

First structural characterisation of a 2,1,12-MC₂B₉ metallocarborane, [2,2,2-(NMe₂)₃-*closo*-2,1,12-TaC₂B₉H₁₁]. Trends in boron NMR shifts on replacing a {BH} vertex with a metal {ML_n} vertex in icosahedral carboranes

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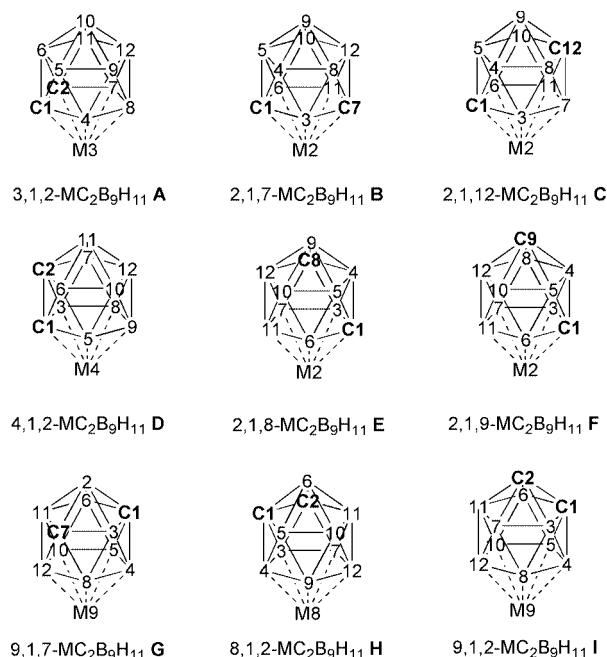
Reactions of M(NMe₂)₅ (M = Ta or Nb) with *nido*-2,9-C₂B₉H₁₃ and the salt [Me₃NH][*nido*-7,9-C₂B₉H₁₂] gave the isomeric dicarbollide complexes [2,2,2-(NMe₂)₃-*closo*-2,1,12-MC₂B₉H₁₁] (M = Ta **1**, Nb **4**) and [2,2,2-(NMe₂)₃-*closo*-2,1,7-MC₂B₉H₁₁] (M = Ta **2**, Nb **5**) respectively. The structures of **1** and **2** were determined by single crystal X-ray diffraction and **1** represents the first structurally characterised example of a 2,1,12-MC₂B₉ metallocarborane. Comparison of ¹¹B NMR data of the tantalum complexes, along with the isomeric [3,3,3-(NMe₂)₃-*closo*-3,1,2-TaC₂B₉H₁₁] **3**, with that of 1,2-, 1,7- and 1,12-C₂B₁₀H₁₂, reveals that the metal vertex {Ta(NMe₂)₃}, on replacing a {BH} vertex, influences significantly the boron NMR shifts of the neighbouring and antipodal cage atoms. Based on this observation the assignments of the reported peaks in the boron NMR data for the seven isomers of (η⁵-C₅H₅)CoC₂B₉H₁₁ are tentatively predicted.

Introduction

Hundreds of metallocarboranes have been synthesized since they were first reported by Hawthorne and co-workers in the 1960s.^{1,2} The most commonly studied metallocarboranes are those with an icosahedral MC₂B₉ cage. The 3,1,2-, 2,1,7- and 2,1,12-MC₂B₉ (A, B and C) cages are generated by base removal of the most positive boron atom of the three icosahedral carboranes, 1,2-, 1,7- and 1,12-C₂B₁₀H₁₂ respectively followed by addition of a metal fragment. Of these, metallocarboranes consisting of the 3,1,2-MC₂B₉ cage A are the most widely studied with over 300 structures determined by X-ray crystallography, followed by those containing 2,1,7-MC₂B₉ B geometries with some 30 structures known.³ Dicarbollide complexes containing the 2,1,12-MC₂B₉ C type are limited to those containing cobalt, rhodium and nickel at the metal vertex and no structural characterisation has been reported.^{4–12} Metallocarboranes with other MC₂B₉ cage conformations (D–I) are synthesized *via* cage rearrangements^{4,5,7,13,14} and compounds with 4,1,2- (D) and 2,1,8-MC₂B₉ (E) cages have been structurally determined.^{15,16}

