

Sterically encumbered charge-compensated carbaboranes: synthesis and reactivity

Molecular structures of 7-Ph-11-SMe₂-7,8-*nido*-C₂B₉H₁₀ and 1-Ph-3,3-(CO)₂-7-SMe₂-3,1,2-*closo*-RhC₂B₉H₈^{1,2}

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Abstract

Reaction between K[7-Ph-7,8-*nido*-C₂B₉H₁₁] and dmsO in H₂SO₄ affords a mixture of the isomers 7-Ph-9-SMe₂-7,8-*nido*-C₂B₉H₁₀ (**1a**) and 7-Ph-11-SMe₂-7,8-*nido*-C₂B₉H₁₀ (**1b**). Similarly, starting from K[7,8-Ph₂-7,8-*nido*-C₂B₉H₁₀], the diphenyl analogue 7,8-Ph₂-9-SMe₂-7,8-*nido*-C₂B₉H₉ (**2**) was produced. These three new *nido* carbaboranes have been characterised spectroscopically, including ¹¹B–¹¹B COSY and ¹H–¹H NOESY experiments, and by a single crystal diffraction study on **1b**. Deprotonation of **1a** followed by addition of [RhCl(CO)₂]₂ affords the carbametallaborane 1-Ph-3,3-(CO)₂-7-SMe₂-3,1,2-*closo*-RhC₂B₉H₉ (**3**), characterised by IR and ¹H and ¹¹B NMR spectroscopies and by a crystallographic study. © 1997 Elsevier Science S.A.

Keywords: Boron; Rhodium; Carbaboranes; Steric effects; Crystal structure

1. Introduction

Recently we have been interested in the use of sterically crowded carbaboranes to induce polytopal deformations or isomerisations in carbametallaboranes derived from them. These investigations have centred around the di-anionic {7,8-Ph₂-7,8-*nido*-C₂B₉H₉}²⁻ fragment, in which steric congestion can result in the isolation of products in which the C_{cage}–C_{cage} connectivity is formally broken (pseudocloso compounds) [2] or those in which cage carbon isomerisation has occurred [3]. However, these investigations are often lim-

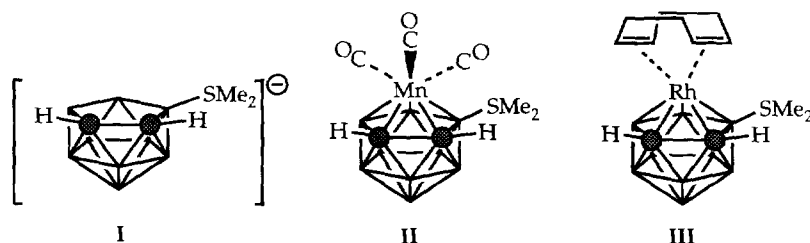
ited to metal fragments which have a formal 2+ charge, as these give products which are overall neutral and thus easily separable by chromatographic techniques. We are interested in extending this chemistry to metal fragments with a formal 1+ charge, and thus sought a suitable mono-anionic carbaborane ligand.

We have previously shown that the ‘charge-compensated’ carbaborane anion [9-SMe₂-7,8-*nido*-C₂B₉H₁₀]⁻ ([carb’]⁻, **I**) can be combined with monocationic metal fragments to give stable, neutral products. Thus, reaction between [*fac*-Mn(NCMe)₃(CO)₃][BPh₄] and Tl[carb’] affords [4-SMe₂-3,3,3-(CO)₃-3,1,2-*closo*-MnC₂B₉H₁₀] (**II**) [4] and between [RhCl(η²,η²-cod)]₂ and Tl[carb’] affords [4-SMe₂-3-(η²,η²-cod)-3,1,2-*closo*-RhC₂B₉H₁₁] (**III**) [5]. **II** and **III** constituting carbametallaborane analogues of the well-known cyclopentadienyl complexes CpMn(CO)₃ and CpRh(η²,η²-cod) respectively.

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¹ Dedicated to the memory of Professor Yuri T. Struchkov, in recognition of his many outstanding contributions to structural chemistry.

² Steric effects in heteroboranes. Part 14. For part 13 see Ref. [1].



Whilst there is current interest in metal complexes of charge-compensated carbaboranes [6], we are not aware of any reports describing crowded charge-compensated species.

We report here the synthesis of three new carbaboranes which are sterically encumbered derivatives of carb^hH, their full characterisation by NMR spectroscopy (including assignment by ¹¹B–¹¹B COSY, and ¹H–¹H NOESY experiments), and, for one, the results of a single crystal X-ray diffraction study. We also report the synthesis and characterisation of the first transition metal complex of one of them.

2. Experimental

2.1. Synthesis of new compounds

2.1.1. General

All experiments were carried out under a dry, oxygen-free dinitrogen atmosphere, using Schlenk line techniques, although all the new compounds reported are stable to the ambient atmosphere both as solids and as solutions. All solvents were dried over the appropriate drying agents immediately prior to use: CH₂Cl₂, CaH₂; thf, Na wire–benzophenone; 40–60 °C and 60–80 °C light petroleum fractions, Na wire; diethyl ether, Na wire–benzophenone. Microanalyses were performed by Napier University. Chromatography columns (3 × 25 cm) were packed with silica (Kieselgel 60, 200 to 400 mesh). The compounds [RhCl(CO)]₂ [7], K[7-Ph-7,8-*nido*-C₂B₉H₁₁] [8] and K[7,8-Ph₂-7,8-*nido*-C₂B₉H₁₀]³ were prepared by the published procedures or slight modifications thereof.

2.1.2. Infrared spectroscopy

Infrared spectra were recorded from CH₂Cl₂ solutions, using 0.1 mm solution cells and a Nicolet Impact 400 FTIR spectrophotometer.

³ Synthesis of K[7,8-Ph₂-7,8-*nido*-C₂B₉H₁₀] adapted from that given for K[7-Ph-7,8-*nido*-C₂B₉H₁₁] in Ref. [8].

2.1.3. NMR spectroscopy

¹H NMR spectra were recorded on a Bruker AC 200 spectrometer. ¹¹B spectra (one- and two-dimensional), ¹H NOE and ¹H–¹H NOESY experiments were recorded on a Bruker DPX 400 spectrometer. Measurements were recorded at 297 K from CDCl₃ solutions unless otherwise stated. Proton chemical shifts are reported relative to residual protio solvent in the sample, and ¹¹B shifts (at 128.0 MHz) are relative to external BF₃ · OEt₂.

2.1.4. 7-Ph-9-SMe₂-7,8-*nido*-C₂B₉H₁₀ (**1a**) and 7-Ph-11-SMe₂-7,8-*nido*-C₂B₉H₁₀ (**1b**)

K[7-Ph-7,8-*nido*-C₂B₉H₁₁] (1.30 g, 5.2 mmol) was dissolved in a mixture of H₂O (5 cm³) and dmsO (1.5 cm³) to afford a clear solution and cooled in an ice bath. H₂SO₄ (conc., 5.5 cm³) was added dropwise under N₂ to the cooled solution over 15 min and the resulting sticky solid was stirred for 4 days under N₂ to afford a white precipitate. H₂O (20 cm³) was added to the suspension, which was then filtered. The solid thus recovered was washed twice with H₂O and dissolved in CH₂Cl₂ (50 cm³). The resulting solution was dried over MgSO₄ and then reduced in vacuo to ca. 5 cm³. It was then filtered through a short plug of silica (5 cm) and finally purified by column chromatography (CH₂Cl₂:60–80 petroleum ether, 3:2) to afford the colourless materials 7-Ph-9-SMe₂-7,8-*nido*-C₂B₉H₁₀ (9-supercarb^hH, **1a**), mass 0.156 g, yield 11% (first eluted) and 7-Ph-11-SMe₂-7,8-*nido*-C₂B₉H₁₀ (11-supercarb^hH, **1b**), mass 0.104 g, yield 7%. Diffraction-quality single crystals of **1b** were grown by the slow diffusion of a CH₂Cl₂ solution and 60–80 petroleum ether at –30 °C.

