SYNTHESIS AND/OR MOLECULAR STRUCTURES OF SOME SIMPLE 2,1,7- AND 2,1,12-RUTHENA- AND COBALTACARBORANES

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Dedicated to Dr Bohumil Štíbr on the occasion of his 70th birthday in recognition of his many outstanding contributions to boron chemistry.

The ruthenacarboranes 2-(*p*-cymene)-2,1,7-*closo*-RuC$_2$B$_9$H$_{11}$ (**2**) (*p*-cymene = 1-methyl-4-iso-propylbenzene) and 2-(*p*-cymene)-2,1,12-*closo*-RuC$_2$B$_9$H$_{11}$ (**3**) have been synthesised by simple metallation of [7,9-*nido*-C$_2$B$_9$H$_{11}$]$^{2-}$ and [2,9-*nido*-C$_2$B$_9$H$_{11}$]$^{2-}$, respectively. In preparing the known cobaltacarborane 2-(η-C$_5$H$_5$)-2,1,12-*closo*-CoC$_2$B$_9$H$_{11}$ (**6**), the new bis(dicarbollide) [2,2'-Co(1,12-*closo*-C$_2$B$_9$H$_{11}$)$_2$]$^-$ (as its [(η-C$_5$H$_5$)$_2$Co]$^+$ salt; **7**) was also formed. Molecular structures of **2**, **3**, **6** and **7** and that of the known compound 2-(η-C$_5$H$_5$)-2,1,7-*closo*-CoC$_2$B$_9$H$_{11}$ (**5**) have been determined. Patterns in ⟨δ(^{11}B)⟩, the weighted average ^{11}B NMR chemical shift, of these metallacarboranes, together with those in 3-(*p*-cymene)-3,1,2-*closo*-RuC$_2$B$_9$H$_{11}$ (**1**) and 3-(η-C$_5$H$_5$)-3,1,2-*closo*-CoC$_2$B$_9$H$_{11}$ (**4**) are discussed in relation to ⟨δ(^{11}B)⟩ in the parent carboranes 1,2-*closo*-C$_2$B$_{10}$H$_{12}$, 1,7-*closo*-C$_2$B$_{10}$H$_{12}$ and 1,12-*closo*-C$_2$B$_{10}$H$_{12}$. The similarity between the ^{1}H and ^{11}B spectra of **6** and **7** confirm the isolobality of the [C$_5$H$_5$]$^-$ and [C$_2$B$_9$H$_{11}$]$^{2-}$ ligands. An electrochemical study of **7** confirms that trends in the potential of the Co^{III}/Co^{II} couple for the series of isomers of (η-C$_5$H$_5$)CoC$_2$B$_9$H$_{11}$ are reproduced for the bis(dicarbollides) [Co(C$_2$B$_9$H$_{11}$)$_2$]$^-$. The molecular structures of compounds **1–3** as a family and **4–6** as a family provide a unique opportunity to consider structural patterns in simple isomeric metallacarboranes.
Keywords: Metallacarboranes; Carboranes; Boron clusters; X-ray diffraction; Crystallography; Electrochemistry; Cobalt; Ruthenium.

A vast amount of data on icosahedral (transition-)metallacarboranes exists in the literature since these compounds were first reported in the 1960s[1]. Metalladicarboranes, with MC$_2$B$_9$ cores, dominate the field and, of the vari-

ous isomers of MC_2B_9 which are known, the 3,1,2-MC_2B_9 family (**I**) heavily outweighs all others. 3,1,2-MC_2B_9 metallacarboranes are afforded by metallation of the [7,8-*nido*-$C_2B_9H_{11}$]$^{2-}$ anion, itself produced by simple deboronation of 1,2-*closo*-$C_2B_{10}H_{12}$. Deboronation of 1,7-*closo*-$C_2B_{10}H_{12}$ affords [7,9-*nido*-$C_2B_9H_{11}$]$^{2-}$, metallation of which gives 2,1,7-MC_2B_9 metallacarboranes (**II**), whilst deboronation of 1,12-*closo*-$C_2B_{10}H_{12}$ yields [2,9-*nido*-$C_2B_9H_{11}$]$^{2-}$ which in turn would give rise to 2,1,12-MC_2B_9 metalla-carboranes (**III**).

3,1,2-MC_2B_9 (**I**)   2,1,7-MC_2B_9 (**II**)   2,1,12-MC_2B_9 (**III**)
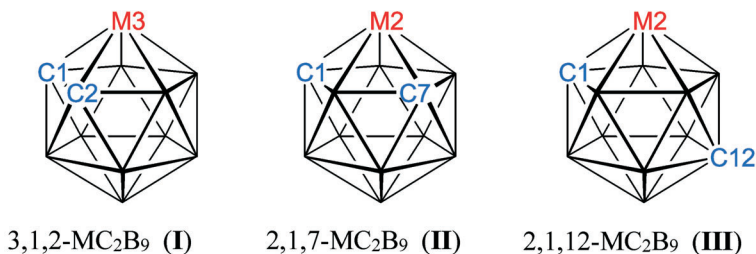
In this article we report the syntheses and complete characterisation of simple metallacarboranes of types **II** and **III** from metallation of [7,9-*nido*-$C_2B_9H_{11}$]$^{2-}$ and [2,9-*nido*-$C_2B_9H_{11}$]$^{2-}$, respectively, with the {Ru(*p*-cymene)}$^{2+}$ fragment (*p*-cymene = 1-methyl-4-isopropylbenzene). We compare 2-(*p*-cymene)-2,1,7-*closo*-$RuC_2B_9H_{11}$ (**2**) and 2-(*p*-cymene)-2,1,12-*closo*-$RuC_2B_9H_{11}$ (**3**) with each other and with the previously charac-terised type **I** analogue 3-(*p*-cymene)-3,1,2-*closo*-$RuC_2B_9H_{11}$ (**1**)[2]. We wanted further to compare these ruthenacarboranes with the corresponding cobaltacarboranes formed by metallation with {Co(η-C_5H_5)}$^{2+}$ so we have prepared the previously reported but not previously crystallographically-characterised species 2-(η-C_5H_5)-2,1,7-*closo*-$CoC_2B_9H_{11}$ (**5**)[3] and 2-(η-C_5H_5)-2,1,12-*closo*-$CoC_2B_9H_{11}$ (**6**)[3,4], which we further compare with the fully characterised species 3-(η-C_5H_5)-3,1,2-*closo*-$CoC_2B_9H_{11}$ (**4**)[5]. In the course of this work we serendipitously also prepared the salt [(η-C_5H_5)$_2$Co]-[2,2'-Co(1,12-*closo*-$C_2B_9H_{11}$)$_2$] (**7**), which is also described.