Despite the enormous number of icosahedral MC₂B₉ metallocarboranes known, ¹¹B NMR chemical shift assignments of these are sparse. Assignments determined by 2-D ¹¹B–¹¹B COSY spectroscopy have been reported for metallocarboranes with 3,1,2-C₂B₉ cages A, [Cl₃TaC₂B₉H₁₁] and [X₂Ta(C₂B₉H₁₁)₂] (X = Me, F or Cl) derivatives,^{17,18} [(C₅H₅)CoC₂B₉H₁₁],¹⁹ [(C₆-Me₆)RuC₂B₉H₁₁],²⁰ [(C₅Me₅)RhC₂B₉H₁₁] and derivatives,^{19,21} [(C₅Me₅)IrC₂B₉H₁₁]¹⁹ and [(C₅H₅)Mo(C₃H₃)C₂B₉H₉].²²

Here we report the syntheses and characterisation of the new tantalum compounds [2,2,2-(NMe₂)₃-*closo*-2,1,12-TaC₂B₉H₁₁] **1** and [2,2,2-(NMe₂)₃-*closo*-2,1,7-TaC₂B₉H₁₁] **2**. The structure of complex **1** was determined by single crystal X-ray diffraction and this represents the first structurally characterised example of a 2,1,12-MC₂B₉ metallocarborane; the structure of **2** has also been determined. Along with the recently reported isomer



[3,3,3-(NMe₂)₃-*closo*-3,1,2-TaC₂B₉H₁₁] **3**,²³ this study demonstrates the first fully assigned ¹¹B and ¹H NMR data for a series of metallocarboranes incorporating 3,1,2-, 2,1,7- and 2,1,12-MC₂B₉ cages (A–C) and reveals clear trends in the ¹¹B NMR chemical shifts on replacing a {BH} vertex in the isomeric carboranes 1,2-, 1,7- and 1,12-C₂B₁₀H₁₂ by the metal vertex {Ta(NMe₂)₃}. These trends include data for the new niobium compounds [2,2,2-(NMe₂)₃-*closo*-2,1,12-NbC₂B₉H₁₁] **4** and [2,2,2-(NMe₂)₃-*closo*-2,1,7-NbC₂B₉H₁₁] **5** synthesized here, and the previously reported isomer [3,3,3-(NMe₂)₃-*closo*-3,1,2-NbC₂B₉H₁₁] **6**. From this study, the assignments of the reported

Table 1 ^{11}B NMR chemical shift data (δ) for isomeric $\text{MC}_2\text{B}_9\text{H}_{11}$ complexes [$\text{M} = \text{BH}$, $\text{Ta}(\text{NMe}_2)_3$ or $\text{Nb}(\text{NMe}_2)_3$]^a

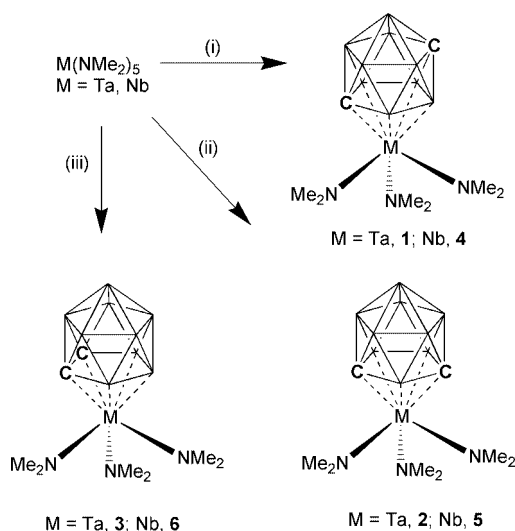
2,1,12-MC ₂ B ₉	B7,11	B3,6	B4,5	B8,10	B9	Average	
M = BH	−14.7	−14.7	−14.7	−14.7	−14.7	−14.7	
Ta(NMe ₂) ₃	−4.1	−6.2	−13.7	−14.2	−19.3	−10.6	
difference	10.6	8.5	1.0	0.5	−4.6		
Nb(NMe ₂) ₃	−4.5	−5.9	−13.4	−14.2	−17.6	−10.4	
difference	10.2	8.8	1.3	0.5	−2.9		
2,1,7-MC ₂ B ₉	B6,11	B3	B4,8	B5,12	B10	B9	Average
M = BH	−13.1	−16.8	−13.1	−6.4	−10.3	−10.3	−11.4
Ta(NMe ₂) ₃	−5.2	−11.8	−13.1	−5.9	−11.1	−16.9	−9.8
difference	7.9	5.0	0.0	0.5	−0.8	−6.6	
Nb(NMe ₂) ₃	−4.7	−11.4	−12.9	−5.8	−11.4	−15.6	−9.1
difference	8.4	5.4	0.2	0.6	−1.1	−5.3	
3,1,2-MC ₂ B ₉	B4,7	B8	B9,12	B5,11	B6	B10	Average
M = BH	−15.0	−10.6	−3.8	−15.0	−16.1	−10.6	−11.7
Ta(NMe ₂) ₃	−5.7	1.7	−3.4	−13.8	−13.8	−16.2	−8.2
difference	9.3	12.3	0.4	1.2	2.3	−5.6	
Nb(NMe ₂) ₃	−6.1	3.3	−2.9	−13.2	−13.2	−14.4	−7.4
difference	9.9	13.9	0.9	1.8	2.9	3.8	

