Synthesis and characterisation of *pseudocloso* iridium and ruthenium diphenyl carbaboranes. Molecular structures of 1,2-Ph_2-3-(η-C_6H_6)-3,1,2-*pseudocloso*-$RuC_2B_9H_9$ and 1,2-Ph_2-3-(cym)-3,1,2-*pseudocloso*-$RuC_2B_9H_9$ (cym = *p*-cymene) and individual gauge for localised orbitals calculations on carbametallaboranes‡

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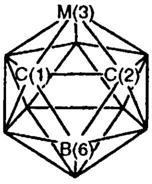
The syntheses and characterisations of 1,2-Ph_2-3-(η-C_5Me_5)-3,1,2-*pseudocloso*-$IrC_2B_9H_9$ **1**, 1,2-Ph_2-3-(η-C_6H_6)-3,1,2-*pseudocloso*-$RuC_2B_9H_9$ **2**, 1,2-Ph_2-3-(cym)-3,1,2-*pseudocloso*-$RuC_2B_9H_9$ (cym = *p*-cymene) **3** and 1,2-Ph_2-3-(η-C_6Me_6)-3,1,2-*pseudocloso*-$RuC_2B_9H_9$ **4** are reported from the reactions between $Tl_2[7,8\text{-}Ph_2\text{-}$*nido*-7,8-$C_2B_9H_9]$ and either $[\{IrCl_2(C_5Me_5)\}_2]$ or the appropriate $[\{RuCl_2(arene)\}_2]$ species. By ^{11}B NMR spectroscopy all these compounds have *pseudocloso* geometries, in which the C(1) $\cdots$ C(2) connectivity is broken and an approximately square M(3)C(1)B(6)C(2) face is generated. Crystallographic studies on **2** and **3** confirm this suggestion. It is suggested that distortion in these species arises from steric crowding between the C_{phenyl} substituents, forced to adopt conformations with high θ values by the presence of the η-bonded substituent at M(3). Individual gauge for localised orbitals calculations, reported for the first time on transition-metal heteroboranes, reasonably reproduce the (previously assigned) ^{11}B NMR chemical shifts of 3-(η-C_5Me_5)-3,1,2-*closo*-$RhC_2B_9H_{11}$, and allow a tentative assignment of those of 1,2-Ph_2-3-(η-C_5Me_5)-3,1,2-*pseudocloso*-$RhC_2B_9H_9$.

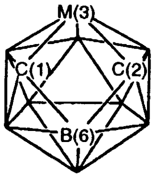
In a previous paper in this series[2] we discussed how the successive introduction of phenyl and methyl substituents at the cage carbon atoms in 3-(arene)-3,1,2-ruthenadicarbaboranes caused distortion of the essentially icosahedral cluster framework. Evidence was presented to show the beginnings of a deformation from *closo* (**I**) towards *pseudocloso* (**II**), under which the C(1)–C(2) connectivity lengthens and the M(3) $\cdots$ B(6) distance shortens, there being an associated small, but measurable, shift to higher frequency of the average ^{11}B NMR shift. We have already shown§,[3] that in 1,2-Ph_2-3-(η-C_5Me_5)-3,1,2-*pseudocloso*-$RhC_2B_9H_9$ a full *pseudocloso* structure is afforded, and have ascribed the cause of this unusual structure to the relief of intramolecular steric congestion between the cage phenyl groups, forced to lie nearly coplanar by the demands of the metal-bound C_5Me_5 ligand. Moreover, in 1,2-Ph_2-3-(η-C_5Me_5)-3,1,2-*pseudocloso*-$RhC_2B_9H_9$ the weighted-average ^{11}B NMR shift is +6.0 ppm, at very high frequency compared to that (−8.6 ppm) in the undistorted analogue 3-(η-C_5Me_5)-3,1,2-*closo*-$RhC_2B_9H_{11}$.[4]

Unfortunately, however, the structure determination of 1,2-Ph_2-3-(η-C_5Me_5)-3,1,2-*pseudocloso*-$RhC_2B_9H_9$ was of relatively low precision, the result of crystallographic disorder that was impossible to model completely. Moreover, we could never obtain an ^{11}B–^{11}B correlation (COSY) NMR spectrum of this species by which to assign specific boron resonances more fully to investigate the high frequency shifts.

In the present contribution we report the synthesis of 1,2-Ph_2-3-(η-C_5Me_5)-3,1,2-$IrC_2B_9H_9$, the simple iridium analogue of our initial *pseudocloso* species, prepared in the (ultimately unsuccessful) hope of being able to obtain a more accurate crystal structure of this family of compound. We also report a series of (arene)Ru congeners, crystallographic and spectroscopic study of which has allowed us to investigate any effects on cluster structure of changes in the steric demand of the metal-bonded η-polyene ligand. Although all the above species are further examples of *pseudocloso* carbametallaboranes it was again not possible to assign ^{11}B spectra through traditional (COSY) means, and so we have taken the slightly unusual step of tentatively assigning the spectrum of a typical *pseudocloso* carbametallaborane from the results of individual gauge for localised orbitals (IGLO) calculations.[5]



I (*closo*)



II (*pseudocloso*)

Experimental

Synthesis and characterisation

All reactions were carried out under an atmosphere of dry, oxygen-free nitrogen using standard Schlenk techniques, with some subsequent manipulations carried out in the open laboratory. Unless otherwise stated, all solvents were dried and distilled under N_2 just prior to use. The NMR spectra were recorded on Bruker WP200SY or WH360 spectrometers as $CDCl_3$ solutions at 298 K, chemical shifts being reported

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‡ Steric Effects in Heteroboranes. Part 11.[1]

§ Note that the signs of two of the ^{11}B NMR chemical shifts of compound **II** reported in Table 1 of reference 3 are in error, and should read +10.3 (2 B) and +4.0 (2 B).

relative to external $SiMe_4$ (^1H) or $BF_3{\cdot}OEt_2$ (^{11}B, ^{11}B-{^1H}). Infrared spectra were recorded as reference solutions in CH_2Cl_2 on a Perkin-Elmer 598 spectrophotometer. Microanalyses were performed by the departmental service. The starting materials $Tl_2[7,8\text{-}Ph_2\text{-}\textit{nido}\text{-}7,8\text{-}C_2B_9H_9]$,[3] $[\{IrCl_2(C_5Me_5)\}_2]$,[6] $[\{RuCl_2(C_6H_6)\}_2]$,[7] $[\{RuCl_2(cym)\}_2]$ (cym = *p*-cymene, 4-isopropyltoluene)[8] and $[\{RuCl_2(C_6Me_6)\}_2]$[8] were prepared by literature methods or slight variants thereof.