EXPERIMENTAL

Synthesis – General

Experiments were performed under dry, oxygen-free N_2 using standard Schlenk techniques, with some subsequent manipulation in the open laboratory. Solvents were freshly distilled over CaH_2 (CH_2Cl_2) or Na wire (THF, 60-80 petroleum ether) and were degassed (3 × freeze-pump-thaw cycles) before use, or were stored over 4 Å molecular sieves ($CDCl_3$). Preparative

thin layer chromatography (TLC) employed 20 × 20 cm Kieselgel 60 F_{254} glass plates. IR spectra were recorded from CH_2Cl_2 solutions or KBr disks using a Perkin Elmer Spectrum RX FT spectrophotometer (ν_{max}, cm^{-1}). NMR spectra at 400.1 MHz (^1H, chemical shifts relative to $SiMe_4$), or 128.4 MHz (^{11}B, chemical shifts relative to $BF_3 \cdot OEt_2$) were recorded on a Bruker DPX400 spectrometer from $CDCl_3$ or $(CD_3)_2CO$ solutions at ambient temperature. Chemical shifts are given in ppm (δ-scale) and coupling constants (J) in Hz. Elemental analyses were determined by the departmental service. Electron impact mass spectra were recorded using a Kratos Concept mass spectrometer. The starting materials [Ru(p-cymene)Cl$_2$]$_2$ [6], Li$_2$[7,9-nido-C$_2$B$_9$H$_{11}$] [7], and Li$_2$[2,9-nido-C$_2$B$_9$H$_{11}$] [4], were prepared by published methods or slight variants thereof. All other reagents and solvents were supplied commercially and were used as received.

2-(p-Cymene)-2,1,7-closo-RuC$_2$B$_9$H$_{11}$ (2)

A solution of [Ru(p-cymene)Cl$_2$]$_2$ (0.306 g, 0.50 mmol) in THF (20 ml) was slowly added to a solution of Li$_2$[7,9-nido-C$_2$B$_9$H$_{11}$] (0.146 g, 1.00 mmol) in THF (20 ml) at 0 °C. The reaction mixture was allowed to warm slowly to room temperature and then stirred overnight. Volatiles were removed in vacuo and the resulting brown solid dissolved in the minimum amount of CH_2Cl_2 and filtered through Celite®. Further purification involved preparative TLC with a mixed eluent of CH_2Cl_2/40–60 petroleum ether (2:1) yielding a yellow mobile band at R_F 0.45 which was recovered as a yellow solid, compound 2. Yield 0.150 g (41%). For C$_{12}$H$_{25}$B$_9$Ru (367.70) calculated: 39.2% C, 6.85% H; found: 40.3% C, 7.09% H. IR: 2541. ^1H NMR (CDCl$_3$): 5.80–5.60 (2 × d, 4 H, J = 6, CH$_3$**C$_6$H$_4$**CH(CH$_3$)$_2$), 3.70 (br s, 2 H, CH$_{cage}$), 2.70 (sept., 1 H, J = 7, CH$_3$C$_6$H$_4$**CH**(CH$_3$)$_2$), 2.20 (s, 3 H, **CH$_3$**C$_6$H$_4$CH(CH$_3$)$_2$), 1.30 (d, 6 H, J = 7, CH$_3$C$_6$H$_4$CH(**CH$_3$**)$_2$). ^{11}B{^1H} NMR (CDCl$_3$): –0.62 (1 B), –5.50 (2 B), –11.16 (1 B), –14.50 (2 B), –15.82 (1 B), –20.19 (2 B), ⟨δ(^{11}B)⟩ = –12.0. EIMS: M$^+$ envelope centred on m/z 368.

2-(p-Cymene)-2,1,12-closo-RuC$_2$B$_9$H$_{11}$ (3)

Similarly, [Ru(p-cymene)Cl$_2$]$_2$ (0.306 g, 0.50 mmol) and Li$_2$[2,9-nido-C$_2$B$_9$H$_{11}$] (0.146 g, 1.00 mmol) were reacted in THF. Work-up as for 2 afforded a yellow mobile band at R_F 0.55 recovered as a yellow solid, compound 3. Yield 0.213 g (58%). For C$_{12}$H$_{25}$B$_9$Ru (367.70) calculated: 39.2% C, 6.85% H; found: 39.0% C, 6.95% H. IR: 2563. ^1H NMR (CDCl$_3$): 5.70–5.60 (2 × d, 4 H, J = 6, CH$_3$**C$_6$H$_4$**CH(CH$_3$)$_2$), 2.52 (sept., 1 H, J = 6, CH$_3$C$_6$H$_4$**CH**(CH$_3$)$_2$), 2.52 (br s, 1 H, CH$_{cage}$), 2.05 (s, 3 H, **CH$_3$**C$_6$H$_4$CH(CH$_3$)$_2$), 1.78 (br s, 1 H, CH$_{cage}$), 1.05 (d, 6 H, J = 6, CH$_3$C$_6$H$_4$CH(**CH$_3$**)$_2$). ^{11}B{^1H} NMR (CDCl$_3$): –3.92 (1 B), –7.48 (2 B), –8.82 (2 B), –19.35 (2 B), –21.39 (2 B), ⟨δ(^{11}B)⟩ = –13.1. EIMS: M$^+$ envelope centred on m/z 364.

2-(η-C$_5$H$_5$)-2,1,7-closo-CoC$_2$B$_9$H$_{11}$ (5)

A 1 M solution of Na[C$_5$H$_5$] (0.30 ml, 0.30 mmol) in THF was added to a solution of Li$_2$[7,9-nido-C$_2$B$_9$H$_{11}$] (0.146 g, 1.00 mmol) in THF (20 ml) at 0 °C and stirred for 15 min followed by the addition of a slurry of CoCl$_2$ (0.455 g, 3.50 mmol) in THF (10 ml). The reaction mixture was allowed to warm slowly to room temperature, the flask was opened to the air, and the product stirred overnight. Volatiles were removed in vacuo and the resulting brown solid worked-up as for compound 2 to yield a yellow mobile band at R_F 0.55 recovered as a yellow solid, compound 5. Yield 0.038 g (15%). For C$_7$H$_{16}$B$_9$Co (256.44) calculated:

32.8% C, 6.29% H; found: 32.6% C, 6.37% H. IR: 2529. ^{1}H NMR (CDCl$_3$): 4.72 (s, 5 H, C$_5$H$_5$), 3.78 (br s, 2 H, CH$_{cage}$). ^{11}B{^{1}H} NMR (CDCl$_3$): –2.15 (1 B), –2.93 (2 B), –9.49 (1 B), –12.26 (2 B), –13.95 (1 B), –17.44 (2 B), $\langle\delta(^{11}B)\rangle$ = –9.6. EIMS: M$^+$ envelope centred on m/z 257.