^a All chemical shifts are in ppm. Italicised values (differences) are the difference between the chemical shift of the metallocarborane and that of the same vertex in the parent $\text{C}_2\text{B}_{10}\text{H}_{12}$.

peaks in the ^{11}B NMR data for the seven isomers of $[(\eta^5\text{-C}_5\text{H}_5)\text{CoC}_2\text{B}_9\text{H}_{11}]$ are tentatively predicted.

Results and discussion

The reactions of $\text{Ta}(\text{NMe}_2)_5$ with the neutral carborane *nido*-2,9- $\text{C}_2\text{B}_9\text{H}_{13}$ and the salt $[\text{Me}_3\text{NH}][\text{nido-7,9-}\text{C}_2\text{B}_9\text{H}_{12}]$ gave the isomeric dicarbollide complexes $[\text{2,2,2-(NMe}_2)_3\text{-}\text{closo-2,1,12-TaC}_2\text{B}_9\text{H}_{11}]$ **1** and $[\text{2,2,2-(NMe}_2)_3\text{-}\text{closo-2,1,7-TaC}_2\text{B}_9\text{H}_{11}]$ **2** respectively in high yields (Scheme 1). The new metallocar-



Scheme 1 The synthesis of the isomeric metallocarboranes $[\text{2,2,2-(NMe}_2)_3\text{-}\text{closo-2,1,12-MC}_2\text{B}_9\text{H}_{11}]$ ($\text{M} = \text{Ta}$, **1**; Nb , **4**) and $[\text{2,2,2-(NMe}_2)_3\text{-}\text{closo-2,1,7-MC}_2\text{B}_9\text{H}_{11}]$ ($\text{M} = \text{Ta}$, **2**; Nb , **5**) and the previously reported $[\text{3,3,3-(NMe}_2)_3\text{-}\text{closo-3,1,2-MC}_2\text{B}_9\text{H}_{11}]$ ($\text{M} = \text{Ta}$, **3**; Nb , **6**). Reagents: (i) *nido*-2,9- $\text{C}_2\text{B}_9\text{H}_{13}$, (ii) $[\text{Me}_3\text{NH}][\text{nido-7,9-}\text{C}_2\text{B}_9\text{H}_{12}]$, (iii) *nido*-7,8- $\text{C}_2\text{B}_9\text{H}_{13}$.

boranes were identified by ^{11}B , ^1H and ^{13}C NMR spectroscopy and structurally characterised by single crystal X-ray diffraction. The solution-state ^1H and ^{13}C NMR data for the three tantalum compounds **1–3** revealed single peaks for the NMe_2 groups indicating that rotation about the Ta–N bonds is fast at ambient temperature in these compounds.

Good quality 2-D ^{11}B – ^{11}B COSY and ^{11}B – ^1H correlation NMR spectra were obtained from these compounds, along with $[\text{3,3,3-(NMe}_2)_3\text{-}\text{closo-3,1,2-TaC}_2\text{B}_9\text{H}_{11}]$ **3** synthesized from $\text{Ta}(\text{NMe}_2)_5$ and *nido*-7,8- $\text{C}_2\text{B}_9\text{H}_{13}$,²³ and these spectra have allowed their ^{11}B and ^1H chemical shifts to be assigned. For more than one isomer of a MC_2B_9 -type metallocarborane, *i.e.* **1** (**C**), **2** (**B**) and **3** (**A**), boron data have been assigned here for the first time and are listed in Table 1. As these three TaC_2B_9 cages are shown to have *closo* geometries by X-ray diffraction,²³ it is possible to compare the differences in the boron chemical shifts caused by replacing a boron vertex with a metal vertex in the three *closo*- $\text{C}_2\text{B}_{10}\text{H}_{12}$ isomers. Average shift differences of +8.9 ppm (max./min. 12.3 to 5.0) for neighbouring borons, −5.6 (−4.6 to −6.6) for antipodal and +0.6 (2.3 to −0.8) for other (butterfly) borons were found (Table 1). Clearly there are strong neighbouring and antipodal effects on the boron chemical shifts on replacing a $\{\text{BH}\}$ vertex with a $\{\text{Me}_2\text{N}\}_3\text{Ta}\}$ vertex in all cases.