1,2-Ph$_2$-3-(η-C$_5$Me$_5$)-3,1,2-*pseudocloso*-IrC$_2$B$_9$H$_9$ 1. A mixture of $[\{IrCl_2(C_5Me_5)\}_2]$ (0.30 g, 0.38 mmol) and $Tl_2[7,8\text{-}Ph_2\text{-}\textit{nido}\text{-}7,8\text{-}C_2B_9H_9]$ (0.50 g, 0.74 mmol) in CH_2Cl_2 (20 cm^3) were gradually warmed to room temperature from −196 °C in a foil-covered Schlenk tube, and left to stir overnight. The resulting orange–red solution was filtered and concentrated to *ca.* 2 cm^3 *in vacuo*. Preparative thin layer chromatography (TLC) on silica, eluting with CH_2Cl_2–hexane (60:40), revealed two mobile bands, one orange–red with R_f *ca.* 0.8 and one yellow with R_f 0.35, but only the former was present in sufficient amount for collection. After isolation this was further purified by recrystallisation (CH_2Cl_2–hexane at −30 °C) to afford dark pink *plates* of 1,2-Ph$_2$-3-(η-C$_5$Me$_5$)-3,1,2-*pseudocloso*-IrC$_2$B$_9$H$_9$, **1**. Yield 0.09 g, 20% (Found: C, 45.6; H, 6.05. Calc. for $C_{24}H_{34}B_9Ir$: C, 47.1; H, 5.60%). IR (CH_2Cl_2) ν_{max} at 2890 (C–H) and 2550 cm^{-1} [s (br), B–H]. NMR: ^1H, δ 7.26–7.15 (m, 10 H, C_6H_5) and 1.24 (s, 15 H, CH_3); ^{11}B-{^1H}, δ 25.29 (1 B), 12.50 (2 B), 11.41 (1 B), −3.58 (4 B) and −17.88 (1 B).

1,2-Ph$_2$-3-(η-C$_6$H$_6$)-3,1,2-*pseudocloso*-RuC$_2$B$_9$H$_9$ 2. Similarly, to a mixture of $[\{RuCl_2(C_6H_6)\}_2]$ (0.12 g, 0.24 mmol) and $Tl_2[7,8\text{-}Ph_2\text{-}\textit{nido}\text{-}7,8\text{-}C_2B_9H_9]$ (0.33 g, 0.48 mmol) at −196 °C in a foil-covered Schlenk tube was added CH_2Cl_2 (20 cm^3). The mixture was allowed to warm to room temperature and stirred for 15 h. The mixture was filtered and the orange filtrate concentrated to *ca.* 2 cm^3 *in vacuo*. Preparative TLC (CH_2Cl_2–hexane, 60:40), revealed a complex mixture of bands. The most mobile and intense of these (orange, R_f 0.7) was collected and recrystallised by solvent diffusion (CH_2Cl_2–hexane, 1:4, −30 °C) to yield 1,2-Ph$_2$-3-(η-C$_6$H$_6$)-3,1,2-*pseudocloso*-RuC$_2$B$_9$H$_9$, **2**, as well formed orange *crystals*. Yield 0.04 g, 18% (Found: C, 51.1; H, 5.70. Calc. for $C_{20}H_{25}B_9Ru$: C, 51.8; H, 5.40%). IR (CH_2Cl_2) ν_{max} at 2525 cm^{-1} [s (br), B–H]. NMR: ^1H, δ 7.66–7.11 (m, 10 H, C_6H_5) and 5.58 (s, 6 H, C_6H_6); ^{11}B-{^1H}, δ 28.16 (1 B), 15.09 (2 B), 13.53 (1 B), −0.27 (2 B), −1.61 (2 B) and −19.84 (1 B).

1,2-Ph$_2$-3-(cym)-3,1,2-*pseudocloso*-RuC$_2$B$_9$H$_9$ 3. Using an analogous procedure to that employed above, a mixture of $[\{RuCl_2(cym)\}_2]$ (0.20 g, 0.33 mmol) and $Tl_2[7,8\text{-}Ph_2\text{-}\textit{nido}\text{-}7,8\text{-}C_2B_9H_9]$ (0.45 g, 0.66 mmol) in CH_2Cl_2 (20 cm^3) were warmed from −196 °C in a foil-covered Schlenk tube, and left to stir for 15 h. Filtration yielded a deep red solution which was concentrated to *ca.* 2 cm^3. Preparative TLC (CH_2Cl_2–hexane, 60:40) afforded only a single band (orange, R_f = 0.85), subsequently collected and recrystallised [hexane into a CH_2Cl_2 solution (4:1) at −30 °C] to afford large, perfectly formed, dark orange *crystals* of 1,2-Ph$_2$-3-(cym)-3,1,2-*pseudocloso*-RuC$_2$B$_9$H$_9$, **3**. Yield 0.05 g, 15% (Found: C, 53.6; H, 6.05. Calc. for $C_{24}H_{33}B_9Ru$: C, 55.5; H, 6.40%). IR (CH_2Cl_2) ν_{max} at 2580 cm^{-1} [s (br), B–H]. NMR: ^1H, δ 7.59–7.19 (m, 10 H, C_6H_5), 5.38–5.13 (m, 4 H, $MeC_6\mathit{H}_4CHMe_2$), 2.05 (sept, 1 H, $^3J_{HH}$ 7, $MeC_6H_4C\mathit{H}Me_2$), 1.54 (s, 3 H, $\mathit{Me}C_6H_4CHMe_2$) and 1.02 (d, 6 H, $^3J_{HH}$ 7 Hz, $MeC_6H_4CH\mathit{Me}_2$); ^{11}B-{^1H}, δ 30.32 (1 B), 15.58 (2 B), 12.57 (1 B), −0.45 (2 B), −1.41 (2 B) and −20.13 (1 B).

1,2-Ph$_2$-3-(η-C$_6$Me$_6$)-3,1,2-*pseudocloso*-RuC$_2$B$_9$H$_9$ 4. This, too, was synthesised in a similar manner. A mixture of $[\{RuCl_2(C_6Me_6)\}_2]$ (0.16 g, 0.24 mmol) and $Tl_2[7,8\text{-}Ph_2\text{-}\textit{nido}\text{-}7,8\text{-}C_2B_9H_9]$ (0.33 g, 0.48 mmol) in CH_2Cl_2 (20 cm^3) was allowed to warm from −196 °C before being stirred overnight at room temperature. The resulting dark brown solution and grey precipitate were separated by filtration and the filtrate concentrated to *ca.* 2 cm^3 *in vacuo*. Preparative TLC (CH_2Cl_2–hexane, 60:40) revealed several mobile bands. The most abundant and mobile (R_f = 0.75) was collected and the solid product recrystallised from CH_2Cl_2–hexane (1:4) at −30 °C to yield poor quality red *needles* of 1,2-Ph$_2$-3-(η-C$_6$Me$_6$)-3,1,2-*pseudocloso*-RuC$_2$B$_9$H$_9$, **4**. Yield 0.04 g, 17% (Found: C, 56.3; H, 7.64. Calc. for $C_{26}H_{37}B_9Ru$: C, 57.0; H, 6.81%). IR (CH_2Cl_2) ν_{max} at 2900 (C–H) and 2525 cm^{-1} [s (br), B–H]. NMR: ^1H, δ 7.52–7.18 (m, 10 H, C_6H_5) and 1.59 (s, 18 H, C_6Me_6); ^{11}B-{^1H}, δ 32.69 (1 B), 15.93 (2 B), 12.28 (1 B), 0.24 (2 B), −0.95 (2 B) and −17.85 (1 B).