2-(η-C$_5$H$_5$)-2,1,12-*closo*-CoC$_2$B$_9$H$_{11}$ (**6**) and [(η-C$_5$H$_5$)$_2$Co][2,2′-Co(1,12-*closo*-C$_2$B$_9$H$_{11}$)$_2$] (**7**)

Reagents and reaction conditions were as for **5** except Li$_2$[2,9-*nido*-C$_2$B$_9$H$_{11}$] was used. Initial column chromatography on silica eluting with CH$_2$Cl$_2$/40–60 petroleum ether (3:1) yielded two mobile yellow bands which were collected, combined, and further purified by TLC, eluting with CH$_2$Cl$_2$/40–60 petroleum ether (4:1).

Major component, compound **6**: R_F 0.80, yield 0.038 g (15%). For C$_7$H$_{16}$B$_9$Co (256.44) calculated: 32.8% C, 6.29% H; found: 33.5% C, 6.27% H. IR: 2552. ^{1}H NMR ((CD$_3$)$_2$CO): 5.50 (s, 5 H, C$_5$H$_5$), 2.89 (br s, 1 H, CH$_{cage}$), 2.18 (br s, 1 H, CH$_{cage}$). ^{11}B{^{1}H} NMR ((CD$_3$)$_2$CO): –3.39 (1 B), –4.69 (2 B), –6.66 (2 B), –15.93 (2 B), –19.17 (2 B), $\langle\delta(^{11}B)\rangle$ = –10.7. EIMS: M$^+$ envelope centred on m/z 257.

Minor component, salt **7**: R_F 0.20, yield 0.020 g (4%). For C$_{14}$H$_{32}$B$_{18}$Co$_2$ (512.88) calculated: 32.8% C, 6.29% H; found: 31.6% C, 6.40% H. IR: 2570. ^{1}H NMR ((CD$_3$)$_2$CO): 5.82 (s, 10 H, C$_5$H$_5$), 2.95 (br s, 2 H, CH$_{cage}$), 2.15 (br s, 2 H, CH$_{cage}$). ^{11}B{^{1}H} NMR ((CD$_3$)$_2$CO): –3.38 (2 B), –5.02 (4 B), –6.41 (4 B), –16.84 (4 B), –19.79 (4 B), $\langle\delta(^{11}B)\rangle$ = –11.1.

Crystallography

Single crystals of **2**, **3**, **5**, **6** and **7** were obtained by slow diffusion of 40–60 petroleum ether into a CH$_2$Cl$_2$ solution of the compound at 23 °C and were studied at 100 ± 2 K on a Bruker X8 APEX2 diffractometer equipped with graphite-monochromated MoKα radiation (λ = 0.71069 Å). Intensity data were corrected for absorption semi-empirically from symmetry-equivalent and repeated reflections. Structures were solved by direct and difference Fourier methods and refined[8] by full-matrix least-squares against F^2. Compounds **2**, **3**, **5** and **6** all crystallise with two independent molecules per asymmetric fraction of the unit cell (labelled **A** and **B**) whilst in salt **7** both ions have crystallographically-imposed 2/*m* (C_{2h}) symmetry. In all cases unambiguous distinction could be made between cage B and cage C atoms on the twin bases of refined (as B) U_{eq} values and interatomic distances. Compounds **2**, **5** and **6** and salt **7** were fully ordered. In **3** cage **A** is ordered but there is partial disorder in cage **B**, with major and minor components, 62.5:37.5, related by rotation about the metal-cage axis. In **5** there is a relatively high mosaic spread (although this could not be resolved into different domains). Nevertheless, whilst refinement for all structures was completed with all non-hydrogen atoms assigned anisotropic displacement parameters, an isotropic restraint had to be applied to 16 atoms in **5**. In salt **7**, H atoms were located from difference Fourier maps and freely refined. In all other structures, H atoms (except for those bound to the disordered atoms in **3B**) were set in idealised positions (B–H 1.12 Å, C–H [cage] 1.12 Å, C–H [arene, Cp] 0.95 Å, C–H [Me] 0.98 Å, C–H [tertiary] 1.00 Å). For **3B**, H atoms bound to the disordered atoms C/B1, C/B3, C/B10 and C/B12 were restrained to C/B–H distances of 1.10(2) Å. In every case, H atom thermal parameters were set to 1.2 U_{eq} of the attached B or C atom except for Me groups (1.5 U_{eq}). Table I contains further experimental details. CCDC 777410 (**2**), 777411 (**3**), 777412 (**5**), 777413 (**6**) and 777414 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic

Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

Electrochemistry

Electrochemical measurements were performed in a standard three-electrode cell with an Ag|AgCl reference electrode, a Pt micro-working electrode (diameter 0.25 mm) and a Pt rod counter electrode. Electrochemical data were captured on a Dell Pentium III desktop PC with General Purpose Electrochemistry system (GPES) version 4.8 connected to an Autolab PGSTAT30 potentiostat. All studies were carried out in 0.3 M [n-Bu$_4$N][BF$_4$]/CH$_2$Cl$_2$ and solutions were purged with N$_2$ for 15 min before each experiment and kept under an N$_2$ blanket during the experiment. Potentials were calculated using differential pulse voltammetry and data were recorded using a scan rate of 0.1 V s^{-1}. Ferrocene was used as the internal stan-

