Synthesis, characterisation and molecular structures of the *closo* and *pseudocloso* heptamethylindenyl carbarhodaboranes 1-Ph-3-(η-C_9Me_7)-3,1,2-*closo*-$RhC_2B_9H_{10}$ and 1,2-Ph_2-3-(η-C_9Me_7)-3,1,2-*pseudocloso*-$RhC_2B_9H_9$. Experimental assignment of the ^{11}B NMR spectrum of a *pseudocloso* carbametallaborane†

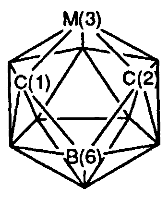
Ulrich Grädler,[a] Andrew S. Weller,[a] Alan J. Welch *,[a] and David Reed[b]

[a] *Department of Chemistry, Heriot-Watt University, Edinburgh EH14 4AS, UK*
[b] *Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ, UK*

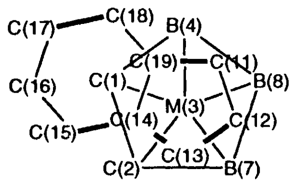
The reaction between [{$RhCl_2$(η-C_9Me_7)}$_2$] and Tl_2[7-Ph-8-R-7,8-*nido*-$C_2B_9H_9$] (R = H or Ph) in CH_2Cl_2 afforded the heptamethylindenyl carbarhodaboranes 1-Ph-3-(η-C_9Me_7)-3,1,2-$RhC_2B_9H_{10}$ **1** and 1,2-Ph_2-3-(η-C_9Me_7)-3,1,2-$RhC_2B_9H_9$ **2**, respectively, in good yields. The ^{11}B NMR chemical shifts of **1** and **2** showed that they possess *closo* and *pseudocloso* structures, respectively. Compound **1** was found to be fluctional in solution at room temperature *via* rotation of the Ph substituent, but cooling below *ca.* 230 K arrested this process, presumably by locking the indenyl ligand into its preferred cisoid conformation and preventing phenyl rotation. An X-ray diffraction study of a single crystal of **1** confirmed both the *closo* nature of the cage and the cisoid conformation, but additionally showed that, of two possible cisoid conformations, the one adopted places the cage phenyl substituent underneath the six-membered ring of the indenyl group. Compound **2** was also subjected to crystallographic analysis, which confirmed the *pseudocloso* nature of the cage. Again, the relative conformation of the two η-bonded ligands is cisoid. An ^{11}B–^{11}B COSY spectrum of compound **2**, the first to be recorded from a *pseudocloso* species, allowed experimental assignment of the ^{11}B chemical shifts which were in excellent agreement with those previously obtained theoretically.

We have recently shown that carbametallaboranes 1,2-Ph_2-3-(η-L)-3,1,2-$MC_2B_9H_9$ (M = Rh[3] or Ir,[1] L = C_5Me_5; M = Ru,[1] L = C_6H_6, *p*-cymene or C_6Me_6) adopt *pseudocloso* structures; those in which the C(1)–C(2) connectivity is lengthened (typically to *ca.* 2.5 Å) and M(3) ··· B(6) is shortened (typically to < 3 Å) as a consequence of steric crowding between the cage-bound phenyl groups, forced to lie nearly coplanar by the presence of the η-bonded substituent at M(3) (**I**). This geometric change from the regular *closo* structure predicted by the polyhedral skeletal electron pair theory[4] appears to be accompanied by a substantial change in the electronic structure of the cluster, since the weighted-average ^{11}B NMR chemical shift of a 12-vertex *pseudocloso* carbametallaborane is *ca.* δ +6, at considerably higher frequency than that of related *closo* species, *ca.* δ −10. The ^{11}B spectrum of a number of *closo* compounds 3-(η-L)-3,1,2-$MC_2B_9H_{11}$ have been assigned by ^{11}B–^{11}B correlation spectroscopy (COSY) experiments[5,6] but we have hitherto never been successful in obtaining useful COSY results of *pseudocloso* compounds, although a tentative assignment for 1,2-Ph_2-3-(η-C_5Me_5)-3,1,2-$RhC_2B_9H_9$ was made on the basis of the novel application of individual gauge for localised orbitals (IGLO) calculations to carbametallaboranes.[1]

Prior to this, we have synthesised and characterised a number of indenyl carbametallaboranes 1-R-2-R′-3-(η-C_9H_7)-3,1,2-$MC_2B_9H_9$ (M = Co or Rh). For the parent molecule (R = R′ = H, M = Co) we showed[7] that the theoretically and experimentally preferred conformation was that in which the indenyl ring junction carbon atoms lay cisoid (cisoid implies a *cis*-staggered arrangement of the two η-bonded rings) to the cage carbon atoms (**II**), but that this conformation could be overridden by steric crowding if the cage was doubly carbon substituted, since in 1,2-$(CH_2OMe)_2$-3-(η-C_9H_7)-3,1,2-$CoC_2B_9H_9$ the indenyl ligand is rotated about the M(3) ··· B(10) axis to the next-best staggered conformation.[8]



I



II

The foregoing considerations clearly identify 1,2-Ph_2-3-(η-C_9H_7)-3,1,2-$MC_2B_9H_9$ as potentially interesting molecules. Such species would be expected to suffer substantial steric crowding but have at least two possible ways (adoption of a *pseudocloso* structure and/or indenyl rotation) of relieving that crowding. However, until recently we have been dissuaded from the attempted synthesis of these interesting targets because of the very low yields anticipated. Indenyl carbacobaltaboranes are typically prepared, very inefficiently, from a Co^{III}–$[C_9H_7]^-$–$[RR'C_2B_9H_9]^{2-}$ mixture,[7,8] whilst indenyl carbarhodabo-

---

† Steric Effects in Heteroboranes. Part 12.[1] Also, Indenyl Carbametallaboranes. Part 4.[2]

ranes are afforded by the reaction between '$[RhCl_2(C_9H_7)]_x$' and $[RR'C_2B_9H_9]^{2-}$ in even poorer yields since the rhodium-containing precursor is both inhomogeneous and of limited solubility; by-products with $\{(C_9H_7)Rh(C_9H_6)\}$ fragments σ-bonded to cage B atoms tend to predominate.[2]

The recent communication[9] of the soluble, molecular species $[\{RhCl_2(\eta\text{-}C_9Me_7)\}_2]$, prepared in good yield by the reaction between C_9Me_7H[10] and $RhCl_3{\cdot}3H_2O$, has now afforded a solution to this problem. In this paper we describe the use of $[\{RhCl_2(\eta\text{-}C_9Me_7)\}_2]$ to prepare 1-Ph-3-(η-C_9Me_7)-3,1,2-$RhC_2B_9H_{10}$ and 1,2-Ph_2-3-(η-C_9Me_7)-3,1,2-$RhC_2B_9H_9$, and structural analyses of these products by NMR spectroscopy and X-ray diffraction. We also report the first experimental assignment of the ^{11}B NMR spectrum of a *pseudocloso* carbametallaborane by the ^{11}B–^{11}B COSY method, providing confirmation of the results of our previous IGLO-based prediction.[1]

Experimental

Synthesis and characterisation

General. All initial experiments were carried out under an inert, oxygen-free dinitrogen atmosphere, using standard Schlenk-line techniques. Subsequent manipulations were performed open to the air. All solvents were dried over the appropriate drying agents and distilled prior to use. Microanalyses were performed by the departmental service at Edinburgh University. Preparative thin layer chromatography (TLC) was performed using glass plates coated with Kieselgel 60 F_{254} (0.2 mm thick), prewashed with pure eluant. Heptamethylindene (C_9Me_7H)[10] and the complex $[\{RhCl_2(\eta\text{-}C_9Me_7)\}_2]$[9] were prepared as described. The salts Tl_2[7-Ph-7,8-*nido*-$C_2B_9H_{10}$][11] and Tl_2[7,8-Ph_2-7,8-*nido*-$C_2B_9H_9$][3] were prepared as described previously.