Crystallographic studies

All measurements were carried out at room temperature on an Enraf-Nonius CAD4 diffractometer equipped with graphite-monochromated Mo-Kα X-radiation ($\bar{\lambda}$ = 0.710 69 Å) and operating in the ω–2θ mode.

Table 1 lists details of unit cell data for compounds **1**–**3**, and, in the cases of compounds **2** and **3**, intensity data collection and structure refinement. 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 (CADABS[9]) no crystal decay in either case.

Both structures were solved without difficulty by Patterson (metal atom) and Fourier-difference (all other non-H atom) methods (SHELX 76[10]), and refined by full-matrix least squares (SHELXTL[11]). The correct polarity of the crystal of compound **2** was confirmed by the Flack *x* parameter, −0.01(3) at final convergence. Following initial isotropic convergence, an empirical absorption correction (DIFABS[12]) was applied to each data set. In the case of compound **2** the single (crystallographically independent) phenyl ring was treated as a regular, planar hexagon (C–C 1.39 Å) and H atoms bound to it were set in idealised positions (C–H 0.93 Å). Atoms of the η-C_6 ring were freely refined with H atoms again in idealised sites. Cage H atoms were set 1.10 Å from B on a radial extension, and all H atoms were given isotropic displacement parameters riding at 1.2 × *U*(C or B). In compound **3** the phenyl rings and the cage H atoms were treated as for **2**. Carbon atoms of cym were freely refined, with H atoms ideally positioned [C–H 0.93 for aryl C; 0.96 for methyl C; 0.98 Å for C(341)]. In both structures all non-H atoms were refined with anisotropic thermal parameters, and in the final stages of refinement 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 appear 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.

Theoretical calculations

The model compounds studied were *closo* 3-(η-C$_5$Me$_5$)-3,1,2-RhC$_2$B$_9$H$_{11}$ and *pseudocloso* 3-(η-C$_5$Me$_5$)-3,1,2-RhC$_2$B$_9$H$_9$. Non-hydrogen atom skeletons of each were taken from references 4 and 3 (molecule B) respectively, and adjusted to C_s molecular symmetry. Hydrogen atoms were set in idealised positions with B–H 1.185 and C–H 1.085 Å.

Chemical shifts have been calculated with the IGLO method[5] employing the following contracted basis sets: Rh, relativistic multi-electron (ME) fit effective core potential with a valence [8s7p6d]/(6s5p3d) basis;[13] all other atoms DZ (double zeta),

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

	1	**2**	**3**
Formula	$C_{24}H_{34}B_9Ir$	$C_{20}H_{25}B_9Ru$	$C_{24}H_{33}B_9Ru$
M	612.05	463.78	519.89
System	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/a$	*Pnma*	*Cc*
a/Å	17.751(6)	16.770(8)	8.939(8)
b/Å	18.4286(20)	12.7763(21)	20.020(10)
c/Å	18.197(4)	9.8380(18)	14.210(6)
β/°	118.637(16)	90	101.45(5)
U/Å^3	5224.7	2107.8	2492.3
Z	8 (2 independent)	4	4
D_c/g cm^{-3}	1.556	1.461	1.385
μ(Mo-Kα)/cm^{-1}	51.03	7.34	6.28
F(000)	2400	936	1064
$\theta_{orientation}$/°	8–12	11–12	8–13
$\theta_{data\ collection}$/°		1–25	1–25
hkl ranges		−19 to 19, −15 to 15, 0–11	0–10, 0–23, −16 to 16
ω scan speeds/° min^{-1}		0.82–2.35	0.87–2.35
Data measured		4751	2424
Period/h		112	40
Unique data		1936	2338
g_1		0.0424	0.0360
g_2		2.14	0.65
R (all data)		0.0762	0.0250
Data observed [$F_o > 4\sigma(F_o)$]		1348	2224
R (observed data)		0.0399	0.0219
*wR*2		0.0976	0.0543
S		1.045	1.092
Variables		130	281
Maximum, minimum residues/e Å^{-3}		0.49, −0.30	0.61, −0.22

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

Atom	*x*	*y*	*z*
Ru(3)	1930(1)	2500	1636(1)
C(1)	1665(3)	1528(3)	3344(5)
C(12)	216(2)	1026(2)	3557(3)
C(13)	−402(1)	312(3)	3390(4)
C(14)	−248(2)	−668(2)	2835(4)
C(15)	523(2)	−934(2)	2448(4)
C(16)	1140(2)	−220(2)	2616(4)
C(11)	987(2)	760(2)	3170(3)
C(31)	928(4)	1962(5)	239(6)
C(32)	1621(5)	1432(5)	−74(6)
C(33)	2285(5)	1962(5)	−432(5)
B(4)	2581(3)	1316(4)	2837(5)
B(5)	2265(3)	1347(4)	4619(6)
B(6)	1610(5)	2500	4581(7)
B(8)	3132(5)	2500	2570(8)
B(9)	3236(3)	1829(4)	4148(5)
B(10)	2662(5)	2500	5341(8)