TABLE I
Crystallographic data

Parameter	2	3	5	6	7
Formula	C$_{12}$H$_{25}$B$_9$Ru	C$_{12}$H$_{25}$B$_9$Ru	C$_7$H$_{16}$B$_9$Co	C$_7$H$_{16}$B$_9$Co	C$_{14}$H$_{32}$B$_{18}$Co$_2$
M.w.	367.68	367.68	256.42	256.42	512.84
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_12_12_1$	$P2_1/n$	$C2/c$	$P2_1/c$	$C2/m$
a, Å	9.9271(5)	19.9654(16)	21.9632(19)	11.7649(19)	17.2591(8)
b, Å	18.2247(9)	8.1130(8)	13.8017(11)	13.141(2)	10.8043(5)
c, Å	18.4082(8)	20.9806(16)	16.1380(14)	15.981(3)	6.4162(3)
β, °		100.183(4)	98.213(4)	100.311(5)	93.412(2)
U, Å^3	3330.4(3)	3344.9(4)	4841.7(7)	2430.7(7)	1194.32(10)
Z	8	8	16	8	2
$F(000)$, e	1488	1488	2080	1040	520
D_{calc}, g cm^{-3}	1.467	1.460	1.407	1.401	1.426
μ(MoKα), mm^{-1}	0.926	0.922	1.375	1.369	1.393
θ_{max}, °	38.57	35.96	23.25	26.31	32.21
No. of data measured	138428	134925	32587	26806	14885
No. of unique data	17257	15687	3469	4238	2078
R_{int}	0.0306	0.0396	0.0596	0.1031	0.0300
R, $wR2$ (obs. data)	0.0199, 0.0419	0.0278, 0.0508	0.0970, 0.2187	0.0587, 0.1321	0.0261, 0.0639
S	1.025	1.028	1.305	1.031	1.050
Abs. str. parameter	–0.007(11)				
Variables	403	561	307	307	113
E_{max}, E_{min}, e Å^{-3}	1.217, –0.438	0.755, –1.052	1.144, –1.798	0.985, –0.921	0.502, –0.670

dard and all potentials are referenced to the saturated calomel electrode against which the ferrocene/ferrocinium couple is at 0.55 V.

RESULTS AND DISCUSSION

Chart 1 summarises the new species prepared (**2**, **3** and **7**) and also shows the known metallacarboranes, **1**, **4**, **5** and **6**, with which these compounds are compared.
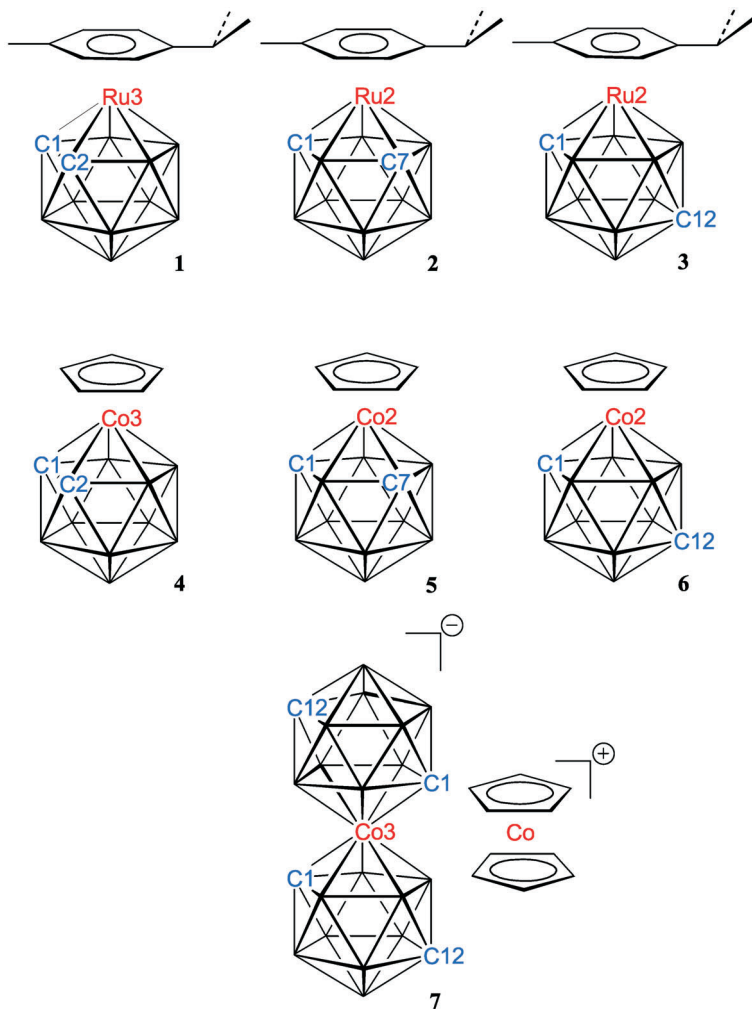
CHART 1

Reaction between $[Ru(p\text{-cymene})Cl_2]_2$ and $Li_2[7,9\text{-}nido\text{-}C_2B_9H_{11}]$ in THF affords $2\text{-}(p\text{-cymene})\text{-}2,1,7\text{-}closo\text{-}RuC_2B_9H_{11}$ (**2**) as the only chromatographically-mobile product, in reasonable yield. The compound was initially characterised by IR spectroscopy, mass spectrometry, microanalysis and ^1H and ^{11}B NMR spectroscopies. The first three of these require no comment. The ^1H NMR spectrum reveals only a single CH_{cage} resonance and a single doublet for the isopropyl methyl groups suggesting time-averaged C_s molecular symmetry in solution, and, in full agreement with this, the $^{11}B\{^1H\}$ NMR spectrum affords six resonances with relative ratios 1:2:1:2:1:2, from high frequency to low frequency.

Similarly, $[Ru(p\text{-cymene})Cl_2]_2$ reacts with $Li_2[2,9\text{-}nido\text{-}C_2B_9H_{11}]$ to afford $2\text{-}(p\text{-cymene})\text{-}2,1,12\text{-}closo\text{-}RuC_2B_9H_{11}$ (**3**), the 2,1,12- analogue of compound **2**. Again there is clear evidence of C_s molecular symmetry by NMR spectroscopy, but this time two CH_{cage} resonances are observed in the ^1H spectrum and there are five resonances, 1:2:2:2:2, in the $^{11}B\{^1H\}$ spectrum.