For **1a**: C₁₀H₂₁B₉S requires %C, 44.4; %H, 7.82. Found: %C, 43.9; %H, 7.58. IR: ν_{max} 2524 cm⁻¹. NMR: ¹H, δ 7.35–7.13 (m, 5H, Ph), 3.06 (s br, 1H, cage-CH), 2.82 (s, 3H, SMe), 2.62 (s, 3H, SMe) ppm; ¹¹B δ –1.69 (d, 1B, J(HB) 134 Hz), –3.74 (s, 1B), –6.10 (d, 1B, J(HB) 147 Hz), –11.53 (d, 2B, J(HB) 135 Hz) (coincident signal), –20.24 (d, 1B, J(HB) 147 Hz), –23.63 (d, 1B, J(HB) 142 Hz), –26.05 (d, 1B, J(HB) 97 Hz), –31.65 (d, 1B, J(HB) 142 Hz) ppm.

For **1b**: $C_{10}H_{21}B_9S$ requires %C, 44.4; %H, 7.82. Found: %C, 44.0; %H, 7.54. IR: ν_{\max} 2517 cm^{-1} . NMR: 1H , δ 7.23–7.11 (m, 5H, Ph), 2.46 (s br, 1H, cage-CH), 2.35 (s, 3H, SMe), 2.33 (s, 3H, SMe) ppm; ^{11}B δ –1.82 (s br, 2B) (co-incident signal), –8.17 (d, 1B, $J(HB)$ 150 Hz), –11.59 (d, 1B, $J(HB)$ 175 Hz), –13.63 (d, 1B, $J(HB)$ 145 Hz), –18.76 (d, 1B, $J(HB)$ 147 Hz), –23.51 (d, 1B, $J(HB)$ 140 Hz), –26.45 (d, 1B, $J(HB)$ 102 Hz), –32.31 (d, 1B, $J(HB)$ 141 Hz) ppm.

2.1.5. 7,8-Ph₂-9-SMe₂-7,8-nido-C₂B₉H₉ (2)

$K[7,8-Ph_2-7,8-nido-C_2B_9H_{10}]$ (1.10 g, 3.4 mmol) was dissolved in H₂O (1 cm³) and dmsO (4.5 cm³) and cooled to 0°C. To this solution H₂SO₄ (conc., 4.5 cm³) was added dropwise over 15 min and the resulting sticky, off-white, solid stirred at room temperature under N₂ for 6 days. The white suspension that formed was diluted with H₂O (20 cm³), and the precipitate collected by filtration and washed with two portions of water. The resulting white solid was dissolved in CH₂Cl₂ (50 cm³) and dried over MgSO₄. Concentration of the resulting solution to ca. 5 cm³ and subsequent column chromatography (silica, CH₂Cl₂) afforded 7,8-Ph₂-9-SMe₂-7,8-nido-C₂B₉H₉ (super²carb¹H, **2**), mass 0.150 g, yield 13%, as a white solid.

$C_{16}H_{25}B_9S$ requires %C, 55.42; %H, 7.27. Found: %C, 53.41; %H, 7.13. IR: ν_{\max} 2530 cm^{-1} . NMR: 1H , δ 7.19 (m, 2H, Ph), 6.86 (m, 8H, Ph), 2.61 (s, 3H, SMe), 2.22 (s, 3H, SMe) ppm; ^{11}B δ –1.43 (s, br, 2B) (co-incident signal), –4.77 (d, 1B, $J(HB)$ 148 Hz), –12.05 (s br, 2B) (co-incident signal), –17.92 (d, 1B, $J(HB)$ 145 Hz), –22.79 (d, 1B, $J(HB)$ 140 Hz), –26.44 (d, 1B, $J(HB)$ 94 Hz), –31.88 (d, 1B, $J(HB)$ 142 Hz) ppm.

2.1.6. 1-Ph-3,3-(CO)₂-7-SMe₂-3,1,2-closo-RhC₂B₉H₉ (3)

A solution of Na[7-Ph-9-SMe₂-7,8-nido-C₂B₉H₉] (generated from 0.110 g, 0.40 mmol 9-supercarb¹H and NaH in thf) was added to a frozen (–196°C) solution of [RhCl(CO)₂]₂ (0.078 g, 0.20 mmol) in thf (10 cm³). The mixture was allowed to warm to room temperature and then stirred for a further 2 h until infrared spectroscopy demonstrated that all the starting material had been consumed. Solvent was removed in vacuo and the resulting solid redissolved in CH₂Cl₂ and filtered through Celite. The resulting solution was reduced to ca. 2 cm³ in vacuo and applied to a chromatography column. Elution with CH₂Cl₂:40–60°C petroleum ether (3:2) afforded a single orange band. Removal of solvent and recrystallisation from CH₂Cl₂:60–80°C petroleum ether afford orange microcrystals of 1-Ph-3,3-(CO)₂-7-SMe₂-3,1,2-closo-RhC₂B₉H₉ (**3**), mass 0.077 g, yield 45%. Diffraction-quality single crystals were obtained

by the slow diffusion of a CH₂Cl₂ solution and 60–80 petroleum ether at –30°C.

$C_{12}H_{20}B_9O_2RhS$ requires %C, 33.7; %H, 4.68. Found: %C, 32.9; %H, 4.82. IR: ν_{\max} 2545 cm^{-1} (m br, BH), 2048 cm^{-1} (vs, CO), 1990 cm^{-1} (s, CO). NMR: 1H , δ 7.19–6.98 (m, 5H, Ph), 3.67 (s br, 1H, cage-CH), 2.88 (s, 3H, SMe), 2.52 (s, 3H, SMe) ppm; ^{11}B δ –2.38 (s, 1B), –6.01 (d, 1B, $J(HB)$ 164 Hz), –7.54 (d br, 2B, $J(HB)$ ca. 140 Hz) (co-incident signal), –10.46 (d, 1B, $J(HB)$ 153 Hz), –11.70 (d, 1B, $J(HB)$ 147 Hz), –12.84 (d, 1B, $J(HB)$ 162 Hz), –15.07 (d br, 1B, $J(HB)$ ca. 150 Hz), –22.27 (d, 1B, $J(HB)$ 149 Hz) ppm.