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

Atom	*x*	*y*	*z*
C(1)	3193(4)	556(2)	1773(3)
C(2)	3136(5)	1705(2)	1172(3)
Ru(3)	2500	1405(1)	2500
B(4)	1432(5)	468(2)	1918(3)
B(5)	2117(5)	205(2)	861(3)
B(6)	3309(5)	912(2)	681(3)
B(7)	1347(6)	1892(3)	1157(4)
B(8)	272(5)	1210(2)	1532(4)
B(9)	211(6)	524(2)	721(4)
B(10)	1384(6)	753(2)	−81(3)
B(11)	2050(6)	1573(2)	127(3)
B(12)	177(6)	1340(2)	286(4)
C(102)	4329(3)	−369(1)	2885(2)
C(103)	5573(4)	−734(1)	3361(2)
C(104)	7038(3)	−570(2)	3248(2)
C(105)	7259(2)	−41(2)	2658(2)
C(106)	6015(3)	325(1)	2182(2)
C(101)	4550(2)	161(1)	2295(2)
C(202)	5807(3)	2032(1)	999(2)
C(203)	6956(3)	2505(2)	1045(3)
C(204)	6717(3)	3157(1)	1318(3)
C(205)	5328(3)	3335(1)	1546(3)
C(206)	4179(3)	2861(1)	1501(2)
C(201)	4418(3)	2210(1)	1227(2)
C(31)	1417(6)	2044(2)	3522(3)
C(32)	1531(6)	1370(2)	3822(3)
C(33)	2922(5)	1039(2)	3999(3)
C(34)	4310(6)	1371(2)	3979(3)
C(35)	4189(6)	2026(2)	3620(3)
C(36)	2763(5)	2348(2)	3370(3)
C(311)	−79(7)	2408(3)	3313(4)
C(341)	5803(5)	1026(2)	4355(3)
C(342)	7189(6)	1382(3)	4127(4)
C(343)	5968(6)	945(3)	5443(3)

i.e. B, C,[14] [7s3p]/(4s2p), H, [3s]/(2s). The theoretical ^{11}B chemical shifts have been referenced to $BF_3{\cdot}OEt_2$.[15]

Results and Discussion

The reaction between [{IrCl$_2$(η-C$_5$Me$_5$)}$_2$] and Tl$_2$[7,8-Ph$_2$-*nido*-7,8-C$_2$B$_9$H$_9$] in CH_2Cl_2 affords 1,2-Ph$_2$-3-(η-C$_5$Me$_5$)-3,1,2-IrC$_2$B$_9$H$_9$, compound **1**, as the major product isolated in reasonable yield following work up involving TLC. It was characterised by microanalysis and IR and NMR (^{1}H, ^{11}B-{^{1}H}) spectroscopies, the last revealing relatively high-frequency chemical shifts typical[3] of a *pseudocloso* 3,1,2-MC$_2$B$_9$ polyhedron. Thus, the weighted-average ^{11}B chemical shift in **1** is δ +6.1, which should be compared with the equivalent value of δ −11.7 in the related *closo* species 3-(η-C$_5$Me$_5$)-3,1,2-IrC$_2$B$_9$H$_{11}$.[4]

Preliminary crystallographic data on compound **1** (Table 1) show it to be isomorphous with the previously characterised rhodium analogue 1,2-Ph$_2$-3-(η-C$_5$Me$_5$)-3,1,2-RhC$_2$B$_9$H$_9$[3] whose molecular structure is poorly defined because of a complex crystallographic disorder which was impossible satisfactorily to model. Given that it is highly likely that similar disorder would be manifest in the crystal structure of **1**, coupled

Table 4 Interatomic distances (Å) and selected interbond angles (°) in compound **2**

Ru(3)–C(1)	2.136(4)	Ru(3)–B(4)	2.208(6)
Ru(3)–B(8)	2.216(9)	Ru(3)–C(32)	2.227(6)
Ru(3)–C(33)	2.229(5)	Ru(3)–C(31)	2.277(6)
C(1)–C(11)	1.512(5)	C(1)–B(5)	1.625(7)
C(1)–B(4)	1.637(7)	C(1)–B(6)	1.742(6)
C(31)–C(31A)	1.374(13)	C(31)–C(32)	1.380(9)
C(32)–C(33)	1.350(9)	C(33)–C(33A)	1.376(14)
B(4)–B(8)	1.793(7)	B(4)–B(9)	1.818(8)
B(4)–B(5)	1.832(8)	B(5)–B(10)	1.765(7)
B(5)–B(9)	1.802(8)	B(5)–B(6)	1.838(7)
B(6)–B(10)	1.916(11)	B(8)–B(9)	1.781(9)
B(9)–B(9A)	1.714(11)	B(9)–B(10)	1.743(9)
C(1A)–Ru(3)–C(1)	71.1(2)	C(1)–Ru(3)–B(4)	44.2(2)
B(4)–Ru(3)–B(8)	47.8(2)	C(32)–Ru(3)–C(33)	35.3(2)
C(33)–Ru(3)–C(33A)	36.0(4)	C(32)–Ru(3)–C(31)	35.7(2)
C(31A)–Ru(3)–C(31)	35.1(3)	C(11)–C(1)–B(5)	117.5(4)
C(11)–C(1)–B(4)	124.3(3)	B(5)–C(1)–B(4)	68.3(3)
C(11)–C(1)–B(6)	120.1(4)	B(5)–C(1)–B(6)	66.1(3)
C(11)–C(1)–Ru(3)	116.4(3)	B(4)–C(1)–Ru(3)	70.2(2)
B(6)–C(1)–Ru(3)	98.4(2)	C(16)–C(11)–C(1)	119.3(2)
C(12)–C(11)–C(1)	120.7(2)	C(31A)–C(31)–C(32)	119.4(4)
C(33)–C(32)–C(31)	120.4(6)	C(32)–C(33)–C(33A)	120.1(4)
B(8)–B(4)–B(9)	59.1(4)	C(1)–B(4)–B(5)	55.5(3)
B(9)–B(4)–B(5)	59.2(3)	C(1)–B(4)–Ru(3)	65.5(2)
B(8)–B(4)–Ru(3)	66.3(3)	B(10)–B(5)–B(9)	58.5(4)
C(1)–B(5)–B(4)	56.1(3)	B(9)–B(5)–B(4)	60.0(3)
C(1)–B(5)–B(6)	60.0(3)	B(10)–B(5)–B(6)	64.2(4)
C(1)–B(6)–C(1A)	91.0(4)	C(1)–B(6)–B(5)	53.9(2)
B(5)–B(6)–B(10)	56.0(3)	B(9A)–B(8)–B(9)	57.5(4)
B(9)–B(8)–B(4)	61.1(3)	B(4)–B(8)–Ru(3)	65.9(3)
B(9A)–B(9)–B(10)	60.6(2)	B(9A)–B(9)–B(8)	61.3(2)
B(10)–B(9)–B(5)	59.7(3)	B(8)–B(9)–B(4)	59.7(3)
B(5)–B(9)–B(4)	60.8(3)	B(9)–B(10)–B(9A)	58.9(4)
B(9)–B(10)–B(5)	61.8(3)	B(5)–B(10)–B(6)	59.7(3)

Symmetry transformation used to generate equivalent (A) atoms: $x, -y + \frac{1}{2}, z$.

with the possibility of a further reduction in precision through increased X-ray absorption effects (Ir *versus* Rh), compound **1** was regarded as a poor contender for an accurate structure determination of a *pseudocloso* compound, and intensity data were not recorded.