NMR spectroscopy. One-dimensional NMR spectra were recorded on Bruker AC 200 and DPX 400 spectrometers at Heriot-Watt University and a Bruker WH 360 spectrometer at Edinburgh University. The last was also used for the low-temperature and two-dimensional (COSY) experiments. Measurements were recorded at 297 K in $CDCl_3$ solutions unless otherwise indicated. Proton shifts are reported relative to external $SiMe_4$ with ^{11}B recorded relative to external $BF_3{\cdot}OEt_2$ at 128.00 MHz or 115.56 MHz.

Infrared spectroscopy. Infrared spectra were recorded from CH_2Cl_2 solutions in 0.1 mm solution cells using a Nicolet Impact 400 FTIR instrument.

Syntheses

1-Ph-3-(η-C_9Me_7)-3,1,2-*closo*-$RhC_2B_9H_{10}$ 1. The compounds $[\{RhCl_2(\eta\text{-}C_9Me_7)\}_2]$ (0.136 g, 0.18 mmol) and Tl_2[7-Ph-7,8-*nido*-$C_2B_9H_{10}$] (0.329 g, 0.53 mmol) were added to a frozen (−196 °C) solution of CH_2Cl_2 (10 cm^3) and the reaction mixture left to warm slowly to room temperature. After stirring for 18 h under dinitrogen, the solution was left to settle, and the supernatant removed *via* syringe. The solvent was evaporated to *ca.* 2 cm^3 volume *in vacuo*, and the resulting orange solution applied to preparative TLC plates. Development with CH_2Cl_2 afforded one major yellow mobile band which was recrystallised from CH_2Cl_2–pentane (1:2 ratio) at −30 °C to afford orange *crystals* of 1-Ph-3-(η-C_9Me_7)-3,1,2-*closo*-$RhC_2B_9H_{10}$ (yield 0.045 g, 48%) (Found: C, 54.5; H, 7.0. Calc. for $C_{24}H_{36}B_9Rh$: C, 54.9; H, 6.9%). IR ν_{max} 2547 cm^{-1} (B–H). NMR (CD_2Cl_2): ^1H, δ 7.15 (t, 1 H, Ph), 7.05 (apparent t, 2 H, Ph), 6.45 (d, 2 H, Ph), 3.55 (s br, 1 H, CH), 2.55 (s, 3 H, Me), 2.35 (s, 6 H, 2Me), 2.15 (s, 3 H, Me), 1.90 (s, 3 H, Me), 1.85 (s, 3 H, Me) and 1.80 (s, 3 H, Me); ^{11}B, δ 10.35 [d, 1 B, *J*(HB) 150], −1.09 [d, 1 B, *J*(HB) 148], −2.38 [d, 2 B, *J*(HB) 155], −9.64 [d, 2 B, *J*(HB) 138], −15.48 [d, 1 B, *J*(HB) 154], −17.56 [d, 1 B, *J*(HB) 154] and −20.61 [d, 1 B, *J*(HB) 154 Hz]; $^{11}B\text{-}\{^1H\}$, δ 10.35 (1 B), −1.09 (1 B), −2.38 (2 B), −9.64 (2 B), −15.48 (1 B), −17.56 (1 B) and −20.61 (1 B).

1,2-Ph_2-3-(η-C_9Me_7)-3,1,2-*pseudocloso*-$RhC_2B_9H_9$ 2. The compounds $[\{RhCl_2(\eta\text{-}C_9Me_7)\}_2]$ (0.085 g, 0.11 mmol) and Tl_2[7,8-Ph_2-7,8-*nido*-$C_2B_9H_9$] (0.190 g, 0.25 mmol) were added to a frozen (−196 °C) solution of CH_2Cl_2 (10 cm^3) and the reaction mixture left to warm slowly to room temperature. After stirring for 18 h under dinitrogen, the solution was allowed to settle, and the supernatant removed *via* syringe. The solvent was reduced to *ca.* 2 cm^3 volume *in vacuo*, and the resulting orange-brown solution applied to preparative TLC plates. Development with CH_2Cl_2 afforded one major orange band, which was recrystallised from CH_2Cl_2–ethyl acetate (1:2) at −30 °C to afford orange *crystals* of 1,2-Ph_2-3-(η-C_9Me_7)-3,1,2-*pseudocloso*-$RhC_2B_9H_9$ (yield 0.037 g, 52%) (Found: C, 59.8; H, 6.7. Calc. for $C_{30}H_{40}B_9Rh$: C, 59.9; H, 6.7%). IR ν_{max} 2514 cm^{-1} (B–H) NMR: ^1H, δ 7.20 (m, 6 H, Ph), 7.05 (m, 4 H, Ph), 2.10 (s, 6 H, 2 Me), 1.95 (s, 3 H, Me), 1.90 (s, 6 H, 2Me) and 1.50 (s, 6 H, 2Me); ^{11}B, δ 34.27 [d, 1 B, *J*(HB) 119], 13.27 [d, 1 B, *J*(HB) 128], 9.44 [d, 2 B, *J*(HB) 144], 4.84 [d, 2 B, *J*(HB) 130], −1.64 [d, 2 B, *J*(HB) 136] and −18.47 [d, 1 B, *J*(HB) 151]; $^{11}B\text{-}\{^1H\}$, δ 34.27 (1 B), 13.27 (1 B), 9.44 (2 B), 4.84 (2 B), −1.64 (2 B) and −18.47 (1 B).

Crystallographic studies

All measurements were carried out at room temperature on an Enraf-Nonius CAD4 diffractometer (Edinburgh University) equipped with graphite-monochromated Mo-Kα X-radiation (λ = 0.710 69 Å) and operating in the ω–2θ mode. Crystallographic computing was performed at Heriot-Watt University using the SHELXTL system[12] on a Pentium 90 MHz PC.

Table 1 lists details of unit cell data, intensity data collection and structure refinement for complexes **1** and **2**. In each case the unit-cell parameters and the orientation matrix for data collection were determined by the least-squares refinement of the setting angles of 25 strong, high angle, reflections. Regular remeasurement of the intensities of two check reflections revealed no crystal decay in either case. Data were empirically corrected for absorption by the ψ-scan method.

Both structures were solved without difficulty by direct and Fourier-difference methods, and optimised by full-matrix least-squares refinement (on F^2). Phenyl H atoms were placed in idealised positions (C–H 0.93 Å) and methyl H atoms were treated as idealised rigid groups (C–H 0.96 Å). Cage H atoms were set 1.10 Å from C or B on a radial extension. In the final stages of refinement all non-H atoms were refined with anisotropic displacement parameters, with H atoms given isotropic displacement parameters riding at 1.2 times the equivalent isotropic parameter of their bound (B or C) 'heavy' atom. Data were weighted such that $w^{-1} = [\sigma^2(F_o^2) + (g_1P)^2 + g_2P]$ where $P = [\max(F_o^2 \text{ or } 0) + 2F_c^2]/3$.