2.2. Crystallographic studies

Measurements on single crystals of **1b** and **3** mounted in Lindemann capillaries were carried out at room temperature on a Siemens P4 diffractometer using graphite-monochromated Mo K α radiation ($\lambda =$

Table 1
Crystallographic data and details of refinement

	1b	3
Formula	$C_{10}H_{21}B_9S$	$C_{12}H_{20}B_9O_2RhS$
<i>M</i>	270.62	428.54
System	Monoclinic	Monoclinic
Space group	C2	C2/c
<i>a</i> / Å	17.169(3)	16.171(2)
<i>b</i> / Å	6.9270(10)	7.0161(8)
<i>c</i> / Å	13.856(4)	35.122(4)
β / deg	105.00(2)	103.048(4)
<i>U</i> / Å ³	1591.7(6)	3882.0(8)
<i>Z</i>	4	8
<i>D</i> _{calc}	1.129	1.466
μ (Mo K α)/mm ^{–1}	0.181	0.989
<i>F</i> (000)	568	1712
θ _{orientation} / deg	4.94–11.88	4.99–12.52
θ _{data collection} / deg	1.52–25.00	2.59–25.00
<i>hkl</i> range	–1 to 20, –1 to 8, –16 to 15	–1 to 19, –1 to 8, –41 to 40
ω scan speeds / deg min ^{–1}	1.5–60.0	1.5–40
crystal decay / % (corrected for)	8.42	5.1
Data measured	1917	4138
Unique data (used in refinement)	1738	3198
<i>a</i>	0.0865	0.0302
<i>b</i>	0	5.8336
<i>R</i> , <i>wR</i> ₂ (all data)	0.1482, 0.2240	0.0377, 0.0873
Observed data (<i>I</i> > 2 σ (<i>I</i>))	1031	2706
<i>R</i> , <i>wR</i> ₂ (observed data)	0.0769, 0.1639	0.0287, 0.0763
<i>S</i>	1.086	1.146
Flack <i>x</i> parameter	–0.05(32)	—
Extinction coefficient	—	0.00245(12)
Variables	184	263
<i>E</i> _{max} , <i>E</i> _{min} (e [–] Å ^{–3})	0.45, –0.30	0.31, –0.31

Extinction expression: $F^c = kF_0[1 + 0.001 F_0^2 \lambda^3 / \sin(2\theta)]^{-1/4}$.

Weight expression: $w^{-1} = [\sigma_c^2(F_0)^2 + (aP)^2 + bP]$ where $P = [0.333 \max\{F_0, 0\} + 0.667(F_0)^2]$.

0.71069 Å). Crystallographic computing was via the SHELXTL system [9] on a Pentium 90 MHz PC.

Table 1 lists details of unit cell data, intensity data collection and structure refinement. The unit cell parameters and orientation matrix for data collection were determined by the least squares refinement of 20 and 32 centred reflections respectively, with 2θ ranging from 9.8 to 25°. Data collection by ω -scans. Standard reflections were re-measured every 100 data, and slight crystal decay was found (8% and 5% respectively). Data were corrected for absorption by φ scans. Both structures were solved by direct and difference Fourier methods and refined by full-matrix least squares against F^2 . Cage C atoms not carrying phenyl substituents were identified on the bases of refined (as B) isotropic thermal parameters and interatomic distances. All non-hydrogen atoms were allowed anisotropic thermal motion. Phenyl, methyl and (for **1b**) terminal cage H atom positions were calculated and these atoms allowed to ride on their respective C or B atoms, with isotropic displacement parameters set at 1.2, 1.2 and 1.5 times U_{eq} for the bound atom respectively. The bridging H atom in **1b** was found in a difference Fourier map and allowed to refine subject to both B–H distances being restrained to 1.20(5) Å; for this atom alone the isotropic displacement parameter was fixed at 0.08 Å². For **3**, cage H atoms were found in a difference Fourier and thereafter allowed positional and individual isotropic thermal refinement. Details of extinction and weighting schemes are given in Table 1. Co-ordinates of refined non-hydrogen atoms in **1b** and **3**, together with equiva-

Table 2

Atomic co-ordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å² $\times 10^3$) for **1b**

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
S(1)	2827(1)	2201(4)	2870(2)	39(1)
B(1)	844(7)	–2106(21)	2827(8)	50(3)
B(2)	1587(7)	–992(18)	2294(8)	40(3)
B(3)	549(7)	–902(18)	1641(9)	42(3)
B(4)	10(7)	–623(20)	2521(10)	52(3)
B(5)	643(7)	–458(19)	3743(8)	42(3)
B(6)	1647(7)	–719(17)	3569(8)	38(3)
C(7)	1134(5)	1170(15)	1836(6)	32(2)
C(8)	254(5)	1328(17)	1939(7)	45(3)
B(9)	237(7)	1694(19)	3105(8)	46(4)
B(10)	1294(7)	1592(18)	3842(8)	43(3)
B(11)	1802(6)	1269(17)	2894(6)	30(2)
C(21)	2871(7)	4625(16)	3396(9)	60(3)
C(22)	3530(6)	957(19)	3877(10)	73(4)
C(71)	1277(4)	2058(18)	911(5)	33(2)
C(72)	1053(6)	4062(16)	721(7)	45(3)
C(73)	1187(7)	4916(17)	–97(8)	53(3)
C(74)	1513(6)	4037(20)	–736(8)	56(3)
C(75)	1752(5)	2061(25)	–577(6)	53(3)
C(76)	1614(5)	1154(18)	260(6)	43(3)

U_{eq} is defined as one-third of the trace of the orthogonalised U_{ij} tensor.

Table 3

Atomic co-ordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å² $\times 10^3$) for **3**

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
C(1)	–2075(2)	1277(5)	–6336(1)	42(1)
C(2)	–1278(2)	2736(5)	–6186(1)	39(1)
Rh(3)	–726(1)	95(1)	–6360(1)	40(1)
B(4)	–1819(3)	–798(6)	–6094(1)	45(1)
B(5)	–2564(3)	855(7)	–5963(1)	48(1)
B(6)	–2228(2)	3137(7)	–6045(1)	47(1)
B(7)	–489(2)	1875(5)	–5815(1)	36(1)
B(8)	–800(2)	–480(6)	–5734(1)	39(1)
B(9)	–1783(3)	–245(7)	–5594(1)	49(1)
B(10)	–2041(3)	2227(7)	–5566(1)	50(1)
B(11)	–1228(2)	3529(6)	–5716(1)	42(1)
B(12)	–968(2)	1459(6)	–5423(1)	42(1)
S(1)	612(1)	2903(1)	–5755(1)	44(1)
C(11)	–2613(2)	1450(7)	–6746(1)	53(1)
C(12)	–3199(3)	49(7)	–6885(1)	72(1)
C(13)	–3733(3)	190(10)	–7256(2)	99(2)
C(14)	–3675(3)	1714(12)	–7480(2)	106(2)
C(15)	–3096(4)	3094(11)	–7358(2)	111(2)
C(16)	–2570(3)	2976(8)	–6989(1)	84(2)
C(21)	1292(2)	888(6)	–5609(2)	65(1)
C(22)	854(3)	4225(7)	–5307(1)	67(1)
C(31)	–297(3)	1037(7)	–6786(2)	72(1)
O(31)	–27(4)	1580(7)	–7032(1)	136(2)
C(32)	–326(3)	–2296(6)	–6441(1)	55(1)
O(32)	–83(2)	–3788(5)	–6475(1)	84(1)

U_{eq} is defined as one-third of the trace of the orthogonalised U_{ij} tensor.

lent isotropic thermal parameters, appear in Tables 2 and 3 respectively. Tables of anisotropic thermal parameters and hydrogen atom co-ordinates and complete lists of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

3. Results and Discussion

3.1. Nido carbaboranes

Reaction between $K[7\text{-Ph-}7,8\text{-nido-C}_2\text{B}_9\text{H}_{11}]$ and dmsO (dmsO = dimethylsulphoxide), in concentrated sulphuric acid at room temperature for 4 days, affords the new nido carbaboranes 7-Ph-9-SMe₂-7,8-nido-C₂B₉H₁₀ (**1a**, 9-supercarb'H) and 7-Ph-11-SMe₂-7,8-nido-C₂B₉H₁₀ (**1b**, 11-supercarb'H) in low yields after column chromatography. Compounds **1a** and **1b** are isomers in that the phenyl group is attached to a cage carbon atom either adjacent to the SMe₂-bound boron atom (11-supercarb'H) or separated from it by the other cage carbon atom (9-supercarb'H). Reaction between $K[7,8\text{-Ph-}7,8\text{-nido-C}_2\text{B}_9\text{H}_{10}]$ and dmsO, in concentrated sulphuric acid at room temperature for 6 days, affords the new diphenyl derivative 7,8-Ph₂-9-SMe₂-7,8-nido-C₂B₉H₉ (**2**, super²carb'H) in low yield.