Thus, attention was focussed on potential analogues containing 3-{η-(arene)Ru} fragments. Compounds **2**–**4** (1,2-Ph_2-3-arene-3,1,2-$RuC_2B_9H_9$ where arene = C_6H_6, cym or C_6Me_6 respectively) were all prepared by the reactions between $[\{RuCl_2(arene)\}_2]$ and $Tl_2[7,8\text{-}Ph_2\text{-}nido\text{-}7,8\text{-}C_2B_9H_9]$ in yields of 10–20% after work up involving TLC. Compound **3** was the only mobile product of this reaction, and for **2** and **4** the target materials appeared to be the most abundant species in a mixture of products. As with **1**, compounds **2**–**4** were initially characterised by IR and ^1H and ^{11}B-{^1H} NMR spectroscopies.

At room temperature the ^{11}B NMR spectra of **2**–**4** all support C_s molecular symmetries, since the pattern of resonances is (high-frequency-to-low-frequency) 1 : 2 : 1 : 2 : 2 : 1. The weighted average ^{11}B chemical shifts (δ) are +5.36, +5.58 and +6.40 respectively; again, when compared with the average chemical shift in similar *closo* carbametallaboranes [*e.g.* δ −11.1 in 3-(η-C_6H_6)-3,1,2-$RuC_2B_9H_{11}$,[16] −10.2 in 3-(η-C_6Me_6)-3,1,2-$RuC_2B_9H_{11}$[17]] these values lie substantially to high frequency, suggesting *pseudocloso* structures.

The ^1H NMR spectra of complexes **2** and **4** reveal single resonances for the benzene or hexamethylbenzene ligands (δ 5.58 and 1.59, respectively), indicative of rotation of these η^6-bonded functions that is rapid on the NMR time-scale. One might expect similar rotation of cym in **3**; comparison of the C_s symmetry evident from its ^{11}B NMR spectrum and the C_1 symmetry apparent from a crystallographic study (see below) suggests at least substantial libration of cym in solution.

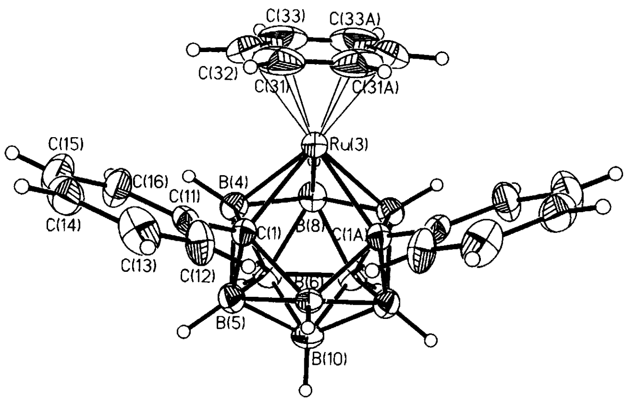
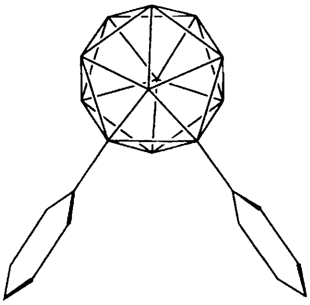


Fig. 1 Perspective view of a single molecule of compound **2** (30% ellipsoids except for H atoms which have an artificial radius of 0.1 Å for clarity); H atoms carry the same number as the B or C atom to which they are bound

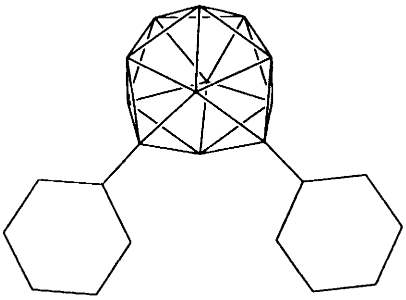
Compounds **2** and **3** were obtained as well formed single crystals, and the molecular structures of each were established unequivocally by diffraction studies. Unfortunately, good quality crystals of **4** could not be grown in spite of numerous attempts.

A perspective view of a single molecule of **2** is presented in Fig. 1, Table 4 lists interatomic distances and selected interbond angles. The molecule has crystallographically imposed C_s symmetry about the plane through Ru(3)B(6)B(8)B(10). Atom labels ending A represent the result of reflection in this plane.

The structural study confirms the prediction of the spectroscopic analysis, *viz.* compound **2** has a *pseudocloso* structure (**II**) nominally derived from a normal, *closo* structure



III θ = 0°



IV θ = 90°

(**I**) by breaking of the C(1)–C(1A) connectivity [in **2** C(1)···C(1A) is 2.485(8) Å]. Since 3-(η-C_6H_6)-3,1,2-$RuC_2B_9H_{11}$,[18] 3-(η-C_6Me_6)-3,1,2-$RuC_2B_9H_{11}$[19] and 1-Ph-3-(mes)-3,1,2-$RuC_2B_9H_{10}$[2] (mes = $C_6H_3Me_3$-1,3,5) all have *closo* structures [C(1)–C(2) 1.626(4)–1.657(10) Å] and the structure of 1-Ph-2-Me-3-(cym)-3,1,2-$RuC_2B_9H_9$ shows[2] that C(1)–C(2) stretching has just begun [average C(1)–C(2) 1.728(15) Å], we believe that the *pseudocloso* structure of **2** results from steric congestion between the cage-bound phenyl groups.

The conformation of phenyl substituents in phenyl 1,2-carbaboranes and their metal complexes is best described by the angle θ, the modulus of the average C_{cage}–C_{cage}–C–C torsion angle.[2] In 1,2-Ph_2-1,2-$C_2B_{10}H_{10}$,[20] the parent carbaborane from which complexes **1**–**4** are derived, the average θ is low (6.5°) and this conformation is maintained[21] in the decapitated anion $[7,8\text{-}Ph_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ (average θ = 13.4°); these low θ conformations are depicted in **III**. Reclosing the *nido* {7,8-Ph_2-7,8-C_2B_9} structure with a {Rh(η-C_5Me_5)}, {Ir(η-C_5Me_5)} or {Ru(C_6H_6)} fragment apparently forces the cage phenyl substituents to lie much more coplanar (θ in **2** is 61.55°), their mutual steric repulsion prising open the C_{cage}–C_{cage} connectivity to produce the *pseudocloso* geometry which is sketched from above in **IV**. In compound **2** the closest approach between phenyl H atoms, H(12)···H(12A), is 2.09 Å,* *cf.* twice the van der Waals radius for H (2.4 Å).