Syntheses of the new niobium complexes $[\text{2,2,2-(NMe}_2)_3\text{-}\text{closo-2,1,12-NbC}_2\text{B}_9\text{H}_{11}]$ **4** and $[\text{2,2,2-(NMe}_2)_3\text{-}\text{closo-2,1,7-NbC}_2\text{B}_9\text{H}_{11}]$ **5** were achieved by the same route as for **1** and **2** respectively, using $\text{Nb}(\text{NMe}_2)_5$ in place of $\text{Ta}(\text{NMe}_2)_5$ (Scheme 1). The niobium derivatives **4**, **5** and the recently reported isomer $[\text{3,3,3-(NMe}_2)_3\text{-}\text{closo-3,1,2-NbC}_2\text{B}_9\text{H}_{11}]$ **6** revealed very similar NMR characteristics as their tantalum analogues **1**, **2** and **3** respectively so their multinuclear NMR data are assigned accordingly.

Molecular structures

The Ta atoms in complexes **1**, **2** and the *closo*-3,1,2-isomer **3** are co-ordinated in a piano-stool fashion by the open CB_4 (in **1**) or C_2B_3 (in **2** and **3**) faces of the dicarbollide ligand and by three dimethylamide ligands. The nitrogen atoms of the latter have planar (sp^2) bond geometry, the Ta–N bond distances indicate $\text{d}(\text{Ta})\leftarrow\text{p}_\pi(\text{N})$ donation. Detailed examination of the molecular structures (Figs. 1 and 2, Table 2) reveals significant differences between the isomers, and the crystal structures of **1**, **2** and **3** are quite different. The orientation of the NMe_2 ligands with respect to the remainder of the metal co-ordination sphere can be described by the dihedral angle τ between the NC_2 and CbTaN planes, where Cb is the centroid of the co-ordinated dicarbollide face. In **1** the N(1)Me_2 ligand

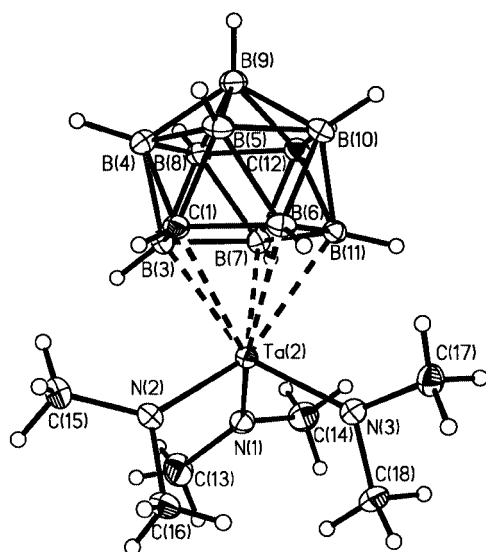


Fig. 1 The molecular structure of [2,2,2-(NMe₂)₃-closo-2,1,12-TaC₂-B₉H₁₁] **1**, showing 50% displacement ellipsoids.

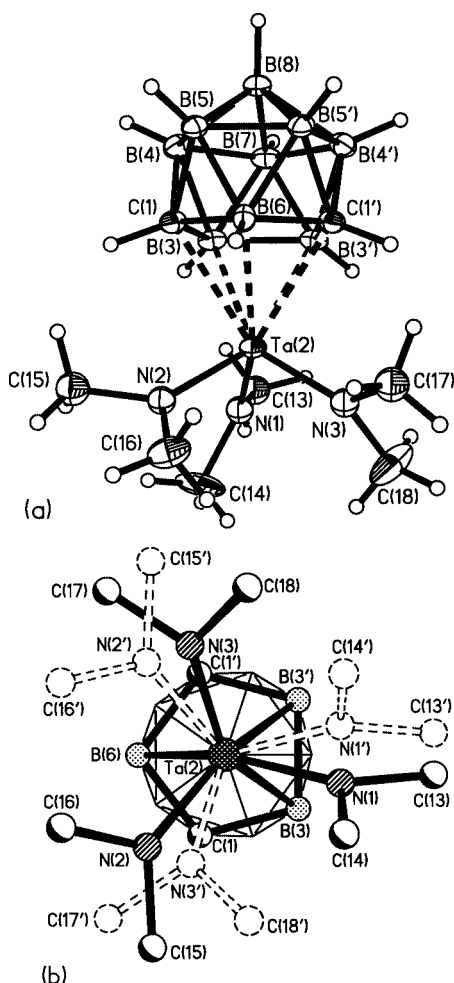


Fig. 2 (a) The molecular structure of [2,2,2-(NMe₂)₃-closo-2,1,7-TaC₂B₉H₁₁] **2**, showing 50% displacement ellipsoids. (b) Disorder in the crystal of **2**: two enantiomers sharing the same site (H atoms are omitted). Atoms, symmetrically generated by the *m* plane, are primed.