Compounds **1a** and **1b** are afforded in the approxi-

mate ratio 60: 40, the greater amount of **1a** formed due to proximity of cage phenyl and SMe_2 groups in **1b**. Both compounds were fully characterised by IR and ^1H and ^{11}B NMR spectroscopies and microanalysis. For **1a**, the ^1H NMR spectrum displays two singlets each of integral-3 at δ 2.82 ppm and δ 2.62 ppm assigned to the magnetically inequivalent sulphur-bound methyl groups, and a broad singlet of integral-1 at δ 3.06 ppm assigned to the cage CH group. In addition resonances due to the cage phenyl substituent are observed as a multiplet between δ 7.35 and 7.13 ppm. The $^{11}\text{B}\{-^1\text{H}\}$ NMR spectrum displays nine inequivalent boron environments between δ -1.69 and δ -31.65 ppm; on retention of proton coupling the peak at δ -3.74 ppm clearly remains a singlet and is thus assigned to the SMe_2 -substituted boron vertex. For **1b**, the two inequivalent methyl groups are observed in the ^1H NMR spectrum at δ 2.35 and δ 2.33 ppm and the cage C-H signal is at δ 2.46 ppm. A multiplet corresponding to five aromatic protons is observed between δ 7.23 and 7.11 ppm. The

$^{11}\text{B}\{-^1\text{H}\}$ NMR spectrum displays eight boron signals with integrals in the ratio 2:1:1:1:1:1:1:1 (high frequency to low frequency) between δ -1.82 and δ -32.31 ppm. The highest frequency resonance (which must be a co-incidence) appears as a broad singlet in the fully proton coupled spectrum, demonstrating that one of its components is due to the SMe_2 -substituted boron atom.

Compound **2** displays resonances in the ^1H NMR spectrum attributable to two phenyl groups and a single SMe_2 group. Thus are observed a multiplet between δ 7.19 and δ 6.86 ppm and two singlets at δ 2.61 ppm and δ 2.22 ppm with relative integrals 10:3:3. In the $^{11}\text{B}\{-^1\text{H}\}$ NMR spectrum, seven resonances are observed between δ -1.43 ppm and δ -31.88 ppm in the ratio 2:1:2:1:1:1:1 (high-to-low frequency, the integral-2 resonances being co-incidences), confirming the asymmetric nature of the molecule, arising from the SMe_2 substitution. Proton coupling caused all five integral-1 resonances to split into doublets and, although the two

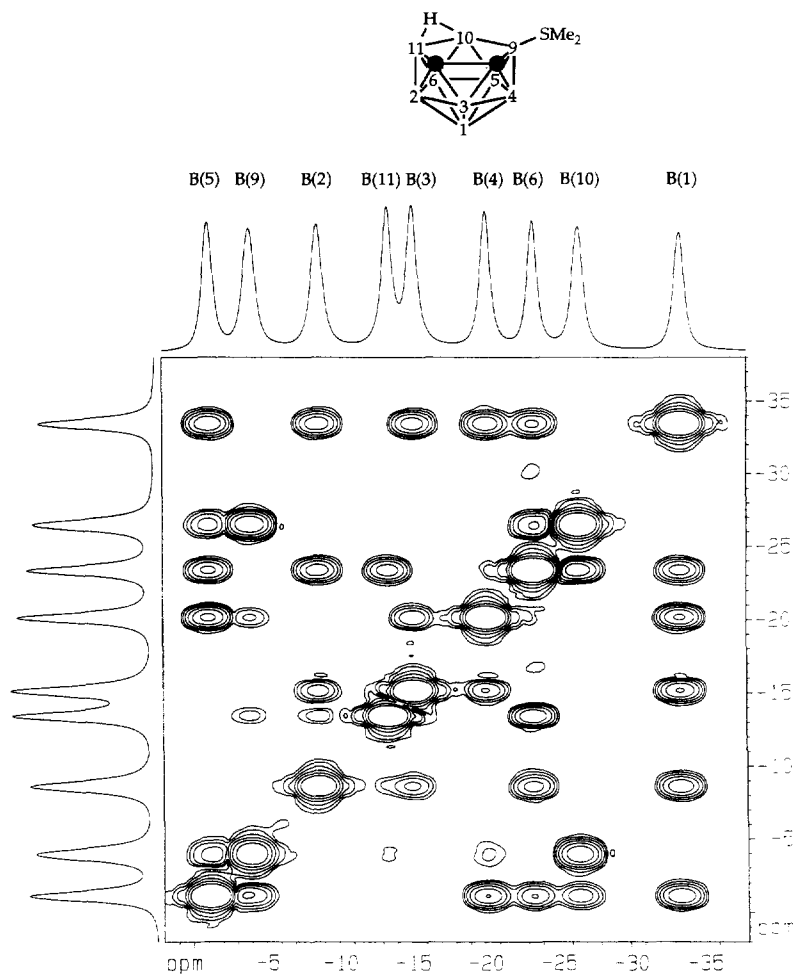
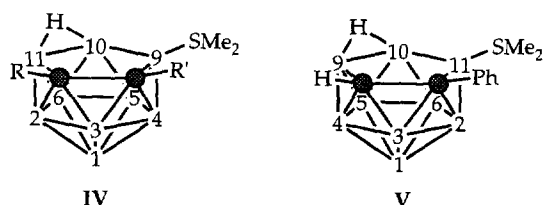


Fig. 1. $^{11}\text{B}\{-^1\text{H}\}$ COSY spectrum of 9- SMe_2 -7,8-*nido*- $\text{C}_2\text{B}_9\text{H}_{11}$ (carb'H) at 128.4 MHz, acquired using a Jeener-type two-pulse COSY sequence with phase cycling to give quad detection in each dimension. 128 FIDs, each of 256 points, were collected, and composite-pulse (WALTZ-16) decoupling of ^1H was applied continuously throughout the acquisition period. The spectrum is displayed in magnitude mode, positive contours only, with the corresponding 1-D $^{11}\text{B}\{-^1\text{H}\}$ spectrum plotted along the F1 and F2 axes.

integral-2 resonances both broadened, coupling was not resolved. Therefore, at this stage we do not know whether the SMe_2 -substituted boron atom in **2** resonates at -1.43 or -12.05 ppm.