As a result of the stretching of the C(1)–C(1A) edge C(1) makes fairly short connections to B(4) and B(5) [1.637(7) and 1.625(7) Å respectively], and B(6) is pulled 0.337 Å out of the (necessarily rigorously flat) B(5)B(9)B(5A)B(9A) plane towards Ru(3), approaching to within 2.946(7) Å of the metal. The B(6)–B(10) connectivity is concomitantly long [1.916(11) Å]. Fig. 2(*a*) shows parameters within the open, nearly square Ru(3)C(1)B(6)C(1A) face that results from, and is characteristic of, the distortion of **2** to a *pseudocloso* structure. The distortion appears to be fairly localised in that, apart from the long C(1)–C(1A) and B(6)–B(10) distances, and short C(1)–B(4), C(1)–B(5) and Ru(3)···B(6) distances noted, lengths within the rest of the polyhedron are generally normal. Thus, the Ru(3)–C(1) and Ru(3)–B lengths in **2** are very similar to those in (undistorted) 3-(η-C_6H_6)-3,1,2-$RuC_2B_9H_{11}$,[18] and B–B lengths [except B(6)–B(10)] are standard, 1.714(11)–1.838(7) Å. The η^6-C_6H_6 ring is planar to within 0.013 Å and almost parallel (dihedral angle 0.3°) to the plane through B(5)B(9)B(5A)B(9A).

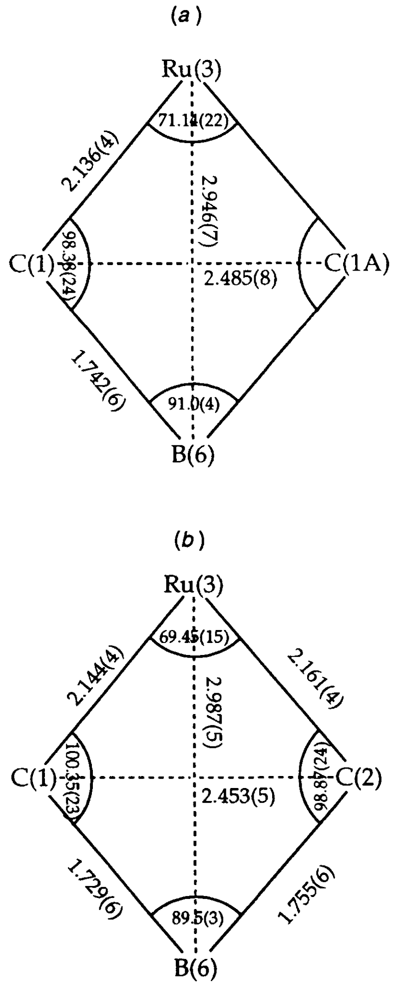


Fig. 2 Geometrical details (Å and °) in the open faces of *pseudocloso* compounds **2** (*a*) and **3** (*b*)

Compound **3** crystallises with no imposed molecular symmetry (although, as previously noted, C_s symmetry is apparent from the ^{11}B NMR spectrum). Fig. 3 shows a perspective view of one molecule and Table 5 lists interatomic distances and selected interbond angles.

As with the benzene analogue **2**, the *p*-cymene compound **3** displays a *pseudocloso* structure, with C(1)···C(2) 2.458(5) and Ru(3)···B(6) 2.987(5) Å. These parameters are, respectively, slightly shorter and slightly longer than the corresponding values in **2**, identifying somewhat less of a *pseudocloso* distortion. Angles in the Ru(3)C(1)B(6)C(2) pseudosquare [detailed in Fig. 2(*b*)], a displacement of B(6) out of the B(5)B(9)B(12)B(11) plane of only 0.286 Å, and a shorter B(6)–B(10) connectivity, 1.869(7) Å, all reflect the reduced distortion in **3** relative to that in **2**. On the other hand, C(1)–B(4,5) and C(2)–B(7,11) lengths in **3** are as short as the equivalent distances in **2**.

It seems likely that the distortion in **3** is smaller because of reduced mutual crowding between the phenyl substituents. For phenyl ring C(101)–C(106) θ is 65.90°, slightly greater than that in **2**, but for C(210)–C(206) it is much less, 43.90°. The closest approach of *ortho* H atoms, H(106)···H(202) is 2.28 Å,* signifying less crowding than in **2**. Thus, rather to our surprise, replacement of η-C_6H_6 in **2** by η(*p*-cymene) in **3** appears to produce, if anything, a rather less crowded molecule.

In **3** the central ring of cym is planar to within 0.033 Å. Both substituent carbon atoms, C(311) (Me group) and C(341) (Pr^i

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* These distances are those between electron-density centroids. *Internuclear* H···H distances will be slightly shorter.

Table 5 Interatomic distances (Å) and selected interbond angles (°) in compound **3**