Final (non-H) atomic positional parameters are given in Tables 2 and 3.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

Results and Discussion

The reaction of $[\{RhCl_2(\eta\text{-}C_9Me_7)\}_2]$ with Tl_2[7-Ph-8-R-7,8-*nido*-$C_2B_9H_9$] (R = H or Ph) in CH_2Cl_2 affords the heptamethylindenyl carbarhodaboranes 1-Ph-3-(η-C_9Me_7)-3,1,2-$RhC_2C_2B_9H_{10}$ **1** and 1,2-Ph_2-3-(η-C_9Me_7)-3,1,2-$RhC_2B_9H_9$ **2**, respectively, in good yields. In these reactions the

Table 1 Crystallographic data and details of data collection and structure refinement

	1	**2**
Formula	$C_{24}H_{36}B_9Rh$	$C_{30}H_{40}B_9Rh$
M	524.73	600.82
System	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
a/Å	10.7256(21)	11.969(5)
b/Å	18.925(4)	19.012(10)
c/Å	13.586(3)	12.877(5)
β/°	113.18(3)	93.79(3)
U/Å^3	2535.1(9)	2923.8(22)
Z	4	4
D_c/g cm^{-3}	1.375	1.365
μ(Mo-Kα)/mm^{-1}	0.686	0.605
F(000)	1080	1240
$\theta_{orientation}$/°	8–12	7–12
$\theta_{data\ collection}$/°	1–25	1–25
hkl range	− 12 to 12, 0–22, 0–16	0–14, 0–22, − 15 to 15
ω scan speeds/° min^{-1}	0.82–2.35	0.87–2.35
Data measured	5265	5607
Unique data	4440	5146
g_1	0.0434	0.0788
g_2	2.15	4.84
R (all data)	0.0797	0.0769
Data observed [$F_o > 4\sigma(F_o)$]	3180	3727
R (observed data)	0.0413	0.0413
wR_2	0.1020	0.1241
S	1.068	0.866
Variables	307	361
Maximum, minimum residue/e Å^{-3}	0.37, −0.40	0.48, −0.30

Table 2 Atomic coordinates (× 10^4) for compound **1**

Atom	x	y	z	Atom	x	y	z
Rh(3)	8 277(1)	945(1)	7 053(1)	C(16)	12 174(5)	930(3)	9 322(4)
C(1)	8 806(4)	1 844(2)	6 303(3)	C(17)	12 371(5)	501(3)	8 515(4)
C(2)	7 991(5)	2 079(3)	7 080(4)	C(18)	11 339(5)	132(3)	7 768(4)
B(4)	7 894(5)	1 226(3)	5 394(4)	C(19)	10 027(5)	155(2)	7 827(4)
B(5)	7 879(6)	2 112(3)	5 003(4)	C(101)	10 313(4)	1 928(2)	6 660(3)
B(6)	7 948(6)	2 650(3)	6 078(5)	C(102)	10 975(5)	1 628(3)	6 075(4)
B(7)	6 497(6)	1 594(4)	6 744(5)	C(103)	12 346(6)	1 741(4)	6 345(5)
B(8)	6 416(6)	1 036(4)	5 625(5)	C(104)	13 069(6)	2 158(4)	7 193(5)
B(9)	6 372(7)	1 628(4)	4 587(5)	C(105)	12 452(5)	2 445(3)	7 792(5)
B(10)	6 389(6)	2 502(4)	5 011(5)	C(106)	11 075(5)	2 334(3)	7 541(4)
B(11)	6 490(6)	2 497(4)	6 333(5)	C(111)	8 417(7)	− 678(3)	6 263(5)
B(12)	5 520(6)	1 842(4)	5 417(5)	C(121)	6 437(6)	− 336(3)	7 383(5)
C(11)	8 753(5)	− 174(3)	7 200(4)	C(131)	7 799(5)	722(3)	9 275(4)
C(12)	7 834(5)	− 23(3)	7 697(4)	C(151)	10 712(6)	1 411(3)	10 226(4)
C(13)	8 465(5)	452(2)	8 559(4)	C(161)	13 385(6)	1 338(4)	10 084(5)
C(15)	10 947(5)	966(3)	9 395(3)	C(171)	13 788(6)	458(4)	8 519(5)
C(14)	9 853(4)	560(2)	8 662(3)	C(181)	11 511(7)	− 284(4)	6 886(6)

thallium carbaborane is used in excess (> 2 equivalents) to ensure total conversion of the rhodium-containing precursor. The excess $Tl_2[7\text{-}Ph\text{-}8\text{-}R\text{-}7,8\text{-}$*nido*$\text{-}C_2B_9H_9]$ is effectively insoluble in CH_2Cl_2, and compounds **1** and **2** are the major products isolated following work up involving preparative TLC.

Thus $[\{RhCl_2(\eta\text{-}C_9Me_7)\}_2]$ is shown to be an excellent precursor for indenyl carbarhodaboranes, much superior to '$[RhCl_2(\eta\text{-}C_9H_7)]_x$' previously used[2] to prepare 1-Ph-3-(η-C_9H_7)-3,1,2-$RhC_2B_9H_{10}$ and 1,2-$(CH_2OMe)_2$-3-(η-C_9H_7)-3,1,2-$RhC_2B_9H_9$ in yields of *ca.* 1% or less. Presumably the homogeneity of $[\{RhCl_2(\eta\text{-}C_9Me_7)\}_2]$ and its solubility in CH_2Cl_2 are important factors in its synthetic utility. In addition, the absence of relatively labile aromatic H atoms means that by-products with indenide units σ-bonded to cage B atoms, as has been observed[2] when using '$[RhCl_2(\eta\text{-}C_9H_7)]_x$', can no longer be formed. Since we are interested in the structural consequences of possible steric crowding between cluster substituents, $\eta\text{-}C_9Me_7$ is further preferred to $\eta\text{-}C_9H_7$.

Compounds **1** and **2** are orange crystalline materials, indefinitely stable in air as solids and stable for long periods as solutions under N_2. Both compounds give satisfactory microanalyses (C, H) and show strong absorptions between 2500 and 2550 cm^{-1} in IR spectra due to B–H stretching.

The $^{11}B\text{-}\{^1H\}$ NMR spectrum of compound **1** reveals seven resonances (relative integrals 1 : 1 : 2 : 2 : 1 : 1 : 1 from high to low frequency) consistent with an asymmetric molecule, the integral-2 resonances being coincident. The weighted-average chemical shift is δ −7.6, indicative[1] of a *closo* structure. On retention of proton coupling each resonance is split into a doublet with J(HB) 138–155 Hz.

At room temperature the ^1H NMR spectrum of **1** shows, in addition to six singlet resonances (1 coincident) between δ 2.6 and 1.8 (Me groups) and a broad integral-1 singlet at δ 3.55 (cage C–H), only three resonances in the aromatic region. These appear as a triplet (1 H) centred at δ 7.15, an apparent triplet (2 H) centred on δ 7.05 and a doublet (2 H) centred at δ 6.45, all couplings being *ca.* 7 Hz. They are assigned, respectively, to the *para*, *meta* and *ortho* protons of the phenyl ring clearly undergoing rotation about the C(1)–C(101) bond which is

Table 3 Atomic coordinates (× 10^4) for compound **2**

Atom	x	y	z	Atom	x	y	z
Rh(3)	2434(1)	929(1)	1708(1)	C(19)	4181(4)	786(2)	1031(4)
C(1)	2186(4)	2040(2)	1753(3)	C(111)	2973(5)	342(4)	−663(4)
C(2)	1546(4)	1207(3)	3084(4)	C(121)	2138(6)	−734(3)	950(6)
B(4)	1582(5)	1724(3)	683(4)	C(131)	3327(6)	−487(3)	3118(5)
B(5)	996(5)	2414(3)	1456(4)	C(151)	5150(5)	643(4)	3942(4)
B(6)	1310(5)	2084(3)	2773(4)	C(161)	6778(5)	1631(4)	3146(5)
B(7)	824(5)	673(3)	2305(5)	C(171)	6592(5)	2078(3)	1003(5)
B(8)	743(5)	943(3)	931(5)	C(181)	4769(5)	1565(4)	−436(4)
B(9)	83(5)	1786(3)	824(5)	C(101)	3199(4)	2509(2)	1808(4)
B(10)	−135(5)	2067(3)	2087(5)	C(102)	3402(5)	2942(3)	970(4)
B(11)	247(5)	1418(3)	2986(5)	C(103)	4269(5)	3425(3)	1036(5)
B(12)	−350(5)	1184(3)	1734(5)	C(104)	4939(5)	3491(3)	1935(5)
C(11)	3309(4)	370(3)	488(4)	C(105)	4766(4)	3061(3)	2751(5)
C(12)	2925(4)	−133(3)	1197(5)	C(106)	3899(4)	2574(3)	2687(4)
C(13)	3451(4)	−4(2)	2195(4)	C(201)	1983(4)	1008(3)	4169(4)
C(14)	4273(4)	555(2)	2107(4)	C(202)	2710(5)	1439(3)	4772(4)
C(15)	5102(4)	860(3)	2820(4)	C(203)	3051(5)	1251(4)	5791(5)
C(16)	5847(4)	1329(3)	2434(4)	C(204)	2663(6)	655(4)	6218(5)
C(17)	5748(4)	1553(3)	1363(4)	C(205)	1909(6)	225(4)	5639(5)
C(18)	4919(4)	1304(3)	685(4)	C(206)	1591(5)	403(3)	4636(5)

unrestricted on the NMR time-scale at room temperature. On progressive cooling the signal centred at δ 6.45 broadens at 256 K, is indistinguishable from the baseline at 233 K, reappears as two broad peaks centred at δ 6.8 and 5.9 at 218 K and is fully resolved into two doublets at 203 K. Under the same conditions the resonance centred at δ 7.05 broadens and splits into two integral-1 apparent triplets centred at δ 7.00 and 7.10. Selective decoupling experiments carried out at 203 K allowed full assignment of the aromatic region as follows:

δ 7.15 (apparent t), H(104) (*para*); 7.10 (apparent t), H(103) (*meta*); 7.00 (apparent t), H(105) (*meta*); 6.78 (d), H(102) (*ortho*); 5.87 (d), H(106) (*ortho*).

Although the NMR data does not allow us to comment on the extent of libration of the indenyl ligand about the metal–cluster axis, we believe that it is likely that the restricted rotation of the phenyl group at low temperatures is a direct result of the indenyl ligand locking into a cisoid conformation above it. The low-temperature spectrum is thus fully consistent with the molecular structure of **1** determined crystallographically (see below).

Compound **1** crystallises with no significant intermolecular contacts. A perspective view of a single molecule, demonstrating the atomic numbering scheme, is shown in Fig. 1 whilst Table 4 lists bond distances and selected interbond angles.

The structural analysis confirms that **1** has a *closo* polyhedral geometry, with C(1)–C(2) 1.674(6) and Rh(3) ··· B(6) > 3.4 Å. The usual molecular reference plane in *closo* 3,1,2-MC$_2$B$_9$ polyhedra is B(5)B(6)B(11)B(12)B(9); this and the upper (C$_2$B$_3$) face are both planar and are parallel. Atom Rh(3) bonds evenly to the carbaborane, with Rh–C/B distances in the region 2.17–2.19 Å. In contrast, but fully expected,[7–10] Rh(3) is slipped by *ca.* 0.16 Å with respect to the indenyl ligand in a direction away from C(14) and C(19). Partial double bond character is clearly evident in C(15)–C(16) and C(17)–C(18).

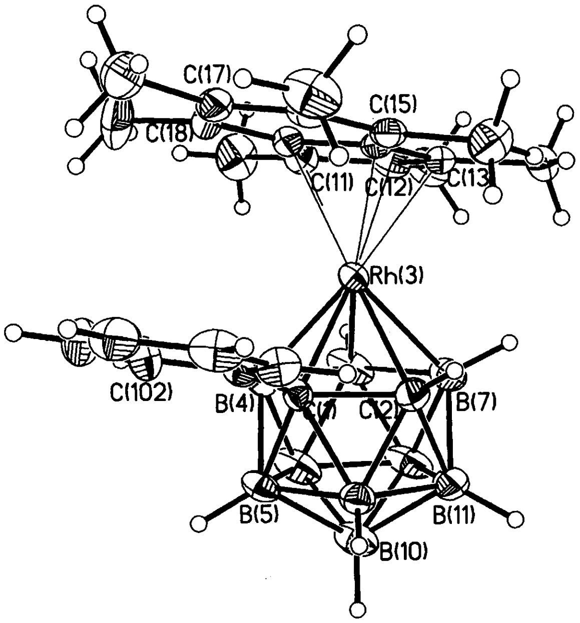


Fig. 1 Perspective view of a single molecule of compound **1** (30% ellipsoids except for H atoms which have an artificial radius of 0.1 Å for clarity). The phenyl ring is numbered cyclically, C(10*i*, *i* = 1–6). Methyl C atoms are numbered C(1*k*1) where *k* denotes the indenyl ring atom, C(1*k*, *k* = 1–3, 5–8) to which they are attached. Cage and phenyl H atoms carry the same number as the atom to which they are bound

The overall molecular conformation is cisoid, with the indenyl junction C atoms as close as possible to the cage C atoms given a mutually staggered arrangement of the two η-bonded rings. We have already shown that this arrangement, which arises directly from relatively weak bonding between the metal atom and (*i*) carbaborane C atoms *versus* carbaborane B atoms, and (*ii*) indenyl junction C atoms *versus* indenyl non-junction C atoms, is predicted and observed in the archetypal indenyl carbametallaborane 3-(η-C$_9$H$_7$)-3,1,2-CoC$_2$B$_9$H$_{11}$.[7] However, in indenyl carbametallaboranes in which one cage C atom is substituted *two* cisoid arrangements are possible; in structure **IIa** Ph is located under the six-membered ring of the indenyl ligand, whilst in **IIb** it lies to one side; conformations **IIa** and **IIb** are related as rotational isomers (of one ligand relative to the other). In 1-Ph-3-(η-C$_9$H$_7$)-3,1,2-CoC$_2$B$_9$H$_{10}$ the solid-state structure[8] accords with **IIb**, and there is convincing evidence that this conformation is also the limiting low-temperature solution one since cage C–H resonates at low frequency (δ 2.08 at 185 K) in the ^{1}H NMR spectrum as a result of lying directly under the six-membered ring. In compound **1** the alternate cisoid arrangement **IIa** is observed, as confirmed by Fig. 2. Thus, not only is the sterically demanding η-C$_9$Me$_7$ ligand not found rotated about the Rh(3) ··· B(10) axis to avoid the Ph substituent, but it also adopts what is presumably the more crowded cisoid alternative. That the observed structure *is* crowded is apparent from the following: the phenyl ring C(101–106), which has a conformation with respect to the carbaborane defined[11] by θ = 78.0°, subtends an elevation angle with respect to the upper C$_2$B$_3$ face of only 20.6°; the plane of the five-membered indenyl ring is tilted by 11.8° with respect to the C$_2$B$_3$ face, away from the phenyl substituent; the

Table 4 Bond lengths (Å) and selected interbond angles (°) in compound **1**

Rh(3)–C(1)	2.170(4)	Rh(3)–C(2)	2.171(5)	B(8)–B(9)	1.788(8)	B(9)–B(10)	1.750(10)
Rh(3)–B(4)	2.192(5)	Rh(3)–B(7)	2.167(6)	B(9)–B(12)	1.756(10)	B(10)–B(11)	1.757(9)
Rh(3)–B(8)	2.174(6)	Rh(3)–C(11)	2.169(5)	B(10)–B(12)	1.772(8)	B(11)–B(12)	1.774(11)
Rh(3)–C(12)	2.162(5)	Rh(3)–C(13)	2.184(4)	C(11)–C(12)	1.426(7)	C(11)–C(19)	1.437(7)
Rh(3)–C(14)	2.293(4)	Rh(3)–C(19)	2.304(5)	C(11)–C(111)	1.515(7)	C(12)–C(13)	1.420(6)
C(1)–C(101)	1.503(6)	C(1)–C(2)	1.674(6)	C(12)–C(121)	1.508(7)	C(13)–C(14)	1.453(6)
C(1)–B(4)	1.703(7)	C(1)–B(5)	1.727(6)	C(13)–C(131)	1.505(6)	C(15)–C(16)	1.360(6)
C(1)–B(6)	1.745(7)	C(2)–B(11)	1.721(7)	C(15)–C(14)	1.429(6)	C(15)–C(151)	1.508(7)
C(2)–B(6)	1.724(7)	C(2)–B(7)	1.745(8)	C(14)–C(19)	1.440(6)	C(16)–C(17)	1.445(7)
B(4)–B(9)	1.743(9)	B(4)–B(5)	1.757(8)	C(16)–C(161)	1.516(7)	C(17)–C(18)	1.364(8)
B(4)–B(8)	1.770(8)	B(5)–B(9)	1.746(8)	C(17)–C(171)	1.520(7)	C(18)–C(19)	1.441(6)
B(5)–B(6)	1.757(8)	B(5)–B(10)	1.765(9)	C(18)–C(181)	1.505(7)	C(101)–C(102)	1.379(6)
B(6)–B(10)	1.752(8)	B(6)–B(11)	1.755(8)	C(101)–C(106)	1.386(6)	C(102)–C(103)	1.384(7)
B(7)–B(12)	1.755(8)	B(7)–B(11)	1.797(9)	C(103)–C(104)	1.359(8)	C(104)–C(105)	1.350(8)
B(7)–B(8)	1.825(10)	B(8)–B(12)	1.766(10)	C(105)–C(106)	1.394(7)		