Before attempting to resolve this question as part of full assignment of the ^{11}B resonances of all new compounds **1a**, **1b** and **2** to specific boron atoms, we have undertaken an ^{11}B - ^{11}B COSY experiment on the parent species carb'H, numbered as in **IV**. This archetypal charge-compensated carbaborane was first prepared [10] in 1978 and structurally characterised a decade later [11].



carb'H	R = R' = H	11-supercarb'H, 1b
9-supercarb'H, 1a	R = Ph; R' = H	
super ² carb'H, 2	R = R' = Ph	

The ^{11}B - ^{11}B COSY spectrum of carb'H, fully proton coupled, is shown in Fig. 1. There are no co-incident resonances in the 1-D ^{11}B spectrum and from comparison of the ^{11}B and ^{11}B - $\{^1\text{H}\}$ spectra it is clear that the resonance at δ 3.99 ppm should be assigned to B(9).

There are three boron atoms (δ -1.14 , -23.42 and -33.46) which show coupling to five others, but only the last couples to B(9), identifying it as B(5). Two boron atoms (δ -13.47 and -15.18) show only three couplings, and must therefore be B(11) and B(3). Only one four-coupled boron (δ -8.65) couples to both of these, identifying it as B(2), and by elimination the other four-coupled boron, B(4), must resonate at δ -20.18 . Confirmation derives from the observation of the expected couplings between B(4)/B(5) and B(4)/B(9), but not between B(2)/B(5) and B(2)/B(9).

Of the two remaining boron atoms with five couplings, only the lower frequency one, δ -33.46 , couples to B(4), identifying it as arising from B(1) and meaning that B(6) resonates at δ -23.42 . Considering the remaining unassigned boron atoms, only one, δ -15.18 , couples to B(1) and must therefore correspond to B(3), and only one, δ -26.54 , couples to B(9), identifying it as due to B(10). This leaves B(11) resonating at δ -13.47 , and couplings to B(2) and B(6) are confirmed. Note that, as anticipated (e.g. see Ref. [12]), no coupling is observed between the H-bridged boron atoms B(10) and B(11). It is interesting to note,

Table 4

Assignment of ^{11}B resonances in the nido-carbaboranes carb'H and the new compounds **1a**, **1b** and **2**

Vertex	Chemical shift \(\delta\) ppm			
	carb'H	1a	1b	2
B(1)	-33.46	-31.65	-32.31	-31.88
B(2)	-8.65	-6.10	-8.17	-4.77
B(3)	-15.18	-11.53	-11.59	-12.05
B(4)	-20.18	-20.24	-18.67	-17.92
B(5)	-1.14	-1.69	-1.82	-1.34
B(6)	-23.42	-23.63	-23.51	-22.79
B(9)	-3.99	-3.74	-1.82	-1.43
B(10)	-26.54	-26.05	-26.45	-26.44
B(11)	-13.47	-11.53	-13.63	-12.05

however, that we do record an off-diagonal peak in the COSY spectrum between B(9) and B(11).

^{11}B - ^{11}B COSY spectra of **1a**, **1b** and **2** (numbered as in **IV** or **V** as appropriate), were similarly analysed, and complete unambiguous assignments were deduced; these are summarised in Table 4. In all cases it is confirmed that SMe_2 substitution occurs at a facial boron atom adjacent to cage carbon. However, these results alone do not afford the relative positions of SMe_2 and phenyl substituents in the case of the supercarb'H isomers, i.e. they do not distinguish between **1a** and **1b**. This was accomplished by analysis of the results of ^1H - ^1H NOESY experiments on both compounds. In the NOESY spectrum of **1a** cross-peaks are observed between phenyl protons and the cage-CH, and also between the cage-CH and both sets of SMe_2 protons. However, no cross-peaks are observed between phenyl and methyl protons. In contrast, for **1b** there are clear cross-peaks between phenyl protons and both the cage C-H and methyl protons.

The stereochemistry of **1b** was unequivocally established as the result of a single crystal X-ray diffraction study. Fig. 2 shows a perspective view of a single molecule of **1b** and demonstrates the atomic numbering scheme used, whilst Table 5 lists selected interatomic distances and interbond angles. Note that in Fig. 2 we have deliberately inverted the chirality of the molecule to facilitate comparison with the view of [carb']⁻ and its metal complexes represented herein by the line diagrams of **I**-**III**.

It is immediately apparent that the structure of **1b** is that of a nido-icosahedral carbaborane in which the B-bound SMe_2 group is adjacent to the C-bound phenyl substituent, confirming the conclusions of the ^{11}B - ^{11}B COSY and ^1H - ^1H NOESY experiments. The B(9)-B(10) edge carries an H-bridge. The two pentagonal belts defined by C(7) to B(11) and B(2) to B(6) are both essentially planar, and lie parallel with respect to one another (angle between mean planes 0.8°). The phenyl and SMe_2 substituents are inclined at angles of 32.5° and 25.1° respectively to the upper pentagonal belt.

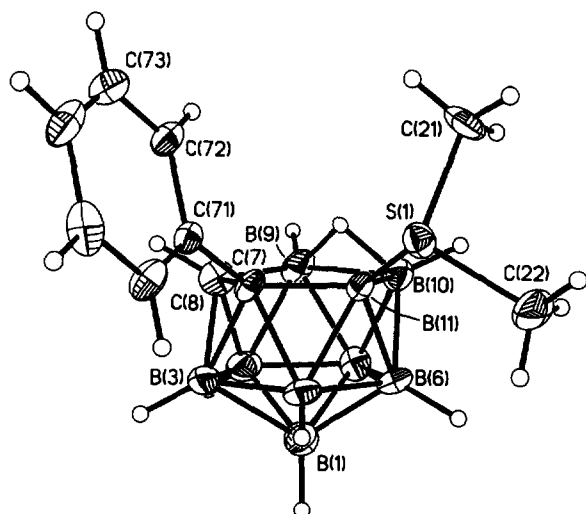


Fig. 2. Perspective view of a single molecule of 7-Ph-11-SMe₂-7,8-nido-C₂B₉H₁₀ (11-supercarb'H, **1b**). Atoms are represented by 30% thermal ellipsoids, except for H atoms which have an artificial radius of 0.1 Å.

Previously we have described parameters that define the conformations of phenyl and SMe₂ substituents in such species, i.e. we have addressed the question of the orientation of Ph and SMe₂ groups about the C_{cage}-C_{phenyl} and B-S bonds. In **1b** the conformation of the phenyl substituent is described by a θ value [13] of 36.0° (θ is the modulus of the average C(8)-C(7)-C(71)-C torsion angles) and that of the SMe₂ substituent by a τ value [14] [τ is the torsion angle C(7)-B(11)-S(1)-lone pair, calculated from the measurable torsion angles C(7)-B(11)-S(1)-C(21) and C(7)-B(11)-S(1)-C(22)] which has a modulus of 21.5°. These twists from conformations defined by $\theta = \tau = 0^\circ$ are conrotatory (anticlockwise in the sense of Fig. 2) and we believe that they are heavily influenced by intramolecular steric crowding. The S(1)-B(11)-X angles are greatest to X = B(6) and X = B(10), reflecting the greater steric demand of Me groups over the S-lone pair of electrons; a similar situation exists in the structures of carb'H itself [11,15], and in its transition metal