C(1)–C(101)	1.512(4)	C(1)–B(5)	1.613(6)	B(5)–B(6)	1.819(7)	B(6)–B(11)	1.814(6)
C(1)–B(4)	1.637(6)	C(1)–B(6)	1.729(6)	B(6)–B(10)	1.869(7)	B(7)–B(8)	1.810(7)
C(1)–Ru(3)	2.144(4)	C(2)–C(201)	1.518(5)	B(7)–B(11)	1.819(7)	B(7)–B(12)	1.825(7)
C(2)–B(11)	1.626(6)	C(2)–B(7)	1.638(7)	B(8)–B(12)	1.775(7)	B(8)–B(9)	1.787(7)
C(2)–B(6)	1.755(6)	C(2)–Ru(3)	2.161(4)	B(9)–B(12)	1.745(7)	B(9)–B(10)	1.756(8)
Ru(3)–B(4)	2.191(4)	Ru(3)–B(7)	2.208(5)	B(10)–B(12)	1.743(7)	B(10)–B(11)	1.751(7)
Ru(3)–C(33)	2.212(4)	Ru(3)–B(8)	2.218(5)	B(11)–B(12)	1.795(7)	C(31)–C(36)	1.403(7)
Ru(3)–C(32)	2.220(5)	Ru(3)–C(36)	2.244(4)	C(31)–C(32)	1.413(6)	C(31)–C(311)	1.499(7)
Ru(3)–C(31)	2.290(5)	Ru(3)–C(35)	2.325(5)	C(32)–C(33)	1.387(7)	C(33)–C(34)	1.412(6)
Ru(3)–C(34)	2.385(5)	B(4)–B(5)	1.809(7)	C(34)–C(35)	1.404(6)	C(34)–C(341)	1.503(7)
B(4)–B(8)	1.833(7)	B(4)–B(9)	1.833(7)	C(35)–C(36)	1.409(7)	C(341)–C(342)	1.519(7)
B(5)–B(10)	1.754(7)	B(5)–B(9)	1.794(7)	C(341)–C(343)	1.532(6)		
C(101)–C(1)–B(5)	117.3(3)	C(101)–C(1)–B(4)	125.4(3)	B(11)–B(7)–B(12)	59.0(3)	C(2)–B(7)–Ru(3)	66.5(2)
B(5)–C(1)–B(4)	67.6(3)	C(101)–C(1)–B(6)	118.1(3)	B(8)–B(7)–Ru(3)	66.2(2)	B(12)–B(8)–B(9)	58.7(3)
B(5)–C(1)–B(6)	65.8(3)	C(101)–C(1)–Ru(3)	117.3(2)	B(12)–B(8)–B(7)	61.2(3)	B(9)–B(8)–B(4)	60.8(3)
B(4)–C(1)–Ru(3)	69.4(2)	B(6)–C(1)–Ru(3)	100.4(2)	B(7)–B(8)–Ru(3)	65.6(2)	B(4)–B(8)–Ru(3)	64.7(2)
C(201)–C(2)–B(11)	117.6(3)	C(201)–C(2)–B(7)	125.0(4)	B(12)–B(9)–B(10)	59.7(3)	B(12)–B(9)–B(8)	60.3(3)
B(11)–C(2)–B(7)	67.7(3)	C(201)–C(2)–B(6)	119.8(3)	B(10)–B(9)–B(5)	59.2(3)	B(8)–B(9)–B(4)	60.8(3)
B(11)–C(2)–B(6)	64.8(3)	C(201)–C(2)–Ru(3)	117.8(3)	B(5)–B(9)–B(4)	59.8(3)	B(12)–B(10)–B(11)	61.8(3)
B(7)–C(2)–Ru(3)	69.5(2)	B(6)–C(2)–Ru(3)	98.9(2)	B(12)–B(10)–B(9)	59.8(3)	B(5)–B(10)–B(9)	61.5(3)
C(1)–Ru(3)–C(2)	69.5(2)	C(1)–Ru(3)–B(4)	44.4(2)	B(11)–B(10)–B(6)	60.0(3)	B(5)–B(10)–B(6)	60.2(3)
C(2)–Ru(3)–B(7)	44.0(2)	B(4)–Ru(3)–B(8)	49.1(2)	B(10)–B(11)–B(12)	58.9(3)	C(2)–B(11)–B(6)	61.0(3)
B(7)–Ru(3)–B(8)	48.3(2)	C(33)–Ru(3)–C(32)	36.5(2)	B(10)–B(11)–B(6)	63.2(3)	C(2)–B(11)–B(7)	56.4(3)
C(32)–Ru(3)–C(31)	36.5(2)	C(36)–Ru(3)–C(31)	36.0(2)	B(12)–B(11)–B(7)	60.7(3)	B(10)–B(12)–B(9)	60.5(3)
C(36)–Ru(3)–C(35)	35.9(2)	C(33)–Ru(3)–C(34)	35.5(2)	B(9)–B(12)–B(8)	61.0(3)	B(10)–B(12)–B(11)	59.3(3)
C(35)–Ru(3)–C(34)	34.6(2)	C(1)–B(4)–B(5)	55.6(3)	B(8)–B(12)–B(7)	60.3(3)	B(11)–B(12)–B(7)	60.3(3)
B(5)–B(4)–B(9)	59.0(3)	B(8)–B(4)–B(9)	58.4(3)	C(106)–C(101)–C(1)	120.1(2)	C(102)–C(101)–C(1)	119.9(2)
C(1)–B(4)–Ru(3)	66.3(2)	B(8)–B(4)–Ru(3)	66.2(2)	C(206)–C(201)–C(2)	118.8(2)	C(202)–C(201)–C(2)	121.2(2)
B(10)–B(5)–B(9)	59.3(3)	C(1)–B(5)–B(4)	56.8(2)	C(36)–C(31)–C(32)	116.6(5)	C(36)–C(31)–C(311)	121.2(5)
B(9)–B(5)–B(4)	61.2(3)	C(1)–B(5)–B(6)	60.1(2)	C(32)–C(31)–C(311)	122.1(5)	C(33)–C(32)–C(31)	121.3(5)
B(10)–B(5)–B(6)	63.0(3)	C(1)–B(6)–C(2)	89.5(3)	C(32)–C(33)–C(34)	122.1(4)	C(35)–C(34)–C(33)	116.2(4)
C(2)–B(6)–B(11)	54.2(2)	C(1)–B(6)–B(5)	54.0(2)	C(35)–C(34)–C(341)	123.9(4)	C(33)–C(34)–C(341)	119.9(4)
B(11)–B(6)–B(10)	56.7(3)	B(5)–B(6)–B(10)	56.8(3)	C(34)–C(35)–C(36)	121.4(5)	C(31)–C(36)–C(35)	121.5(4)
C(2)–B(7)–B(11)	55.8(3)	B(8)–B(7)–B(12)	58.5(3)	C(34)–C(341)–C(342)	114.4(4)	C(34)–C(341)–C(343)	108.0(4)
				C(342)–C(341)–C(343)	110.2(4)		

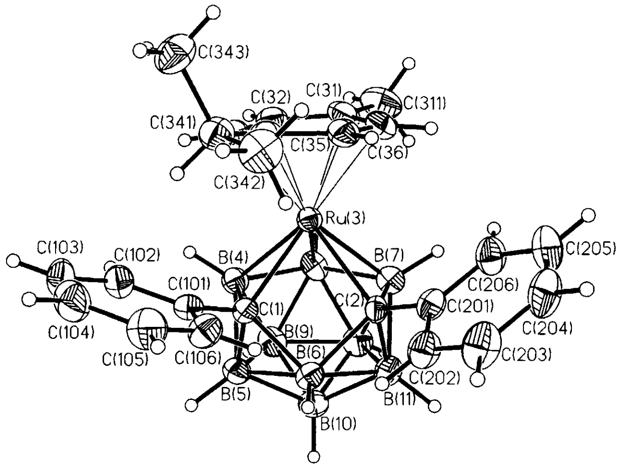

Fig. 3 Perspective view of a single molecule of compound **3** (30% ellipsoids except for H atoms which have an artificial radius of 0.1 Å for clarity); H atoms carry the same number as the B or C atom to which they are bound, except for methyl H atoms [bound to C(311), C(342) and C(343)] which are numbered H(31A–31C) and H(34A–34F)

group) are displaced out of this plane in a direction away from the carbaborane cage, by 0.086 and 0.244 Å respectively. The latter is clearly the more significant and, in the solid state, reflects steric crowding between the Pr^i group and the C(101)–C(106) ring (which consequently displays the greater θ). The C(341)–H(341) vector points towards the C(101)–C(106) ring, and H(341) is only 2.41 Å above the ring plane, *cf.* half the thickness of an aromatic ring plus the van der Waals radius for hydrogen (1.85 + 1.2) of 3.05 Å. It is possible that the fluxional process which renders compound **3** C_s molecular symmetry on the NMR time-scale retains the proximity of H(341) to (necessarily both) phenyl substituents, as H(341) resonates at fairly low frequency [δ 2.05 *cf.* 2.88 in 1-Ph-2-Me-3-(cym)-3,1,2-RuC$_2$B$_9$H$_9$[2]]. A simple oscillation of cym about the Ru(3)B(8)B(10)B(6) plane is all that is required.