B(7)–Rh(3)–C(2)	47.4(2)	C(1)–Rh(3)–C(2)	45.4(2)	B(12)–B(9)–B(8)	59.8(4)	B(6)–B(10)–B(11)	60.0(4)
B(7)–Rh(3)–B(8)	49.7(3)	C(1)–Rh(3)–B(4)	45.9(2)	B(6)–B(10)–B(5)	60.0(3)	B(9)–B(10)–B(5)	59.6(4)
B(8)–Rh(3)–B(4)	47.8(2)	C(12)–Rh(3)–C(11)	38.4(2)	B(9)–B(10)–B(12)	59.8(4)	B(11)–B(10)–B(12)	60.3(4)
C(12)–Rh(3)–C(13)	38.1(2)	C(13)–Rh(3)–C(14)	37.8(2)	C(2)–B(11)–B(6)	59.5(3)	B(6)–B(11)–B(10)	59.8(3)
C(11)–Rh(3)–C(19)	37.3(2)	C(14)–Rh(3)–C(19)	36.5(2)	B(10)–B(11)–B(12)	60.3(4)	C(2)–B(11)–B(7)	59.4(3)
C(101)–C(1)–C(2)	122.1(4)	C(101)–C(1)–B(4)	123.0(4)	B(12)–B(11)–B(7)	58.9(4)	B(7)–B(12)–B(8)	62.4(4)
C(101)–C(1)–B(5)	114.3(4)	B(4)–C(1)–B(5)	61.6(3)	B(9)–B(12)–B(8)	61.0(4)	B(7)–B(12)–B(11)	61.2(4)
C(101)–C(1)–B(6)	112.9(4)	C(2)–C(1)–B(6)	60.5(3)	B(9)–B(12)–B(10)	59.5(4)	B(11)–B(12)–B(10)	59.4(4)
B(5)–C(1)–B(6)	60.8(3)	C(101)–C(1)–Rh(3)	112.3(3)	C(12)–C(11)–C(19)	107.8(4)	C(12)–C(11)–C(111)	122.9(5)
C(2)–C(1)–Rh(3)	67.3(2)	B(4)–C(1)–Rh(3)	67.7(2)	C(19)–C(11)–C(111)	128.8(5)	C(13)–C(12)–C(11)	108.9(4)
C(1)–C(2)–B(6)	61.8(3)	B(11)–C(2)–B(6)	61.2(3)	C(13)–C(12)–C(121)	125.5(5)	C(11)–C(12)–C(121)	125.6(5)
B(11)–C(2)–B(7)	62.5(3)	C(1)–C(2)–Rh(3)	67.3(2)	C(12)–C(13)–C(14)	107.8(4)	C(12)–C(13)–C(131)	123.6(4)
B(7)–C(2)–Rh(3)	66.2(3)	C(1)–B(4)–B(5)	59.9(3)	C(14)–C(13)–C(131)	128.3(4)	C(16)–C(15)–(14)	118.4(4)
B(9)–B(4)–B(5)	59.9(3)	B(9)–B(4)–B(8)	61.2(3)	C(16)–C(15)–C(151)	122.4(5)	C(14)–C(15)–C(151)	119.2(4)
C(1)–B(4)–Rh(3)	66.3(2)	B(8)–B(4)–Rh(3)	65.6(2)	C(15)–C(14)–C(19)	120.6(4)	C(15)–C(14)–C(13)	132.2(4)
C(1)–B(5)–B(4)	58.5(3)	B(9)–B(5)–B(4)	59.7(3)	C(19)–C(14)–C(13)	107.2(4)	C(15)–C(16)–C(17)	121.2(5)
C(1)–B(5)–B(6)	60.1(3)	B(9)–B(5)–B(10)	59.8(4)	C(15)–C(16)–C(161)	121.2(5)	C(17)–C(16)–C(161)	117.6(5)
B(6)–B(5)–B(10)	59.6(3)	C(2)–B(6)–C(1)	57.7(3)	C(18)–C(17)–C(16)	122.3(4)	C(18)–C(17)–C(171)	119.5(5)
C(2)–B(6)–B(11)	59.3(3)	B(10)–B(6)–B(11)	60.1(4)	C(16)–C(17)–C(171)	118.2(5)	C(17)–C(18)–C(19)	117.9(5)
C(1)–B(6)–B(5)	59.1(3)	B(10)–B(6)–B(5)	60.4(4)	C(17)–C(18)–C(181)	122.8(5)	C(19)–C(18)–C(181)	119.3(5)
C(2)–B(7)–B(11)	58.1(3)	B(12)–B(7)–B(11)	59.9(4)	C(11)–C(19)–C(14)	108.0(4)	C(11)–C(19)–C(18)	132.4(5)
B(12)–B(7)–B(8)	59.1(4)	C(2)–B(7)–Rh(3)	66.4(2)	C(14)–C(19)–C(18)	119.5(4)	C(102)–C(101)–C(106)	117.6(4)
B(8)–B(7)–Rh(3)	65.3(3)	B(12)–B(8)–B(9)	59.2(4)	C(102)–C(101)–C(1)	120.2(4)	C(106)–C(101)–C(1)	122.1(4)
B(4)–B(8)–B(9)	58.6(3)	B(12)–B(8)–B(7)	58.5(4)	C(101)–C(102)–C(103)	121.1(5)	C(104)–C(103)–C(102)	120.5(6)
B(4)–B(8)–Rh(3)	66.6(2)	B(7)–B(8)–Rh(3)	64.9(3)	C(105)–C(104)–C(103)	119.6(5)	C(104)–C(105)–C(106)	121.0(5)
B(4)–B(9)–B(5)	60.5(3)	B(5)–B(9)–B(10)	60.6(4)	C(101)–C(106)–C(105)	120.2(5)		
B(10)–B(9)–B(12)	60.7(4)	B(4)–B(9)–B(8)	60.2(3)				

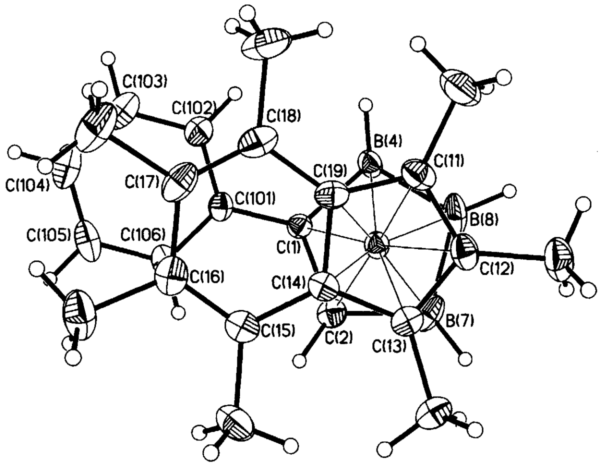
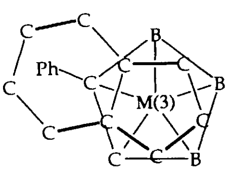


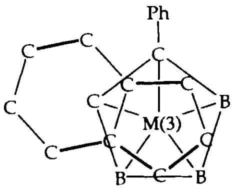
Fig. 2 Top view of compound **1** with the lower half of the carbaborane cage omitted for clarity

C(14–19) plane is further bent away from Ph, subtending a hinge angle with the indenyl pentagon of 3.7°; the methyl pendant C(171) lies displaced nearly 0.1 Å out of the C(14–19) plane away from the carbaborane, whilst C(151), C(161) and C(181) are marginally (0.02–0.06 Å) bent towards it.