Both these reactions have been repeated using $CoCl_2/Na[C_5H_5]$ as the source of the metal-ligand fragment, followed by aerial oxidation (overall this supplies the $\{Co(\eta\text{-}C_5H_5)\}^{2+}$ fragment), although the reactions are not as high-yielding as those using $\{Ru(arene)\}^{2+}$. The compound $2\text{-}(\eta\text{-}C_5H_5)\text{-}2,1,7\text{-}closo\text{-}CoC_2B_9H_{11}$ (**5**) was previously prepared by vapour-phase isomerisation of the $3,1,2\text{-}CoC_2B_9$ isomer and an ^{11}B NMR spectrum at 80.5 MHz reported[3]. We have remade this compound from $Li_2[7,9\text{-}nido\text{-}C_2B_9H_{11}]$, primarily to obtain a sample for a crystallographic study but also to furnish more accurate spectroscopic data. The $^{11}B\{^1H\}$ spectrum of **5** is, unsurprisingly, similar to that of **2** in its 1:2:1:2:1:2 pattern. Equally, $2\text{-}(\eta\text{-}C_5H_5)\text{-}2,1,12\text{-}closo\text{-}CoC_2B_9H_{11}$ (**6**) has been previously prepared in the vapour phase[3] and in solution[4], but we have deliberately repeated its synthesis to afford single crystals. Like compound **4** the cobaltacarborane **6** has a 1:2:2:2:2 pattern in its $^{11}B\{^1H\}$ NMR spectrum.

A minor co-product of **6** is the salt $[(\eta\text{-}C_5H_5)_2Co][2,2'\text{-}Co(1,12\text{-}closo\text{-}C_2B_9H_{11})_2]$ (**7**). The identity of this species remained unknown until we undertook a single-crystal diffraction study (vide supra) since microanalysis and ^1H and ^{11}B NMR spectroscopic data for **6** and **7** are practically identical. However, an early indication that **7** might be a salt was the non-observation of peaks in the EI mass spectrum. Surprisingly, since the analogous $3,1,2\text{-}CoC_2B_9$ anion $[3,3'\text{-}Co(1,2\text{-}closo\text{-}C_2B_9H_{11})_2]^-$ (COSAN) is one of the most widely-studied of all heteroboranes[9], and the analogous 2,1,7- species $[2,2'\text{-}Co(1,7\text{-}closo\text{-}C_2B_9H_{11})_2]^-$ is also well known[5a], we are not aware of a previous report of the $[2,2'\text{-}Co(1,12\text{-}closo\text{-}C_2B_9H_{11})_2]^-$ anion.

Notionally, compounds **1** and **4** represent simple derivatives of 1,2-*closo*-$C_2B_{10}H_{12}$ in which a {BH} fragment is replaced by an isolobal {Ru(*p*-cymene)} or a {Co(η-C_5H_5)} fragment. Equally, **2** and **5** represent analogues of 1,7-*closo*-$C_2B_{10}H_{12}$ in which similar replacements have occurred, whilst **3** and **6** can be regarded as the consequences of the same replacements in 1,12-*closo*-$C_2B_{10}H_{12}$. The ^{11}B NMR chemical shifts of all eight possible isomers of (η-C_5H_5)CoC$_2$B$_9$H$_{11}$ have been computed[10] and compared to experimental values[3,4,5c] (albeit that in some cases the resolution of the experimental spectra is not particularly high) and patterns in chemical shifts of neighbouring and antipodal (to metal) atoms have been fully discussed[5c,10]. In Table II we simply compare $\langle\delta(^{11}B)\rangle$ values for the three isomeric icosahedral carboranes and compounds **1–6**, where $\langle\delta(^{11}B)\rangle$ is the weighted average boron chemical shift. In every case $\langle\delta(^{11}B)\rangle$ moves to high frequency on substitution of {BH} by a metal fragment, but the more so for {Co(η-C_5H_5)} than for {Ru(*p*-cymene)}, presumably reflecting the higher formal oxidation state of Co in **4–6** (Co[III]) compared to that of Ru in **1–3** (Ru[II]). Certainly, $\langle\delta(^{11}B)\rangle$ for the ferracarborane 3-(η-C_6H_6)-3,1,2-*closo*-FeC$_2$B$_9$H$_{11}$[11] (–10.3 ppm) is closer to that for the ruthenacarborane **1** than the cobaltacarborane **4**.

The ^{1}H and ^{11}B NMR spectra of neutral **6** and salt **7** are practically superimposable. Hawthorne's original impetus for the synthesis of metallacarboranes[12] was his perceptive recognition of a similarity between the

TABLE II
Comparison of average ^{11}B NMR chemical shifts

Compound	$\langle\delta(^{11}B)\rangle$	Solvent reference
1,2-*closo*-$C_2B_{10}H_{12}$	–11.1	CDCl$_3$, 22
3-(*p*-cymene)-3,1,2-*closo*-RuC$_2$B$_9$H$_{11}$ (**1**)	–10.5	CDCl$_3$, 2
3-(η-C_5H_5)-3,1,2-*closo*-CoC$_2$B$_9$H$_{11}$ (**4**)	–7.3	CD$_2$Cl$_2$, 5c
1,7-*closo*-$C_2B_{10}H_{12}$	–12.4	CDCl$_3$, 22
2-(*p*-cymene)-2,1,7-*closo*-RuC$_2$B$_9$H$_{11}$ (**2**)	–12.0	CDCl$_3$, this work
2-(η-C_5H_5)-2,1,7-*closo*-CoC$_2$B$_9$H$_{11}$ (**5**)	–9.6	CDCl$_3$, this work
1,12-*closo*-$C_2B_{10}H_{12}$	–14.7	CDCl$_3$, 10
2-(*p*-cymene)-2,1,12-*closo*-RuC$_2$B$_9$H$_{11}$ (**3**)	–13.1	CDCl$_3$, this work
2-(η-C_5H_5)-2,1,12-*closo*-CoC$_2$B$_9$H$_{11}$ (**6**)	–10.7	(CD$_3$)$_2$CO, this work
[(η-C_5H_5)$_2$Co][2,2´-Co(1,12-*closo*-$C_2B_9H_{11}$)$_2$] (**7**)	–11.1	(CD$_3$)$_2$CO, this work

bonding capabilities of $[C_5H_5]^-$ and $[C_2B_9H_{11}]^{2-}$ (later to be expressed as an isolobal analogy)[13]. It is clear from the spectra of **6** and **7** that, indeed, $[C_5H_5]^-$ and $[C_2B_9H_{11}]^{2-}$ really are effectively interchangeable as ligands since their exchanging barely affects the spectra of the other fragment (whether $\{C_5H_5\}$ or $\{C_2B_9H_{11}\}$). Similar conclusions have been reached previously from comparison of the spectra of **4** and $[3,3'-Co(1,2-closo-C_2B_9H_{11})_2]^-$ albeit at lower resolution[14].