is close to the 'horizontal' orientation ($\tau = 90^\circ$) and the other two ligands are close to 'vertical' ($\tau = 0^\circ$); all three are inclined in the same direction to form a chiral propeller conformation. Similar conformations were observed in **3**, as well as in {Ta[(CyN)₂C(NCy)](NMe₂)₃}²⁴ and [Nb(2,6-ⁱPr₂C-

Table 2 Selected bond lengths (Å), bond and dihedral angles (°) for complexes **1** and **2**

	1	2
Ta(2)–N(1)	1.972(2)	1.902(15)
Ta(2)–N(2)	1.983(2)	1.990(14)
Ta(2)–N(3)	1.990(2)	1.994(15)
Ta(2)–C(1)	2.497(2)	2.495(8)
Ta(2)–B(3)	2.446(3)	2.482(9)
Ta(2)–B(6)	2.494(2)	2.447(12)
Ta(2)–B(7)	2.465(2)	—
Ta(2)–B(11)	2.484(2)	—
Ta(2)–Cb	1.986(5)	2.01(1)
C(1)–B(3)	1.688(4)	1.69(1)
B(3)–B(7)	1.772(4)	—
B(7)–B(11)	1.786(3)	—
B(11)–B(6)	1.782(4)	—
C(1)–B(6)	1.674(4)	1.68(1)
B(3)–B(3')	—	1.80(2)
Cb–Ta(2)–N(1)	122.6(2)	118.5(5)
Cb–Ta(2)–N(2)	115.4(2)	118.9(5)
Cb–Ta(2)–N(3)	116.7(2)	119.4(5)
CbTa(2)N(1)/N(1)C(13)C(14)	67.8	28.5
CbTa(2)N(2)/N(2)C(15)C(16)	29.3	60.0
CbTa(2)N(3)/N(3)C(17)C(18)	20.9	55.1

Cb = Centroid of the η^5 -co-ordinated ring.

H₃N)(NMe₂)₃]²⁵ and can be explained by non-degeneracy of the two orthogonal π -donor orbitals of the imide and the C₂B₉H₁₁ or guanidine ligands. The horizontal NMe₂ ligand in **1** or **3** forms a stronger Ta–N bond than the vertical ligands, but the difference is much smaller in **1** (0.015 Å) than in **3** (0.032 Å), where the ligands are much closer to the ideal vertical and horizontal conformations. While in **3** the unique N atom lies *trans* to the most electron-rich (C–C) bond of the dicarbollide and thus close to the local mirror plane of the metallacarborane cage, in **1** the N(1) is *trans* to B(6) and the Cb–Ta(2)–N(1) plane is inclined by 50° to the local mirror plane of the cage, passing through C(1), B(9), C(12) and Ta(2). In the case of 3,1,2-MC₂B₉ metallacarboranes, such as **3**, the orientational preference of the cage with respect to the other ligands on the metal is often described as a strong *trans* influence of the dicarbollide ligand, and has been observed in indenyl,^{26,27} pyrrolyl²⁸ and carbonyl²⁹ complexes. Similar orientational preferences in the isomeric metallacarboranes are less well documented.⁷

Molecules of [2,2,2-(NMe₂)₃-closo-2,1,7-TaC₂B₉H₁₁] **2** (Fig. 2) lie on a crystallographic mirror plane, passing through the Ta(2), B(6), B(7) and B(8) atoms. However, only the metallacarborane cage actually has this symmetry. All three dimethylamide ligands are disordered between two sets of positions, related by the mirror plane. Each set corresponds to one enantiomer of a chiral propeller conformation with one ligand, N(1)Me₂, closer to the vertical and two others to the horizontal conformation. Surprisingly, the Ta(2)–N(1) bond to the unique vertical NMe₂ ligand is shorter than the rest (although the precision is low due to the disorder).

The co-ordinated CB₄ face in complex **1** has an envelope-like distortion, typical for icosahedral metallacarboranes with a metal–CB₄ face bonding (*i.e.* with 4,1,2-MC₂B₉ (**D**),¹⁵ 2,1,8-MC₂B₉ (**E**)¹⁵ and 2,1-MCB₁₀ cages³⁰): the C(1) atom lies 0.08 Å further from Ta(2) than the B₄ plane. In **2** both metal-co-ordinated carbon atoms, C(1) and C(1'), are similarly shifted by 0.09 Å out of the B₃ plane and away from Ta(2).