Again, NMR data for **1** suggest that the **IIa** conformation observed in the solid state agrees with the limiting low-temperature structure in solution. Thus the cage C–H atom does not resonate at particularly low frequency (δ 3.45 at 188 K) but there is evidence that the chemical shifts of the *ortho* phenyl H atoms are affected by the influence of the indenyl ligand. However, in an idealised **IIa** arrangement H(102) and H(106) would experience the indenyl ligand equally. Although Fig. 2 shows that H(106) is rather more eclipsed by indenyl than H(102) the difference is small and unlikely to be maintained in solution, even at low temperature. Consequently, the relatively low frequency of the resonance due to H(106) cannot arise solely from the proximal indenyl group. In contrast, in conformation **IIb** the influence of the indenyl ligand on the *ortho* H atoms is markedly asymmetric, and it is significant that in the low-temperature limiting spectrum of **1** (arrangement **IIa**) $\Delta(\delta_{ortho})$ is < 0.9 ppm, whereas in 1-Ph-3-(η-C_9H_7)-3,1,2-$CoC_2B_9H_{10}$ (arrangement **IIb**) $\Delta(\delta_{ortho})$ is > 1.3 ppm.[8]



IIa



IIb

For compound **2** both the ^{11}B and ^{1}H NMR spectra suggest time-averaged C_s molecular symmetry at room temperature. Thus, in the ^{1}H spectrum, four signals (relative integrals

2 : 1 : 2 : 2, high frequency to low frequency) are observed for the methyl protons, and in the aromatic region two multiplets are observed centred at δ 7.20 (6 H) and 7.05 (4 H), the latter presumably arising from the *ortho* phenyl H atoms; since this does not appear as a simple doublet (by comparison with the room temperature spectrum of **1**) we conclude that the cage phenyl groups are not able to undergo rotation about the C_{cage}–C_{phenyl} bonds at room temperature. In the $^{11}B-\{^1H\}$ NMR spectrum there are six resonances (1 : 1 : 2 : 2 : 2 : 1) whose weighted-average chemical shift is δ +6.0, immediately identifying it as a *pseudocloso* species.[1] All signals show the expected doublet coupling, *J*(HB) 119–151 Hz, in the ^{11}B spectrum. Assignment of the ^{11}B spectrum from an ^{11}B–^{11}B COSY experiment is presented later.

Fig. 3 shows a perspective view of a single molecule of **2**, Fig. 4 views the indenyl ligand, the metal atom and the upper part of the carbaborane cage from above and Table 5 lists bond distances and selected interbond angles. The molecule is confirmed as having a *pseudocloso* structure, characterised by an extended C(1) ••• C(2), 2.491(6) Å, and a contracted Rh(3) ••• B(6), 2.960(5) Å; these arise from the cage phenyl groups lying reasonably coplanar [θ^{11} = 92.2 and 72.2° for C(101–106) and C(201–206), respectively], prising open the C(1)–C(2) connectivity by steric congestion [H(106) ••• H(202) in the open structure is 2.10 Å] and pulling B(6) *ca.* 0.33 Å out of the plane of B(5)B(11)B(12)B(9). All these parameters are in good agreement with equivalent ones reported in other *pseudocloso* species.[1,3]

As is evident from Fig. 4 the indenyl and (partially opened) carbaborane ligand adopt a mutually cisoid conformation; all that is required to generate the C_s molecular symmetry evident from NMR spectroscopy is a 72° libration of one of the ligands relative to the other about the Rh(3) ••• B(10) axis. Parameters within the indenyl ligand of **2** are similar to those in **1**; the metal atom is slipped by 0.14 Å, the η-bonded C_5 face is inclined to the best plane through B(5)B(11)B(12)B(9) by 7.7° and the six-membered indenyl ring is further tilted, by 6.3°, away from the carbaborane. Atoms C(171) and C(161) are each displaced *ca.* 0.05 Å out of the C_6 indenyl ring plane away from the proximal phenyl group, whereas C(151) and C(181) tip *ca.* 0.10 Å in the opposite direction.

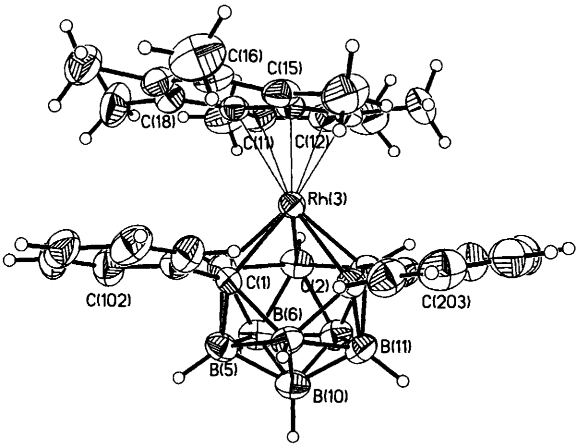


Fig. 3 Perspective view of a single molecule of compound **2** (30% ellipsoids except for H atoms which have an artificial radius of 0.1 Å for clarity). Atomic numbering as for Fig. 1, except that the second phenyl ring is numbered cyclically, C(20*i*)

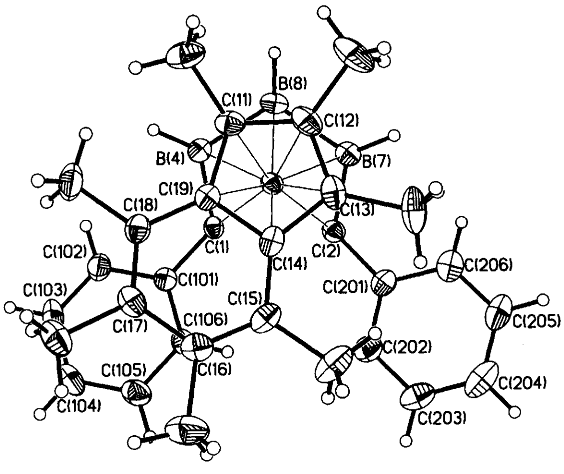


Fig. 4 Top view of compound **2** with the lower half of the carbaborane cage omitted for clarity

The assignment of ^{11}B chemical shifts in *pseudocloso* carbametallaboranes has so far only been possible by computation, and we recently[1] reported the novel application of the IGLO method to this end. Fortunately, compound **2** is the first *pseudocloso* carbametallaborane to yield an ^{11}B–^{11}B (COSY) NMR spectrum, shown in Fig. 5, by which to assign shifts experimentally.

Clearly, the one-dimensional integral-1 peaks (α, β and φ) arise from atoms B(8), B(10) and B(6) and the integral-2 peaks (χ, δ and ε) are due to the pairs B(4,7), B(9,12) and B(5,11). Between α, β and φ the only observed correlation is β/φ, identifying α as due to B(8). Peak α correlates with δ and ε, but not with χ, showing χ as being due to B(5,11), verified by correlations between β/χ and χ/φ. Of β and φ only the former correlates with a second integral-2 resonance (ε), identifying β as arising from B(10) and hence φ from B(6). There is no ε/φ correlation. Peak ε must be due to B(9,12) which, as already noted, correlates strongly with α. By elimination, peak δ arises from B(4,7). It correlates with α (noted), with ε and with χ, as expected.