Table 5
Selected distances (Å) and angles (deg) for **1b**

S(1)C(22)	1.810(11)	S(1)-C(21)	1.824(11)	S(1)-B(11)	1.881(10)
B(1)-B(4)	1.72(2)	B(1)-B(6)	1.77(2)	B(1)-B(3)	1.80(2)
B(1)-B(2)	1.80(2)	B(1)-B(5)	1.81(2)	B(2)-C(7)	1.731(14)
B(2)-B(6)	1.75(2)	B(2)-B(11)	1.77(2)	B(2)-B(3)	1.78(2)
B(3)-C(8)	1.71(2)	B(3)-B(4)	1.72(2)	B(3)-C(7)	1.73(2)
B(4)-C(8)	1.68(2)	B(4)-B(5)	1.76(2)	B(4)-B(9)	1.79(2)
B(5)-B(9)	1.78(2)	B(5)-B(10)	1.79(2)	B(5)-B(6)	1.81(2)
B(6)-B(11)	1.72(2)	B(6)-B(10)	1.79(2)	C(7)-C(71)	1.497(11)
C(7)-C(8)	1.557(11)	C(7)-B(11)	1.613(12)	C(8)-B(9)	1.643(14)
B(9)-B(10)	1.84(2)	B(10)-B(11)	1.770(13)	C(71)-C(76)	1.346(13)
C(71)-C(72)	1.45(2)	C(72)-C(73)	1.350(14)	C(73)-C(74)	1.31(2)
C(74)-C(75)	1.43(2)	C(75)-C(76)	1.392(13)		
C(22)-S(1)-C(21)	100.3(6)	C(22)-S(1)-B(11)	105.2(5)	C(21)-S(1)-B(11)	104.6(5)
B(4)-B(1)-B(3)	58.6(7)	B(6)-B(1)-B(2)	58.6(6)	B(3)-B(1)-B(2)	59.2(6)
B(4)-B(1)-B(5)	59.9(7)	B(6)-B(1)-B(5)	60.7(6)	C(7)-B(2)-B(11)	54.9(6)
B(6)-B(2)-B(11)	58.7(6)	C(7)-B(2)-B(3)	59.1(6)	B(6)-B(2)-B(1)	59.8(6)
B(3)-B(2)-B(1)	60.2(6)	C(8)-B(3)-B(4)	58.7(6)	B(8)-B(3)-C(7)	53.8(6)
C(7)-B(3)-B(2)	59.1(6)	B(4)-B(3)-B(1)	58.6(6)	B(2)-B(3)-B(1)	60.6(6)
C(8)-B(4)-B(3)	60.2(7)	B(3)-B(4)-B(1)	62.8(7)	B(1)-B(4)-B(5)	62.3(7)
C(8)-B(4)-B(9)	56.3(6)	B(S)-B(4)-B(9)	60.1(7)	B(4)-B(S)-B(9)	60.8(7)
B(9)-B(5)-B(10)	62.0(7)	B(4)-B(5)-B(1)	57.7(7)	B(10)-B(5)-B(6)	59.5(6)
(B1)-B(5)-B(6)	58.8(6)	B(11)-B(6)-B(2)	61.1(6)	B(2)-B(6)-B(1)	61.5(6)
B(11)-B(6)-B(10)	60.5(6)	B(1)-B(6)-B(5)	60.5(6)	B(10)-B(6)-B(5)	59.7(7)
C(71)-C(7)-C(8)	115.3(7)	C(71)-C(7)-B(11)	121.6(8)	C(8)-C(7)-B(11)	113.1(7)
C(71)-C(7)-B(2)	120.8(8)	B(11)-C(7)-B(2)	63.7(6)	C(71)-C(7)-B(3)	115.0(8)
C(8)-C(7)-B(3)	62.4(6)	B(2)-C(7)-B(3)	61.8(6)	C(7)-C(8)-B(9)	111.5(8)
B(9)-C(8)-B(4)	65.3(7)	C(7)-C(8)-B(3)	63.8(6)	B(4)-C(8)-B(3)	61.1(7)
C(8)-B(9)-B(4)	58.4(7)	B(5)-B(9)-B(4)	59.1(7)	C(8)-B(9)-B(10)	105.9(7)
B(5)-B(9)-B(10)	59.3(6)	B(11)-B(10)-B(6)	58.0(6)	B(6)-B(10)-B(5)	60.8(7)
B(11)-B(10)-B(9)	101.4(7)	B(5)-B(10)-B(9)	58.8(6)	C(7)-B(11)-B(2)	61.4(6)
B(6)-B(11)-B(2)	60.2(7)	C(7)-B(11)-B(10)	107.9(7)	B(6)-B(11)-B(10)	61.5(6)
C(7)-B(11)-S(1)	116.6(6)	B(6)-B(11)-S(1)	124.1(7)	B(2)-B(11)-S(1)	112.3(6)
B(10)-B(11)-S(1)	127.8(7)	C(76)-C(71)-C(72)	117.6(9)	C(76)-C(71)-C(7)	125.2(10)
C(72)-C(71)-C(7)	117.1(9)	C(73)-C(72)-C(71)	118.7(10)	C(74)-C(73)-C(72)	123.9(12)
C(73)-C(74)-C(75)	119.7(10)	C(76)-C(75)-C(74)	117.2(10)	C(71)-C(76)-C(75)	123.0(11)

complexes [5,14]. The low τ value allows the least sterically-demanding function bound to S to be directed towards the adjacent cage-bound phenyl group, but that there is nevertheless some crowding between them is evidenced by the relatively wide C(71)–C(7)–Y angles when Y = B(11) and Y = B(2), and the relatively long C(7)–B(11) connectivity, 1.613(12) Å, compared with 1.571(4) and 1.582(4) Å for the equivalent distances in

the two crystallographically-independent molecules of carb'H [11].

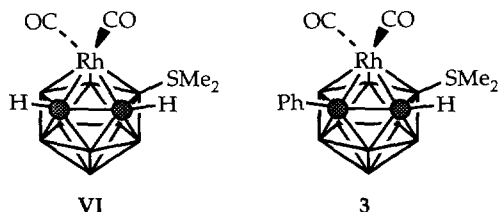
3.2. Carbametallaborane complexes

We have previously shown [5] that reaction between $[\text{RhCl}(\text{CO})_2]_2$ and $\text{Ti}[\text{carb}']$ affords the complex 3,3-(CO)₂-4-SMe₂-closo-3,1,2-RhC₂B₉H₁₀, VI. Similarly,