The geometrical changes in a formerly *closo*-3,1,2-MC$_2$B$_9$ polyhedron forced to adopt a *pseudocloso* structure are interesting and clearly quite substantial. We are also very interested in any changes in the polyhedral electronic structure that are consequent upon these geometrical changes.

In this paper and a previous communication[3] we have consistently noted that the *closo*-to-*pseudocloso* change is accompanied by a substantial movement, typically 15 ppm, to high frequency of the average ^{11}B NMR chemical shift. The ^{11}B spectra of the *closo* carbametallaboranes 3-(η-C$_6$Me$_6$)-3,1,2-RuC$_2$B$_9$H$_{11}$,[17] 3-(η-C$_5$Me$_5$)-3,1,2-RhC$_2$B$_9$H$_{11}$[4] and 3-(η-C$_5$Me$_5$)-3,1,2-IrC$_2$B$_9$H$_{11}$,[4] have all been assigned by ^{11}B–^{11}B COSY experiments, but it has not so far proved possible to obtain useful COSY spectra of our *pseudocloso* compounds. Thus, we do not know by experiment if the *closo*-to-*pseudocloso* change results in all or only some ^{11}B resonances moving to high frequency, nor by how much.

Accordingly, we have attempted to assign the ^{11}B spectrum of a typical *pseudocloso* carbametallaborane,[3] 1,2-Ph$_2$-3-(η-C$_5$Me$_5$)-3,1,2-RhC$_2$B$_9$H$_9$, by an IGLO calculation[5] on a C_s symmetrised model. This is the first time that IGLO calculations have been reported for a transition-metal containing heteroborane, so to check the validity of the method we have also used this approach to calculate the chemical shifts of the related species 3-(η-C$_5$Me$_5$)-3,1,2-RhC$_2$B$_9$H$_{11}$, whose ^{11}B NMR spectrum has already been assigned[17] by a COSY experiment. Results are summarised in Table 6.

Table 6 Experimental and theoretical ^{11}B NMR chemical shifts (ppm) in *closo* and *pseudocloso* carbarhodaboranes

3-(η-C_5Me_5)-3,1,2-$RhC_2B_9H_{11}$			1,2-Ph_2-3-(η-C_5Me_5)-3,1,2-$RhC_2B_9H_9$		
Experimental[a]	Theoretical[b]	Assignment[c]	Experimental[d]	Theoretical[b]	Assignment[e]
−23.4	−27.4	B(6)	−18.0	−30.6	B(6)
−18.6	−19.8	B(5, 11)	+10.3	+9.5	B(5, 11)
−8.3	−4.6	B(9, 12)	−1.2	+0.7	B(9, 12)
−3.5	−12.5	B(4, 7)	+4.0	+5.1	B(4, 7)
−1.8	−9.3	B(10)	+12.9	+10.9	B(10)
+8.6	+2.1	B(8)	+33.1	+25.0	B(8)

[a] Experimental data from ref. 17. [b] IGLO-SCF calculation, double-ζ basis set, C_s symmetrised model with idealised H coordinates. [c] Assignment by ^{11}B–^{11}B COSY NMR spectroscopy (ref. 17). [d] Experimental data from ref. 3. [e] Tentative assignment from IGLO calculation (present study).

In the case of 3-(η-C_5Me_5)-3,1,2-$RhC_2B_9H_{11}$, theory correctly predicts the ordering of the three integral-1 ^{11}B NMR resonances, arising from (high-frequency-to-low-frequency) B(8), B(10) and B(6), although all three signals are calculated to have frequencies which are too low, by an average of 6.9 ppm. The resonance due to B(5,11) is correctly predicted to be the lowest frequency integral-2 resonance and is accurately calculated (Δ only 1.2 ppm), but the relative order of the signals due to B(4,7) and B(9,12) is inverted, the positions of these last two signals being miscalculated by 9.0 and 3.7 ppm respectively. For 3-(η-C_5Me_5)-3,1,2-$RhC_2B_9H_{11}$ as a whole, the maximum and average absolute deviations between experimental and theoretical ^{11}B chemical shifts are 9.0 and 5.0 ppm respectively, considerably larger than found for boranes and carbaboranes at a comparable theoretical level.[15] The weighted-average ^{11}B chemical shift is (experiment) δ −8.6 and (theory) −12.4.

The calculations for 1,2-Ph_2-3-(η-C_5Me_5)-3,1,2-$RhC_2B_9H_9$ afford a weighted-average ^{11}B chemical shift (which is, of course, independent of individual assignments) of δ +4.0, in good agreement with that from experimentation (+6.0) and clearly typical of the value which characterises *pseudocloso* species such as **1**–**4**. In Table 6 we order the experimental shifts so as to produce the best match with those calculated.* Done this way the maximum and average absolute deviations between experiment and theory are 12.6 and 3.4 ppm respectively. The greatest differences are at the extremes of the spectrum [B(8) at highest frequency, Δ = 8.1 ppm; B(6) at lowest frequency, Δ = 12.6 ppm] where both calculated values are too low, reminiscent of the situation with 3-(η-C_5Me_5)-3,1,2-$RhC_2B_9H_{11}$. For the other four resonances the greatest deviation is only 2.0 ppm.

Clearly, the assignment of ^{11}B chemical shifts in this way can only be tentative, and efforts continue to synthesise *pseudocloso* carbametallaboranes whose spectra we can ultimately assign by experiment.† Nevertheless, assuming that the assignment of 1,2-Ph_2-3-(η-C_5Me_5)-3,1,2-$RhC_2B_9H_9$ is correct, we can note that, moving from *closo* 3-(η-C_5Me_5)-3,1,2-$RhC_2B_9H_{11}$ to *pseudocloso* 1,2-Ph_2-3-(η-C_5Me_5)-3,1,2-$RhC_2B_9H_9$, all ^{11}B resonances are shifted to high frequency, by between 7.1 [B(9, 12)] and 28.9 [B(5, 11)] ppm, and future studies, both experimental and theoretical, will be directed towards attempts to understand the origin of these chemical shift changes. At the same time it is clear that systems as complex as 3-(η-C_5Me_5)-3,1,2-$RhC_2B_9H_{11}$ and 1,2-Ph_2-3-(η-C_5Me_5)-3,1,2-$RhC_2B_9H_9$ currently provide a substantial challenge to theory in respect of the accurate calculation of chemical shifts. That challenge will undoubtedly be addressed and overcome as computational methods in this area continue to develop in future years.

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* Such a procedure should always be employed with caution.[22]

† *Note added at proof*: these efforts have now been rewarded.[23]