The complete assignment is given in Table 6 which summarises the ^{11}B chemical shifts in all the *pseudocloso* carbametallaboranes so far characterised. Agreement between the experimental assignment reported here and the tentative assignment[1] based on IGLO calculations for 1,2-Ph_2-3-(η-

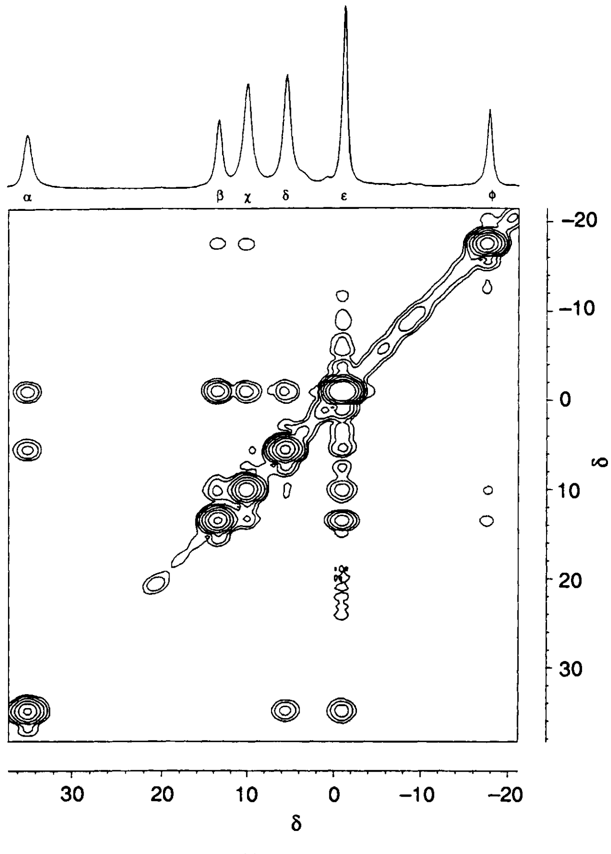


Fig. 5 An 115.56 MHz ^{11}B homonuclear COSY experiment on compound **2**

Table 5 Bond lengths (Å) and selected interbond angles (°) in compound **2**

Rh(3)–C(1)	2.133(4)	Rh(3)–B(7)	2.177(6)	B(10)–B(12)	1.754(9)	B(11)–B(12)	1.776(9)
Rh(3)–C(2)	2.191(5)	Rh(3)–B(8)	2.198(6)	C(11)–C(12)	1.420(7)	C(11)–C(19)	1.452(7)
Rh(3)–B(4)	2.211(6)	Rh(3)–C(12)	2.215(5)	C(11)–C(111)	1.510(7)	C(12)–C(13)	1.414(8)
Rh(3)–C(11)	2.216(5)	Rh(3)–C(13)	2.218(5)	C(12)–C(121)	1.501(7)	C(13)–C(14)	1.458(7)
Rh(3)–C(19)	2.334(5)	Rh(3)–C(14)	2.337(5)	C(13)–C(131)	1.516(7)	C(14)–C(15)	1.429(7)
C(1)–C(101)	1.503(6)	C(1)–B(5)	1.616(7)	C(14)–C(19)	1.450(6)	C(15)–C(16)	1.376(7)
C(1)–B(4)	1.628(7)	C(1)–B(6)	1.737(7)	C(15)–C(151)	1.501(7)	C(16)–C(17)	1.441(7)
C(2)–C(201)	1.507(7)	C(2)–B(11)	1.603(7)	C(16)–C(161)	1.509(7)	C(17)–C(18)	1.363(7)
C(2)–B(7)	1.633(8)	C(2)–B(6)	1.735(7)	C(17)–C(171)	1.514(7)	C(18)–C(19)	1.414(7)
B(4)–B(5)	1.815(8)	B(4)–B(9)	1.820(8)	C(18)–C(181)	1.525(7)	C(101)–C(106)	1.369(7)
B(4)–B(8)	1.833(8)	B(5)–B(10)	1.753(8)	C(101)–C(102)	1.391(7)	C(102)–C(103)	1.384(8)
B(5)–B(9)	1.780(8)	B(5)–B(6)	1.824(8)	C(103)–C(104)	1.370(9)	C(104)–C(105)	1.359(8)
B(6)–B(11)	1.828(8)	B(6)–B(10)	1.889(8)	C(105)–C(106)	1.388(7)	C(201)–C(202)	1.393(7)
B(7)–B(12)	1.823(9)	B(7)–B(11)	1.826(8)	C(201)–C(206)	1.395(7)	C(202)–C(203)	1.396(8)
B(7)–B(8)	1.838(8)	B(8)–B(12)	1.781(8)	C(203)–C(204)	1.354(10)	C(204)–C(205)	1.397(10)
B(8)–B(9)	1.788(8)	B(9)–B(12)	1.741(9)	C(205)–C(206)	1.365(8)		
B(9)–B(10)	1.749(8)	B(10)–B(11)	1.732(9)				
C(1)–Rh(3)–C(2)	70.3(2)	B(7)–Rh(3)–C(2)	43.9(2)	B(5)–B(10)–B(6)	60.0(3)	B(10)–B(11)–B(12)	60.0(4)
B(7)–Rh(3)–B(8)	49.7(2)	C(1)–Rh(3)–B(4)	44.0(2)	C(2)–B(11)–B(7)	56.4(3)	B(12)–B(11)–B(7)	60.8(3)
B(8)–Rh(3)–B(4)	49.1(2)	C(12)–Rh(3)–C(11)	37.4(2)	C(2)–B(11)–B(6)	60.3(3)	B(10)–B(11)–B(6)	64.0(3)
C(12)–Rh(3)–C(13)	37.2(2)	C(11)–Rh(3)–C(19)	37.1(2)	B(9)–B(12)–B(10)	60.0(3)	B(10)–B(12)–B(11)	58.8(3)
C(13)–Rh(3)–C(14)	37.2(2)	C(19)–Rh(3)–C(14)	36.2(2)	B(9)–B(12)–B(8)	61.0(3)	B(11)–B(12)–B(7)	61.0(3)
C(101)–C(1)–B(5)	116.4(4)	C(101)–C(1)–B(4)	124.8(4)	B(8)–B(12)–B(7)	61.3(3)	C(12)–C(11)–C(19)	108.1(4)
C(101)–C(1)–B(6)	117.5(4)	C(101)–C(1)–Rh(3)	118.4(3)	C(12)–C(11)–C(111)	122.1(5)	C(19)–C(11)–C(111)	128.9(5)
B(6)–C(1)–Rh(3)	99.3(3)	C(201)–C(2)–B(11)	114.3(4)	C(13)–C(12)–C(11)	108.9(4)	C(13)–C(12)–C(121)	124.1(6)
C(201)–C(2)–B(7)	123.5(4)	C(201)–C(2)–B(6)	119.7(4)	C(11)–C(12)–C(121)	127.0(6)	C(12)–C(13)–C(14)	108.6(4)
C(201)–C(2)–Rh(3)	122.2(3)	B(6)–C(2)–Rh(3)	97.2(3)	C(12)–C(13)–C(131)	123.1(5)	C(14)–C(13)–C(131)	127.1(5)
C(1)–B(4)–B(5)	55.7(3)	B(5)–B(4)–B(9)	58.6(3)	C(15)–C(14)–C(19)	119.7(4)	C(15)–C(14)–C(13)	133.6(5)
B(9)–B(4)–B(8)	58.6(3)	C(1)–B(4)–Rh(3)	65.5(2)	C(19)–C(14)–C(13)	106.6(4)	C(16)–C(15)–C(14)	118.0(4)
B(8)–B(4)–Rh(3)	65.1(2)	B(10)–B(5)–B(9)	59.3(3)	C(16)–C(15)–C(151)	122.7(5)	C(14)–C(15)–C(151)	119.2(5)
C(1)–B(5)–B(4)	56.3(3)	B(9)–B(5)–B(4)	60.8(3)	C(15)–C(16)–C(17)	121.5(5)	C(15)–C(16)–C(161)	119.8(5)
C(1)–B(5)–B(6)	60.3(3)	B(10)–B(5)–B(6)	63.7(3)	C(17)–C(16)–C(161)	118.7(5)	C(18)–C(17)–C(16)	121.4(5)
C(2)–B(6)–C(1)	91.7(3)	C(1)–B(6)–B(5)	53.9(3)	C(18)–C(17)–C(171)	120.3(5)	C(16)–C(17)–C(171)	118.3(5)
C(2)–B(6)–B(11)	53.4(3)	B(5)–B(6)–B(10)	56.3(3)	C(17)–C(18)–C(19)	118.9(5)	C(17)–C(18)–C(181)	121.9(5)
B(11)–B(6)–B(10)	55.5(3)	C(2)–B(7)–B(11)	54.9(3)	C(19)–C(18)–C(181)	119.2(5)	C(18)–C(19)–C(14)	120.2(4)
B(12)–B(7)–B(11)	58.3(3)	B(12)–B(7)–B(8)	58.2(3)	C(18)–C(19)–C(11)	132.2(4)	C(14)–C(19)–C(11)	107.6(4)
C(2)–B(7)–Rh(3)	68.5(3)	B(8)–B(7)–Rh(3)	65.7(3)	C(106)–C(101)–C(102)	117.4(5)	C(106)–C(101)–C(1)	122.7(4)
B(12)–B(8)–B(9)	58.4(3)	B(9)–B(8)–B(4)	60.3(3)	C(102)–C(101)–C(1)	119.8(4)	C(103)–C(102)–C(101)	120.9(5)
B(12)–B(8)–B(7)	60.5(3)	B(4)–B(8)–Rh(3)	65.8(3)	C(104)–C(103)–C(102)	120.5(5)	C(105)–C(104)–C(103)	119.1(5)
B(7)–B(8)–Rh(3)	64.6(3)	B(12)–B(9)–B(10)	60.4(4)	C(104)–C(105)–C(106)	120.5(6)	C(101)–C(106)–C(105)	121.5(5)
B(10)–B(9)–B(5)	59.6(3)	B(12)–B(9)–B(8)	60.6(3)	C(202)–C(201)–C(206)	117.4(5)	C(202)–C(201)–C(2)	122.4(5)
B(5)–B(9)–B(4)	60.6(3)	B(8)–B(9)–B(4)	61.1(3)	C(206)–C(201)–C(2)	120.0(5)	C(201)–C(202)–C(203)	120.4(6)
B(9)–B(10)–B(5)	61.1(3)	B(11)–B(10)–B(12)	61.3(4)	C(204)–C(203)–C(202)	120.7(6)	C(203)–C(204)–C(205)	120.0(6)
B(9)–B(10)–B(12)	59.6(4)	B(11)–B(10)–B(6)	60.5(3)	C(206)–C(205)–C(204)	119.3(6)	C(205)–C(206)–C(201)	122.2(6)