Trends in boron NMR data for known icosahedral metallacarboranes

The effects on boron NMR shifts of replacing a BH vertex with a metal vertex in the NMR data for 1,2-C₂B₁₀H₁₂ and four 3,1,2-MC₂B₉ cage (**A**) complexes have been compared and

Table 3 Assigned ^{11}B chemical shifts for 3,1,2- $\text{MC}_2\text{B}_9\text{H}_{11}$ complexes^a

3,1,2- MC_2B_9	Ref.	B4,7	B8	B9,12	B5,11	B6	B10	Average
M = BH		−15.0	−10.6	−3.8	−15.0	−16.1	−10.6	−11.7
Ta(NMe ₂) ₃	23	−5.7 9.3	1.7 12.3	−3.4 0.4	−13.8 1.2	−13.8 2.3	−16.2 −5.6	−8.2
Nb(NMe ₂) ₃	23	−6.1 9.9	3.3 13.9	−2.9 0.9	−13.2 1.8	−13.2 2.9	−14.4 −3.8	−7.4
Ir(C ₅ Me ₅)	19	−8.7 6.3	−0.8 9.8	−11.9 −8.1	−21.8 −6.8	−26.4 −10.3	−1.7 8.9	−12.6
Ru(C ₆ Me ₆)	20	−5.4 9.6	4.2 14.8	−9.5 −5.7	−19.8 −4.8	−24.0 −7.9	−2.3 8.3	−10.2
Co(C ₅ H ₅)	19	−4.9 10.1	6.8 17.4	−5.9 −2.1	−16.1 −1.1	−22.4 −6.3	3.5 14.1	−7.3
Rh(C ₅ Me ₅)	19	−3.5 11.5	8.6 19.2	−8.3 −4.5	−18.6 −3.6	−23.4 −7.3	−1.8 8.8	−8.6
TaMe ₂ (C ₂ B ₉ H ₁₁) [−]	18	0.1 15.1	12.9 23.5	0.1 3.9	−11.1 3.9	−14.4 1.7	−8.7 1.9	−3.6
TaF ₂ (C ₂ B ₉ H ₁₁) [−]	18	0.4 15.4	13.2 23.8	1.5 5.3	−7.6 7.4	−10.5 5.6	−10.6 0.0	−2.1
TaCl ₂ (C ₂ B ₉ H ₁₁) [−]	18	−5.6 9.4	26.7 37.3	2.9 6.7	−4.7 10.3	−11.8 4.3	−14.4 −3.8	−1.6
TaCl ₃	17	2.6 17.6	15.8 26.4	7.3 11.1	−3.2 11.8	−5.7 10.4	−5.7 4.9	2.0

^a All chemical shifts are in ppm. Italicised values (differences) are the difference between the chemical shift of the 3,1,2-metallacarborane and that of the same vertex in *ortho*-carborane, 1,2- $\text{C}_2\text{B}_{10}\text{H}_{12}$.

Table 4 Predicted and observed ^{11}B NMR chemical shifts for the isomeric $(\eta\text{-C}_5\text{H}_5)\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})$ complexes

Isomer	Predicted ^a	Observed ^b	Isomer	Predicted	Observed
2,1,7 B	2.0 (B9)	−1.2 (1)	2,1,9 F	1.2 (B7,11)	−0.2 (2)
	−1.6 (B6,11)	−2.9 (2)		−1.6 (B3,6)	−6.8 (2)
	−5.3 (B3)	−9.2 (1)		−9.0 (B12)	−9.7 (1)
	−9.0 (B5,12)	−11.8 (2)		−15.7 (B8,10)	−15.9 (2)
	−12.9 (B10)	−13.3 (1)		−19.4 (B4,5)	−21.4 (2)
2,1,12 C	−15.7 (B4,8)	−16.8 (2)	9,1,7 G	5.1 (B5,12)	0.8 (2)
	−2.4 (B9)	−2.8 (1)		1.2 (B10)	−3.6 (1)
	−3.2 (B7,11,3,6)	−4.6 (2)		−1.6 (B4,8)	−5.8 (2)
		−6.4 (2)		−4.5 (B2)	−6.8 (1)
	−17.3 (B4,5,8,10)	−16.1 (2)		−15.7 (B6,11)	−15.7 (2)
4,1,2 D		−19.3 (2)	8,1,2 H ^c	−19.4 (B3)	−19.8 (1)
	7.7 (B9)	9.5		7.7 (B9,12)	1.1 (2)
	0.9 (B8)	1.5		−3.5 (B4,7)	0.9 (1)
	−2.7 (B11)	−1.5		−3.8 (B6)	−0.2 (1)
	−3.5 (B5)	−4.8		−4.6 (B3)	−4.7 (2)
	−4.6 (B3)	−5.3		−13.2 (B10)	−8.8 (1)
	−6.4 (B12)	−5.9		−17.6 (B5,11)	−14.4 (2)
	13.2 (B10)	−11.2	9,1,12 I ^c	7.7 (B12)	4.2 (1)
	−17.6 (B7)	−18.0		0.9 (B8,10)	0.5 (2)
	−18.7 (B6)	−19.1		−3.5 (B4,5)	−1.8 (2)
2,1,8 E	5.1 (B6)	0.4		−17.6 (B7,11)	−9.6 (2)
	1.2 (B11)	−0.2		−18.7 (B3,6)	−12.4 (2)
	−0.8 (B9)	−1.9			
	−1.6 (B7)	−3.0			
	−5.3 (B3)	−8.3			
	−9.0 (B12)	−10.3			
	−12.9 (B10)	−12.7			
	−15.7 (B5)	−18.4			
	−19.4 (B4)	−19.9			