We have also studied the cobaltacarboranes electrochemically, focussing on the Co^{III}/Co^{II} couple. $E_{1/2}$ values are given in Table III. We have re-measured $E_{1/2}$ (Co^{III}/Co^{II}) for the known species **4**, **5** and **6** and found good agreement with reported values[15]. Thus the reduction occurs at the most negative potential for the 2,1,12- isomer **6**, followed by the 3,1,2- isomer **4**, whilst the easiest isomer to reduce is the 2,1,7- isomer **5**. We confirm that a second reduction (Co^{II}/Co^I) is observed for **4** at –2.01 V (–2.23 V in the literature) but that neither **5** nor **6** show evidence of this second reduction within the electrochemical window available. Voltammetry of salt **7** reveals, in addition to the expected facile Co^{III}/Co^{II} couple for the $[(\eta-C_5H_5)_2Co]^+$ cation (–0.75 V), a reduction wave assigned to the Co^{III}/Co^{II} couple for the $[2,2'-Co(1,12-closo-C_2B_9H_{11})_2]^-$ anion at –1.73 V. Naturally this last potential is substantially more negative than that for the 2,1,12- isomer **6** since the bis(dicarbollide) is anionic. Interestingly, the pattern of reduction potentials displayed by the neutral species **4–6** is repeated for the bis(dicarbollides), since $[3,3'-Co(1,2-closo-C_2B_9H_{11})_2]^-$ and $[2,2'-Co(1,7-closo-C_2B_9H_{11})_2]^-$ are reported to have successively less negative Co^{III}/Co^{II} couples than we find for $[2,2'-Co(1,12-closo-C_2B_9H_{11})_2]^-$, –1.36 and –1.14 V, respectively, in MeCN [16].

TABLE III
Electrode potentials (in V) for the Co^{III}/Co^{II} couple of cobaltacarboranes **4–7**. Reference values are given in parentheses

Compound	Co^{III}/Co^{II}
3-(η-C$_5$H$_5$)-3,1,2-closo-CoC$_2$B$_9$H$_{11}$ (**4**)	–1.08 (–1.22^a, –1.18^b)
2-(η-C$_5$H$_5$)-2,1,7-closo-CoC$_2$B$_9$H$_{11}$ (**5**)	–0.93 (–1.03^a)
2-(η-C$_5$H$_5$)-2,1,12-closo-CoC$_2$B$_9$H$_{11}$ (**6**)	–1.32 (–1.42^a)
[(η-C$_5$H$_5$)$_2$Co][2,2´-Co(1,12-closo-C$_2$B$_9$H$_{11}$)$_2$] (**7**)	–0.75 (–0.81^c), –1.73

^{a} In MeCN, ref.[3] ^{b} In THF, ref.[15] ^{c} In glyme, ref.[15]

Molecular structures of the new species **2**, **3** and **7** and the known compounds **5** and **6** have been determined by single-crystal X-ray diffraction. Figures 1–4 show perspective views of single molecules of **2**, **3**, **5** and **6**, respectively, whilst Fig. 5 is a perspective view of the anion of **7**.

For an icosahedral (transition-)metalladicarborane there are 9 isomeric possibilities (Chart 2). A search of the Cambridge Structural Database (CSD)[17] yields 733 hits on icosahedral MC_2B_9 fragments of which 647 (> 88% of the total) are of the 3,1,2- isomeric type. However, whilst there is a handful of 2,1,7-MC_2B_9 transition metal metalladicarboranes for which structures have been reported (39 examples in the CSD) there are no examples of simple
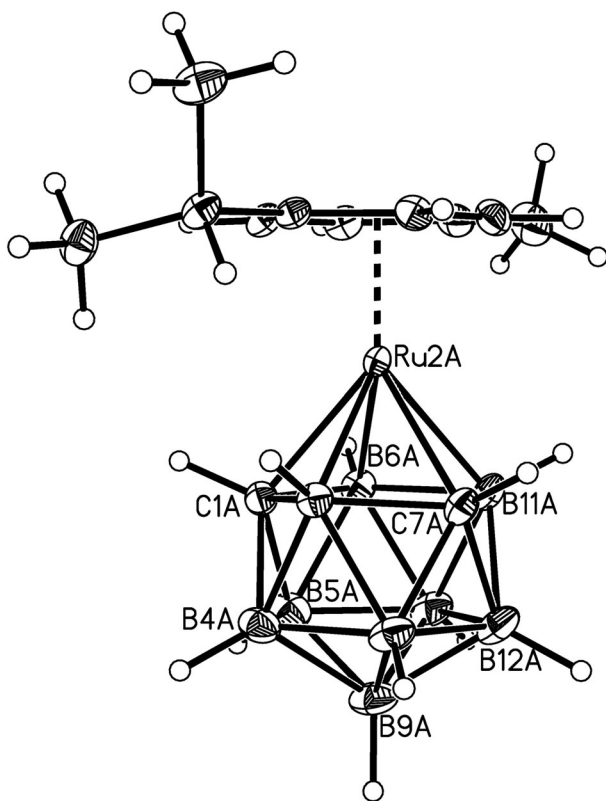
FIG. 1
Perspective view of molecule **A** of 2-(*p*-cymene)-2,1,7-*closo*-RuC$_2$B$_9$H$_{11}$, compound **2**. Molecule **B** is practically superimposable but has a slightly different orientation of the *p*-cymene ligand. Atoms are drawn as 50% probability ellipsoids except for H atoms

