 (19)	B(8)—B(12)—B(9)	60.1 (3)
C(2)—B(3)—B(7)	58.78 (19)	C(1)—C(11)—C(12)	120.3 (3)
B(4)—B(3)—B(8)	60.0 (2)	C(12)—C(11)—C(12^i)	119.2 (3)
B(7)—B(3)—B(8)	60.4 (2)	C(11)—C(12)—C(13)	120.4 (3)
C(1)—B(4)—B(3)	59.11 (19)	C(12)—C(13)—C(14)	120.2 (4)
C(1)—B(4)—B(4^i)	58.61 (19)	C(13)—C(14)—C(13^i)	119.6 (4)
B(3)—B(4)—B(8)	60.0 (2)	C(2)—Si(1)—C(21)	105.48 (16)
B(8)—B(4)—B(9)	59.7 (2)	C(2)—Si(1)—C(22)	110.10 (14)
B(9)—B(4)—B(4^i)	60.2 (2)	C(21)—Si(1)—C(22)	110.48 (17)
C(2)—B(7)—B(3)	59.58 (19)	C(22)—Si(1)—C(22^i)	110.11 (16)
C(2)—B(7)—B(7^i)	58.65 (19)		

Symmetry code: (i) $x, \frac{1}{2} - y, z$.

Methyl, phenyl and cage H atoms were set in idealized positions (C—H = 1.08, B—H = 1.10 Å). A common H-atom displacement parameter, U_{iso} = 0.092 (4) Å^2 at convergence, was refined.

Data reduction and corrections for Lorentz and polarization effects were carried out using CADABS (Gould & Smith,

1986). *SHELXS86* (Sheldrick, 1985) was used to solve the structure (using direct methods for C and B atoms). *SHELX76* (Sheldrick, 1976) was used to refine the structure. Molecular graphics were prepared using *SHELXTL/PC* (Sheldrick, 1990). Molecular-geometry calculations were carried out using *CALC* (Gould & Taylor, 1986).

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Steric Effects in Heteroboranes. VI. 1-Ph-2-tBuMe2Si-1,2-*closo*-C2B10H10

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Abstract

The new icosahedral *closo*-dicarbaborane 1-phenyl-2-(*tert*-butyldimethylsilyl)-1,2-dicarba-*closo*-dodecabor-

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ane(12), $C_{14}H_{30}B_{10}Si$, has been prepared and its structure determined by a crystallographic study. Although some relief from steric crowding is achieved by a bending back of the cage-bound phenyl substituent, the bulk of the *tert*-butyldimethylsilyl group severely restricts any bending back of the silyl moiety. In consequence, some deformation of the cage has resulted. Most significantly, the C_{cage}—C_{cage} connectivity suffers a considerable extension: the C(1)—C(2) distance is 1.745 (6) Å, one of the longest observed in systems of this type.

Comment

In preceding contributions (McGrath & Welch, 1995*a,b*) we presented the molecular structures of 1-Ph-2-Me-1,2-*closo*-C2B10H10 and 1-Ph-2-Br-1,2-*closo*-C2B10H10, respectively, considered as possible (uncrowded and hence relatively undistorted) reference members of a series of 1-Ph-2-*R*-1,2-*closo*-C2B10H10 carbaboranes in which the substituent *R* varies in steric requirement. The preceding paper (McGrath & Welch, 1995*c*) describes the structure of 1-Ph-2-Me3Si-1,2-*closo*-C2B10H10, which exhibits somewhat greater steric congestion. We now report the synthesis and molecular structure of the new carbaborane 1-Ph-2-tBuMe2Si-1,2-*closo*-C2B10H10, (I), where intramolecular crowding to a greater degree is anticipated.
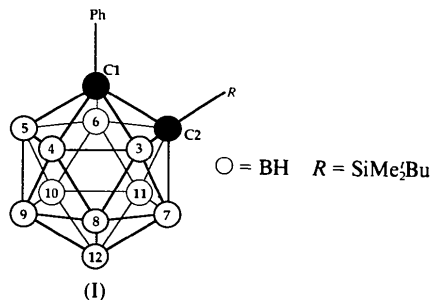

(I)

Fig. 1 shows a perspective view of a single molecule of the title compound and the atomic numbering scheme adopted. Note that for consistency we have again labelled the C_{cage} atom bearing the aryl moiety as C(1). The title compound crystallizes with no close intermolecular contacts.

Gross intramolecular crowding is substantially reduced by the disposition of the trialkylsilyl group, which is oriented such that the tBu group is *anti* to the phenyl ring. Although this brings the tBu moiety close to the carbaborane polyhedron, this situation appears to be less serious than unfavourable steric interaction arising from proximity to the phenyl substituent.

The C(1)—C(11) distance in 1-Ph-2-tBuMe2Si-1,2-*closo*-C2B10H10 is 1.493 (5) Å, essentially the same as in 1-Ph-2-Br-1,2-*closo*-C2B10H10 [1.494 (7) Å], but slightly shorter than in the 2-Me [1.514 (5) Å] and 2-