^a Predicted chemical shifts were calculated by adding the values 12.5 (NE), −2.5 (BE) and 14.1 ppm (AE) to the ^{11}B shifts of $\text{C}_2\text{B}_{10}\text{H}_{12}$ on replacing a BH vertex with a $\text{Co}(\text{C}_5\text{H}_5)$ vertex. ^b Data taken from ref. 5. ^c For these isomers, the observed data are for a derivative of $[(\text{C}_5\text{H}_5)\text{Co}(\text{C}_3\text{H}_6\text{C}_2\text{B}_9\text{H}_9)]$, i.e. $[(\text{C}_5\text{H}_5)\text{Co}(\text{C}_3\text{H}_6\text{C}_2\text{B}_9\text{H}_9)]$.

discussed previously.¹⁹ The assigned ^{11}B chemical shifts of ten *closo*-3,1,2- MC_2B_9 complexes and chemical shift differences with respect to 1,2- $\text{C}_2\text{B}_{10}\text{H}_{12}$ are listed in Table 3. In all cases, except for the $[\text{Cl}_2\text{Ta}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$ anion, there are clear trends in the neighbouring (NE), antipodal (AE) and butterfly (BE) borons on replacing a {BH} vertex with a metal vertex. At this stage it is not clear why the shifts for the $[\text{Cl}_2\text{Ta}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$ anion differ significantly from the related tantalum anions, $[\text{F}_2\text{Ta}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$ and $[\text{Me}_2\text{Ta}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$.¹⁸

Despite the vast quantity of reported boron NMR data for isomeric MC_2B_9 metallacarboranes, there are very few examples of isomeric complexes where chemical shift data have been assigned by ^{11}B – ^{11}B COSY. The thermolysis of 3-(C_5H_5)-*closo*-3,1,2- $\text{CoC}_2\text{B}_9\text{H}_{11}$ leads to 7 of the 9 possible isomeric metallacarboranes, all of which have been separated,⁵ and the ^{11}B chemical shifts of the 3,1,2 isomer have been assigned.¹⁹ This series of isomeric complexes provides a unique case where we are able to use the assigned spectra of the 3,1,2 isomer

Table 5 ^{11}B NMR chemical shifts for 2,1,12-MC₂B₉H₁₁ metallacarboranes^a

	Ref.	B3,6/B7,11		B4,5/B8,10		B9	Average
M = BH		−14.7	−14.7	−14.7	−14.7	−14.7	−14.7
Ta(NMe ₂) ₃	This work	−4.1	−6.2	−13.7	−14.2	−19.3	−10.6
<i>difference</i>		<i>10.6</i>	<i>8.5</i>	<i>1.0</i>	<i>0.5</i>	<i>−4.6</i>	
Nb(NMe ₂) ₃	This work	−4.5	−5.9	−13.4	−14.2	−17.6	−10.4
<i>difference</i>		<i>10.2</i>	<i>8.8</i>	<i>1.3</i>	<i>0.5</i>	<i>−2.9</i>	
Co(C ₅ H ₅)	12	−4.4	−6.5	−15.6	−18.8	−2.7	−10.4
<i>difference</i>		<i>10.3</i>	<i>8.2</i>	<i>−0.9</i>	<i>−4.1</i>	<i>12.0</i>	
Rh(PPh ₃) ₂ H	38	−6.2	−8.7	−19.4	−19.4	−1.1	−12.1
<i>difference</i>		<i>8.5</i>	<i>6.0</i>	<i>−4.7</i>	<i>−4.7</i>	<i>13.6</i>	
Rh(PPh ₃)(MeCO ₂)	10	3.9	−9.4	−18.6	−20.1	3.9	−9.4
<i>difference</i>		<i>18.6</i>	<i>5.3</i>	<i>−3.9</i>	<i>−5.4</i>	<i>18.6</i>	
Rh(PPh ₃)(CO) [−]	7	−23.9	−25.1	−10.9	−17.1	−14.6	−18.7
<i>difference</i>		<i>−9.2</i>	<i>−10.4</i>	<i>3.8</i>	<i>−2.4</i>	<i>0.1</i>	
Ni(PPh ₃) ₂	11	−20.0	−20.0	−10.1	−14.9	−8.1	−15.3
<i>difference</i>		<i>−5.3</i>	<i>−5.3</i>	<i>4.6</i>	<i>−0.2</i>	<i>6.6</i>	