{(η^5-C_5H_5)M}-containing compounds or {(arene}M}-containing species with only H substituents on the cage C and B atoms, the nearest analogues being 2-(η^4-C_5Me_5)-2,1,7-*closo*-NiC$_2$B$_9$H$_{11}$ [18] and 1,7-Me$_2$-2-(η-C_6H_5Me)-2,1,7-*closo*-FeC$_2$B$_9$H$_9$ [19]. Hence structural characterisations of the simple 2,1,7-MC$_2$B$_9$ species **2** and **5** are worthwhile. Moreover, there is only one crystallographic example of a 2,1,12-MC$_2$B$_9$ compound, 2,2,2-(NMe$_2$)$_3$-2,1,12-*closo*-TaC$_2$B$_9$H$_{11}$, and that was produced not from [2,9-*nido*-C$_2$B$_9$H$_{11}$]$^{2-}$ but by direct reaction between 2,9-*nido*-C$_2$B$_9$H$_{13}$ and Ta(NMe$_2$)$_5$ [10]. Consequently, the structural studies of the 2,1,12-MC$_2$B$_9$ compounds **3** and **6** and the bis(2,1,12-MC$_2$B$_9$) anion **7** are of interest. For the sake of completeness it is noted that there are, in the CSD, 9 hits on 4,1,2-MC$_2$B$_9$ and 37 hits on 2,1,8-MC$_2$B$_9$, but no current hits on any of 2,1,9-MC$_2$B$_9$, 9,1,7-MC$_2$B$_9$, 8,1,2-MC$_2$B$_9$ or 9,1,2-MC$_2$B$_9$.
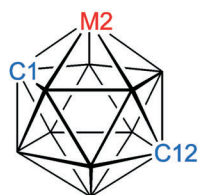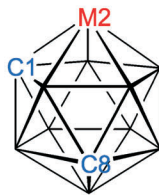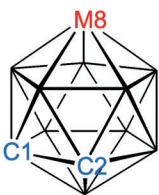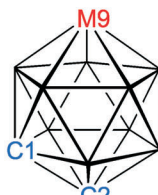

CHART 2

Overall, therefore, compounds **1**, **2** and **3** represent a family of similar icosahedral ruthenacarboranes with, respectively, 3,1,2-, 2,1,7- and 2,1,12-MC_2B_9 architectures, whilst compounds **4**, **5** and **6** represent an analogous family of cobaltacarboranes. Are there patterns within and between the molecular structures of these families? Crystallographic files for **2**, **3**, **5**, **6** and **7** containing comprehensive lists of interatomic distances and angles have been deposited with the Cambridge Crystallographic Data Centre and extensive lists of such parameters will not be reproduced here. Instead, Table IV summarises M–B, M–C, "height" and "fold" for each crystallog-
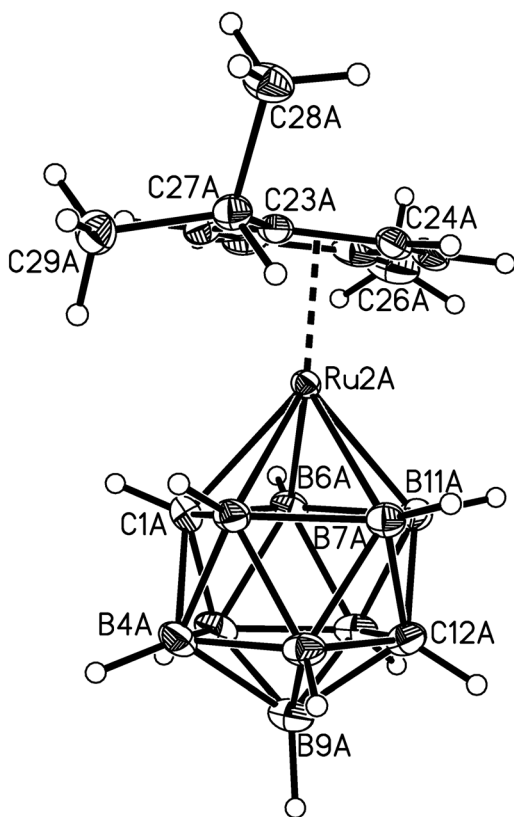

Fig. 2
Perspective view of molecule **A** of 2-(*p*-cymene)-2,1,12-*closo*-$RuC_2B_9H_{11}$, compound **3**. In molecule **B** there is partial disorder of the cage. Atoms are drawn as 50% probability ellipsoids except for H atoms

raphically-independent MC_2B_9 icosahedron in **1–7**. Here "height" is the perpendicular distance from M to the least-squares C_2B_3 or CB_4 carborane face and "fold" is a measure of the envelope folding of the metallabonded face; in every case the C_2B_3 and CB_4 faces fold as described in Fig. 6 [20], with the C atoms slightly below the average plane of the five atoms. Thus θ and $\phi > 0$ for 3,1,2-MC_2B_9 and 2,1,12-MC_2B_9 isomers, θ and $\phi < 0$ for 2,1,7-MC_2B_9 isomers, and "fold" is simply the sum of θ and ϕ.

The ruthenacarborane family **1**, **2** and **3** are all relatively accurately determined but the cobaltacarborane family less so, particularly compound **5**, the crystals of which displayed a relatively wide mosaic spread. Nevertheless, some clear structural patterns are evident in Table IV. The longest Ru–B connectivity is to the central atom, B8, of the 3,1,2- isomer. This isomer also has the shortest Ru–C connectivities if we disregard (partially dis-
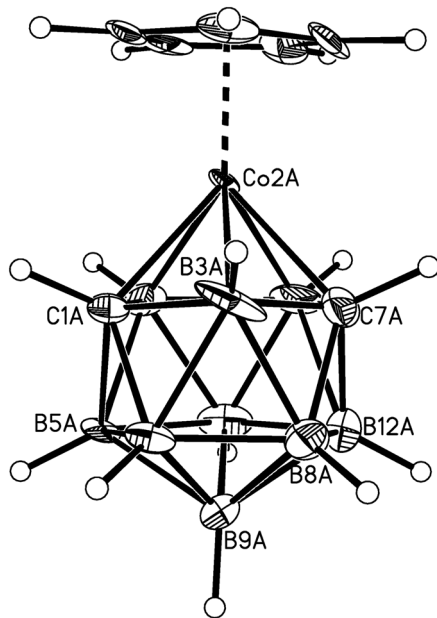

Fig. 3

Perspective view of molecule **A** of 2-(η-C_5H_5)-2,1,7-*closo*-$CoC_2B_9H_{11}$, compound **5**. Molecule **B** is practically superimposable but has a slightly different orientation of the η-C_5H_5 ligand. Atoms are drawn as 30% probability ellipsoids except for H atoms

ordered) **3B**. Similar features are also evident in the cobaltacarborane family. The longest M–C connectivities tend to be in the 2,1,7-MC_2B_9 species, compounds **2** and **5**. The nature of the folding of the metallabonded C_2B_3 or CB_4 carborane ligand face is clearly a function of the isomer type and independent of the metal, with the fold in the 3,1,2- isomers **1** and **4** of ca. +3°, in the 2,1,7- isomers **2** and **5** of ca. –7°, and in the 2,1,12- isomers **3** (except **3B**) and **6** of ca. +5°.