Table 6
Selected distances (Å) and angles (deg) for 3

C(1)–C(11)	1.511(5)	C(1)–C(2)	1.637(4)	C(1)–B(4)	1.689(5)
C(1)–B(5)	1.700(5)	C(1)–B(6)	1.708(6)	C(1)–Rh(3)	2.354(3)
C(2)–B(7)	1.712(5)	C(2)–B(11)	1.726(5)	C(2)–B(6)	1.740(5)
C(2)–Rh(3)	2.203(4)	Rh(3)–C(32)	1.842(4)	Rh(3)–C(31)	1.903(5)
Rh(3)–B(7)	2.245(4)	Rh(3)–B(8)	2.267(4)	Rh(3)–B(4)	2.268(4)
B(4)–B(9)	1.788(6)	B(4)–B(5)	1.804(7)	B(4)–B(8)	1.850(6)
B(5)–B(6)	1.736(6)	B(5)–B(10)	1.747(7)	B(5)–B(9)	1.770(6)
B(6)–B(10)	1.761(6)	B(6)–B(11)	1.784(6)	B(7)–B(12)	1.750(5)
B(7)–B(11)	1.756(5)	B(7)–B(8)	1.769(5)	B(7)–S(1)	1.889(3)
B(S)–B(9)	1.774(6)	B(8)–B(12)	1.802(6)	B(9)–B(12)	1.780(6)
B(9)–B(10)	1.792(7)	B(10)–B(11)	1.775(6)	B(10)–B(12)	1.778(6)
B(11)–B(12)	1.774(6)	S(1)–C(22)	1.792(4)	S(1)–C(22)	1.793(4)
C(11)–C(12)	1.377(6)	C(11)–C(16)	1.380(6)	C(12)–C(13)	1.392(7)
C(13)–C(14)	1.344(8)	C(14)–C(15)	1.348(8)	C(15)–C(16)	1.382(7)
C(31)–O(31)	1.118(5)	C(32)–O(32)	1.134(5)		
C(11)–C(1)–C(2)	119.9(3)	C(11)–C(1)–B(4)	124.9(3)	C(2)–C(1)–B(4)	107.0(3)
C(11)–C(1)–B(5)	118.7(3)	C(2)–C(1)–B(5)	109.3(3)	B(4)–C(1)–B(5)	64.3(3)
C(11)–C(1)–B(6)	112.2(3)	C(2)–C(1)–B(6)	62.6(2)	B(4)–C(1)–B(6)	114.3(3)
B(5)–C(1)–B(6)	61.2(2)	C(11)–C(1)–Rh(3)	109.4(2)	C(2)–C(1)–Rh(3)	64.1(2)
B(4)–C(1)–Rh(3)	65.9(2)	B(7)–C(2)–B(11)	61.4(2)	C(1)–C(2)–B(6)	60.7(2)
B(11)–C(2)–B(6)	62.0(2)	C(1)–C(2)–Rh(3)	74.0(2)	B(7)–C(2)–Rh(3)	68.7(2)
B(11)–C(2)–Rh(3)	127.1(2)	B(6)–C(2)–Rh(3)	130.9(2)	C(32)–Rh(3)–C(31)	89.6(2)
C(32)–Rh(3)–C(2)	170.6(2)	C(31)–Rh(3)–C(2)	99.7(2)	C(32)–Rh(3)–B(7)	129.7(2)
C(31)–Rh(3)–B(7)	117.0(2)	C(2)–Rh(3)–B(7)	45.27(13)	C(32)–Rh(3)–B(8)	94.8(2)
C(31)–Rh(3)–B(8)	158.9(2)	C(2)–Rh(3)–B(8)	76.44(14)	B(7)–Rh(3)–B(8)	46.17(13)
C(32)–Rh(3)–B(4)	98.3(2)	C(31)–Rh(3)–B(4)	151.2(2)	C(2)–Rh(3)–B(4)	73.44(14)
B(7)–Rh(3)–B(4)	78.49(14)	B(8)–Rh(3)–B(4)	48.16(14)	C(32)–Rh(3)–C(1)	133.4(2)
C(31)–Rh(3)–C(1)	114.3(2)	C(2)–Rh(3)–C(1)	41.95(12)	B(7)–Rh(3)–C(1)	75.71(13)
B(8)–Rh(3)–C(1)	76.92(13)	B(4)–Rh(3)–C(1)	42.82(14)	C(1)–B(4)–B(5)	58.1(2)
B(9)–B(4)–B(S)	59.0(2)	B(9)–B(4)–B(8)	58.3(2)	C(1)–B(4)–Rh(3)	71.3(2)
B(8)–B(4)–Rh(3)	65.9(2)	C(1)–B(S)–B(6)	59.6(2)	B(6)–B(5)–B(10)	60.7(3)
B(10)–B(S)–B(9)	61.3(3)	C(1)–B(5)–B(4)	57.5(2)	B(9)–B(5)–B(4)	60.0(3)
C(1)–B(6)–B(5)	59.2(2)	C(1)–B(6)–C(2)	56.7(2)	B(5)–B(6)–B(10)	59.9(3)
C(2)–B(6)–B(11)	58.6(2)	B(10)–B(6)–B(11)	60.1(2)	C(2)–B(7)–B(11)	59.7(2)
B(12)–B(7)–B(11)	60.8(2)	B(12)–B(7)–B(8)	61.6(2)	C(2)–B(7)–S(1)	118.2(2)
B(12)–B(7)–S(1)	123.3(2)	B(11)–B(7)–S(1)	113.1(2)	B(8)–B(7)–S(1)	129.3(2)
C(2)–B(7)–Rh(3)	66.1(2)	B(8)–B(7)–Rh(3)	67.6(2)	S(1)–B(7)–Rh(3)	106.4(2)
B(7)–B(8)–B(12)	58.7(2)	B(9)–B(8)–B(12)	59.7(2)	B(9)–B(8)–B(4)	59.1(2)
B(7)–B(8)–Rh(3)	66.3(2)	B(4)–B(8)–Rh(3)	65.9(2)	B(8)–B(9)–B(12)	60.9(2)
B(5)–B(9)–B(4)	61.0(3)	B(8)–B(9)–B(4)	62.6(2)	B(S)–B(9)–B(10)	58.7(3)
B(12)–B(9)–B(10)	59.7(2)	B(5)–B(10)–B(6)	59.3(2)	B(6)–B(10)–B(11)	60.6(2)
B(11)–B(11)–B(12)	59.9(2)	B(5)–B(10)–B(9)	60.0(3)	B(12)–B(10)–B(9)	59.8(2)
C(2)–B(11)–B(7)	58.9(2)	B(7)–B(11)–B(12)	59.4(2)	B(12)–B(11)–B(10)	60.1(2)
C(2)–B(11)–B(6)	59.4(2)	B(10)–B(11)–B(6)	59.3(2)	B(7)–B(12)–B(11)	59.8(2)
B(11)–B(12)–B(10)	60.0(2)	B(10)–B(12)–B(9)	60.5(3)	B(7)–B(12)–B(8)	59.7(2)
B(9)–B(12)–B(8)	59.4(2)	C(22)–S(1)–C(21)	99.1(2)	C(22)–S(1)–B(7)	108.0(2)
C(21)–S(1)–B(7)	103.5(2)	C(12)–C(11)–C(16)	117.4(4)	C(12)–C(11)–C(1)	118.9(4)
C(16)–C(11)–C(1)	123.6(4)	C(11)–C(12)–C(13)	120.9(5)	C(14)–C(13)–C(12)	119.6(5)
C(13)–C(14)–C(15)	121.3(5)	C(14)–C(15)–C(16)	119.5(6)	C(11)–C(16)–C(15)	121.3(5)
O(31)–C(31)–Rh(3)	178.4(5)	O(32)–C(32)–Rh(3)	177.2(4)		

reaction between $[\text{RhCl}(\text{CO})_2]_2$ and two equivalents of $\text{Na}[9\text{-supercarb}']$ (generated from 9-supercarb' H, **1a**, and NaH in *thf*) affords the new carbametallaborane 1-Ph-3,3-(CO)₂-7-SMe₂-3,1,2-closo-RhC₂B₉H₉, **3**, in moderate yield after work-up by column chromatography.