Table 6 ^{11}B NMR shifts (ppm) and assignments in *pseudocloso* carbametallaboranes 1,2-Ph_2-3-(η-L)-3,1,2-$MC_2B_9H_9$

(η-L)M [Method]	δ [Assignment]						Ref.
(C_5Me_5)Rh [IGLO]	33.1 (1 B) [B(8)]	12.9 (1 B) [B(10)]	10.3 (2 B) [B(5,11)]	4.0 (2 B) [B(4,7)]	−1.2 (2 B) [B(9,12)]	−18.0 (1 B) [B(6)]	1,3
(C_5Me_5)Ir	25.3 (1 B)	12.5 (2 B)	11.4 (1 B)	−3.6 (4 B)		−17.9 (1 B)	1
(C_6H_6)Ru	28.2 (1 B)	15.1 (2 B)	13.5 (1 B)	−0.3 (2 B)	−1.6 (2 B)	−19.8 (1 B)	1
(*p*-cymene)Ru	30.3 (1 B)	15.6 (2 B)	12.6 (1 B)	−0.5 (2 B)	−1.4 (2 B)	−20.1 (1 B)	1
(C_6Me_6)Ru	32.7 (1 B)	15.9 (2 B)	12.3 (1 B)	0.2 (2 B)	−1.0 (2 B)	−17.9 (1 B)	1
(C_9Me_7)Rh [COSY]	34.3 (1 B) [B(8)]	13.3 (1 B) [B(10)]	9.4 (2 B) [B(5,11)]	4.8 (2 B) [B(4,7)]	−1.6 (2 B) [B(9,12)]	−18.5 (1 B) [B(6)]	This work

C_5Me_5)-3,1,2-$RhC_2B_9H_9$ is excellent, confirming the merit of the latter. Much of the spectra of other *pseudocloso* carbametallaboranes can be confidently assigned by comparison. For (η-L)M = (C_6H_6)Ru, (*p*-cymene)Ru and (C_6Me_6)Ru the three highest frequency resonances are clearly due to B(8), B(10) and B(5,11) respectively, with that at lowest frequency arising from B(6). There only remains ambiguity about the precise ordering of the two integral-2 resonances near δ 0, due to either B(4,7) or B(9,12). The position for (η-L)M = (C_5Me_5)Ir is not so well defined, since the relative positions of the signals arising from B(10) and B(5,11) appear inverted and the near-zero chemical shifts are coincident. Nevertheless, the broad pattern of this spectrum is clearly related to those of all the other *pseudocloso* carbametallaboranes.

It is important to have a confident assignment of the ^{11}B spectra of *pseudocloso* carbametallaboranes before embarking on studies designed to probe the electronic structures of these unusually-shaped clusters and to understand how they relate to those of *closo* and *hypercloso*[13,14] species. Such studies are currently underway.

Acknowledgements

We thank the EPSRC (A. S. W.) for support, and the Callery Chemical Company for a generous gift of $B_{10}H_{14}$; U. G. is the recipient of an ERASMUS exchange scholarship from the Philipps University, Marburg, Germany.

References

1 P. T. Brain, M. Bühl, J. Cowie, Z. G. Lewis and A. J. Welch, *J. Chem. Soc., Dalton Trans.*, in the press.
2 Z. G. Lewis and A. J. Welch, *J. Organomet. Chem.*, 1992, **438**, 353.
3 Z. G. Lewis and A. J. Welch, *J. Organomet. Chem.*, 1992, **430**, C45.
4 K. Wade, *Adv. Inorg. Chem. Radiochem.*, 1976, **18**, 1.
5 M. Bown, J. Plesek, K. Base, B. Stibr, X. L. R. Fontaine, N. N. Greenwood and J. D. Kennedy, *Magn. Reson. Chem.*, 1989, **27**, 947.
6 X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy, K. Nestor and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1990, 681.
7 D. E. Smith and A. J. Welch, *Organometallics*, 1986, **5**, 760.
8 Z. G. Lewis, D. Reed and A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 1992, 731.
9 T. B. Marder, personal communication.
10 D. O'Hare, J. C. Green, T. B. Marder, S. Collins, G. Stringer, A. K. Kakker, N. Kaltsoyannis, A. Kuhn, R. Lewis, C. Mehnert, P. Scott, M. Kurmoo and S. Pugh, *Organometallics*, 1992, **11**, 48.
11 J. Cowie, B. D. Reid, J. M. S. Watmough and A. J. Welch, *J. Organomet. Chem.*, 1994, **481**, 283.
12 SHELXTL (PC version 5.0) Siemens Analytical Instruments Inc., Madison, WI, 1994.
13 M. J. Attfield, J. A. K. Howard, A. N. de M. Jelfs, C. M. Nunn and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1987, 2219.
14 N. Carr, D. F. Mullica, E. L. Sappenfield and F. G. A. Stone, *Organometallics*, 1992, **11**, 3697.

Received 4*th August* 1995; *Paper* 5/05432J