Naturally the Ru atom in compounds **1**–**3** is further from the plane of the carborane ligand face than is the Co atom in **4**–**6**. Within each family "height" is least for the 2,1,12- isomer, compounds **3** and **6**. We interpret this in terms of the simple fact that in 2,1,12- isomers the metallabonded face is CB_4 whilst in 3,1,2- and 2,1,7- isomers the face is C_2B_3. Given that the normal pattern of connectivities in (hetero)carboranes is B–B > B–C > C–C [21] this means that the pentagonal ligand faces in **3** and **6** are larger, and the larger the ring the smaller the perpendicular distance to a common metal fragment[13a].
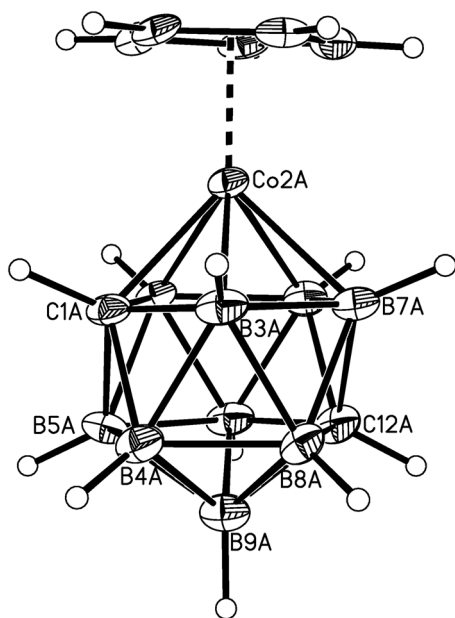

Fig. 4
Perspective view of molecule **A** of 2-(η-C_5H_5)-2,1,12-*closo*-$CoC_2B_9H_{11}$, compound **6**. Molecule **B** is practically superimposable. Atoms are drawn as 50% probability ellipsoids except for H atoms

TABLE IV
Selected molecular parameters for **1**–**7**

Compound	M–B[a], Å	M–C[a], Å	Height, Å	Fold, °
1 (3,1,2-RuC$_2$B$_9$)[b]	2.2154(15) 2.2398(14) 2.2054(14)	2.1732(12) 2.1647(12)	1.625	2.97
2A (2,1,7-RuC$_2$B$_9$)	2.1704(13) 2.2019(13) 2.2008(12)	2.1911(12) 2.1901(11)	1.618	–7.07
2B (2,1,7-RuC$_2$B$_9$)	2.1772(12) 2.1950(13) 2.1897(13)	2.1899(10) 2.1923(11)	1.616	–7.36
3A (2,1,12-RuC$_2$B$_9$)	2.1831(15) 2.1800(16) 2.1746(16) 2.1769(15)	2.1763(14)	1.566	4.68
3B (2,1,12-RuC$_2$B$_9$)[c]	2.1816(17) 2.1841(16) 2.1769(17) 2.1779(16)	2.1704(15)	1.570	1.16
4 (3,1,2-CoC$_2$B$_9$)[d]	2.054(5) 2.106(4) 2.065(5)	1.991(4) 2.005(4)	1.424	2.78
5A (2,1,7-CoC$_2$B$_9$)	2.007(16) 2.036(14) 2.013(18)	2.039(13) 2.015(14)	1.407	–8.25
5B (2,1,7-CoC$_2$B$_9$)	2.013(17) 2.056(19) 2.046(16)	2.032(13) 2.046(12)	1.433	–7.66
6A (2,1,12-CoC$_2$B$_9$)	2.032(7) 2.049(7) 2.055(8) 2.037(7)	2.015(6)	1.378	5.91
6B (2,1,12-CoC$_2$B$_9$)	2.032(7) 2.056(7) 2.060(7) 2.041(7)	2.029(6)	1.387	6.73
7 (2,1,12-CoC$_2$B$_9$)	2.0658(13) 2.0804(12) 2.0804(12)[e] 2.0658(13)[e]	2.0381(16)	1.424	5.64

[a] Order: for 3,1,2-MC$_2$B$_9$ the B atoms are listed B4, B8, B7 and the C atoms C1, C2; for 2,1,7-MC$_2$B$_9$ the B atoms are listed B3, B6, B11 and the C atoms C1, C7; for 2,1,12-MC$_2$B$_9$ the B atoms are listed B3, B7, B11, B6. [b] Ref.[2] [c] Major component of partial disorder. [d] Ref.[5b] [e] By symmetry.
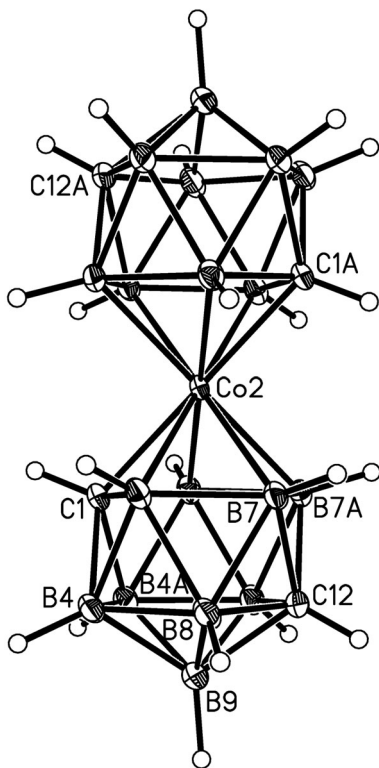
Fig. 5

Perspective view of the anion [2,2'-Co(1,12-*closo*-$C_2B_9H_{11}$)$_2$]$^-$ of salt **7**. The anion has D_{2h} molecular symmetry with the mirror plane passing through C1, Co2, C12 and B9. Atoms are drawn as 50% probability ellipsoids except for H atoms
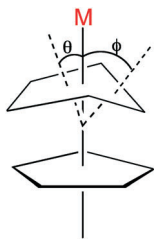

Fig. 6

Definition of θ and φ, the two angles used[20] to describe the folding of carborane ligand faces in metallacarboranes. In Table IV "height" is the perpendicular distance from M to the least-squares plane through the five atoms of the metallabonded face, and "fold" is the sum of θ and φ

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