The new complex displays the expected two CO stretching bands (at 2048 and 1990 cm^{-1}) comparable with those found in **VI** (2040 and 1990 cm^{-1}). The ^1H NMR spectrum exhibits a multiplet of integral-5 centred at δ 7.11 ppm, due to the cage phenyl group, a broad signal of integral-1 at δ 3.66 ppm assigned to the cage C–H proton, and two sharp integral-3 singlets at δ 2.88 and δ 2.56 ppm due to the inequivalent SMe₂ methyl groups. In the $^{11}\text{B}\{-^1\text{H}\}$ NMR spectrum, eight resonances between δ –2.38 ppm and δ –22.27 ppm in the ratio 1:1:2:1:1:1:1:1 (high frequency to low frequency) are observed, confirming the asymmetry expected in the molecule, the highest frequency signal remaining a singlet in the ^{11}B NMR spectrum and arising from the SMe₂-substituted vertex, B(7).

Although we did not expect to observe any severe polytopal deformations in complex **3**, as the phenyl and SMe₂ substituents are not adjacent, a single crystal X-ray diffraction study was carried out to unequivocally

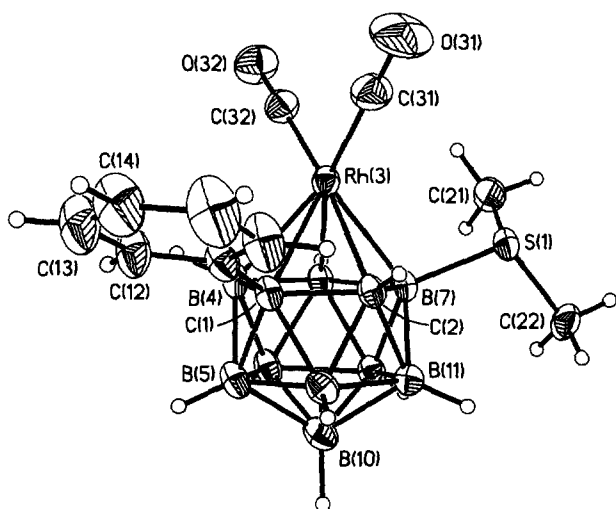


Fig. 3. Perspective view of a single molecule of 1-Ph-3,3-(CO)₂-7-SMe₂-3,1,2-closo-RhC₂B₉H₉ (**3**). Atom representation as in Fig. 2.

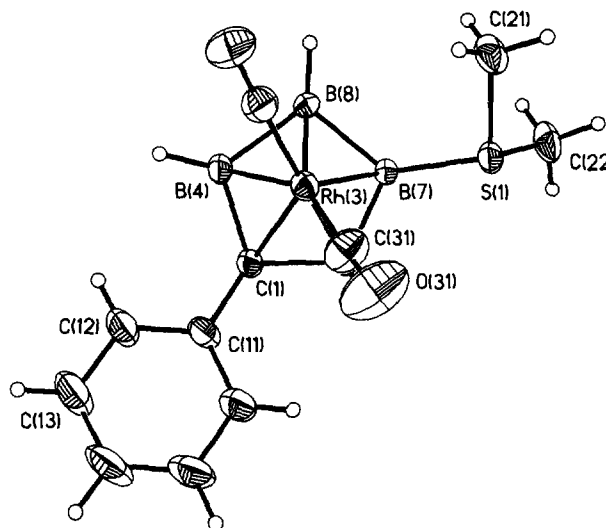


Fig. 4. View of the upper part of **3** showing the conformation of the $\{\text{Rh}(\text{CO})_2\}$ fragment with respect to the C₂B₃ face of the carbaborane.

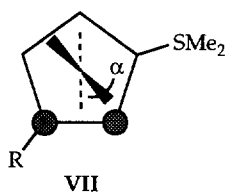
establish the molecular structure of this new complex. Fig. 3 shows a perspective view of compound **3**, demonstrating the atomic numbering scheme, whilst Table 6 lists selected interatomic distances and angles.

The complex displays the expected closo icosahedral structure predicted by electron counting rules [16]. The metal-bonded ligand face $[\text{C}(1)\text{C}(2)\text{B}(7)\text{B}(8)\text{B}(4)]$ is slightly non-planar, being of envelope conformation with C(1) displaced 0.035 Å below the best (least squares) plane. The lower pentagonal belt $[\text{B}(5)\text{B}(6)\text{B}(11)\text{B}(12)\text{B}(9)]$ is planar within experimental error, and essentially parallel (dihedral angle 1.2°) to the upper belt. The Rh atom is 1.73 Å above the upper belt, and slipped [17] by only 0.11 Å with respect to the lower one.

Rh–cage atom distances in **3** are broadly comparable with those in **VI**, but there are notable differences. The Rh–C_{cage} distance to the C atom adjacent to the B-substituted atom is again the shorter, but in **3** by a greater amount, 0.151(5) Å vs. 0.116(4) Å. In contrast, the range of Rh–B distances in **3** is smaller than in **VI**, and Rh–B(SMe₂) is actually the shortest.

Rh–CO distances in **3** are significantly different, Rh–C(31) 1.903(5) Å and Rh–C(32) 1.842(4) Å, mirroring the situation in **VI**. We have previously described [5] the conformation of the $\{\text{ML}_2\}$ fragment in transition metal complexes of carb' in terms of α , defined in the line diagram VII. In **VI** α is ca. 50°, in reasonable agreement with that predicted by frontier orbital analysis [5] (30–36°, lying in a shallow potential well) but possibly reflecting some degree of intermolecular interaction. According to EHMO calculations [18] the frontier MOs of simplified models of $[9\text{-supercarb}']^-$ and of $[11\text{-supercarb}']^-$ (SH₂ replacing SMe₂) are essentially

the same as those previously reported [5] for $[\text{carb}']^-$, and so a similar ML_2 conformation is expected in **3**; the measured α value of 33.6° supports this prediction very well (Fig. 4).



Clearly the Ph and SMe_2 cage substituents in **3** are sufficiently far apart that they are not mutually crowded. This is reflected in the fact that θ and τ values (79.7° and -15.7° , the sign of the latter representing a clockwise rotation about the S–B bond when viewed from sulphur) are, respectively, close to θ values both predicted and observed in 1-Ph-1,2-closo- $\text{C}_2\text{B}_{10}\text{H}_{11}$ [19], and to τ values in $\text{carb}'\text{H}$ [11] and its uncrowded metal complexes [14]. Moreover, the lack of crowding between Ph and SMe_2 groups in **3** allows the electronically preferred metal-fragment conformation to be attained.

It was therefore of interest to investigate the reaction between $[\text{RhCl}(\text{CO})_2]_2$ and the sterically more crowded carbaborane ligands derived by deprotonation of **1b** and **2**, in the anticipation of inducing polytopal deformations and/or isomerisations in the resulting carbametallaboranes.

Reaction between $[\text{RhCl}(\text{CO})_2]_2$ and of $\text{Na}[\text{11-super-carb}']$ or $\text{Na}[\text{super}^2\text{carb}']$ afforded only decomposition products, with no organometallic products isolated. Clearly, the steric pressure from the adjacent SMe_2 and Ph groups in carbametallaboranes derived from **1b** will result in a significantly reduced θ value relative to that in **3**, which in turn will not support the desired metal fragment conformation. The situation would only be exacerbated in carbametallaboranes derived from the extremely sterically encumbered ligand $\text{super}^2\text{carb}'$.

Apart from polytopal deformation or isomerisation, relief from steric crowding in metal complexes of **1b** and **2** could conceivably be gained by a greater lateral slip distortion of the metal away from the cage C atoms. It is well established [20] that increased slip is afforded by exopolyhedral ligands L which are significantly more basic than CO, and further development of the transition metal chemistry of **1a**, **1b** and **2**, taking account of such factors, is currently under way.

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