^a All chemical shifts are in ppm. Italicised values (differences) are the difference between the chemical shift of the 2,1,12-metallacarborane and that of the same vertex in *para*-carborane, 1,12-C₂B₁₀H₁₂.

to predict the chemical shifts of the other isomers using the averaged chemical shift differences (NE, 12.5 ppm; AE, 14.1 and BE, −2.5) generated from the assigned boron NMR peaks of the 3,1,2 isomer.^{5,19} Table 4 compares the predicted boron chemical shifts and assignments with the experimental data. The overall correlation is remarkably good between the predicted and observed data. If the order of the assigned peaks is identical to the order known experimentally for all isomers the error range is between +2.0 to −5.2 ppm. These crude predictions are no worse than the chemical shifts predicted by IGLO computations³¹ on the *static* geometry of 3-(C₅Me₅)-3,1,2-RhC₂B₉H₁₁ obtained by single crystal X-ray diffraction¹⁹ where the error range is between +9.0 to −3.7 ppm.

Perhaps the most informative boron NMR data are those of compounds containing the 2,1,12-MC₂B₉ (C) isomer, where a 2:2:2:2:1 boron peak intensity ratio is expected. The boron peak of intensity 1 is assigned to the antipodal boron atom (B9) whilst the other four peaks correspond to the two pairs of boron atoms (B3,6/7,11) on the neighbouring positions and two pairs on the lower belt (B4,5/B8,10) of the cage. The peaks with the biggest shift differences compared to the boron chemical shift of 1,12-C₂B₁₀H₁₂ ($\delta_{\text{B}} - 14.7$) are presumed to be the neighbouring boron atoms (B3,6/7,11), and demonstrated to be the case in the ^{11}B - ^{11}B COSY assigned spectra of **1** and **4**. Table 5 shows the boron NMR data for these and other 2,1,12-MC₂B₉ derivatives and clearly those complexes with a {ML₂} type vertex such as {Ni(PPh₃)₂} and {Rh(PPh₃)(CO)[−]} do not follow the trend observed for the other complexes. These observations are in agreement with the observation that {L₃M}, {L₅M} and {L₆M} vertices in metallacarboranes listed in Tables 3–5 are isolobal to the {BH} vertex whereas the non-conical {ML₂} vertices, {(Ph₃P)₂Ni} and {(Ph₃P)₂Rh[−]}, are not.³²

The antipodal effect on boron NMR shifts is well known in icosahedral heteroboranes and is thought to be a consequence of the electron density in the cluster surface orbitals.³³ An increase in the electron density in these orbitals is believed to cause a deshielding effect on the chemical shift of the antipodal boron atom. On this basis, the electron density is high in the surface orbitals for the {(C₅H₅)Co} vertex and low for the {(Me₂N)₃Ta} vertex.

The averaged boron shifts of the metallacarboranes in Tables 3 and 5 are similar to C₂B₁₀H₁₂ in many cases, which suggest similarities in the cage electronics between these compounds. Averaged shifts significantly to high frequency (δ 2.0 to −3.6) are found for tantalum derivatives containing the 3,1,2-MC₂B₉ cage, [Cl₃Ta(C₂B₉H₁₁)], [Cl₂Ta(C₂B₉H₁₁)₂][−], [F₂Ta(C₂B₉H₁₁)₂][−] and [Me₂Ta(C₂B₉H₁₁)₂][−], with their chemical shifts for the B10 atoms strongly to high frequency compared to other

shifts, which suggests that these complexes do not contain similar electronic and orbital characteristics to those in C₂B₁₀H₁₂ isomers.

Experimental

All manipulations of air- and moisture-sensitive compounds were performed on a conventional vacuum/nitrogen line using standard Schlenk and cannula techniques or in a nitrogen filled glove box. Elemental analysis was performed by the micro-analytical service within this department. Mass spectra were recorded on a Micromass Autospec instrument operating in EI mode; in each case the highest abundance peak in the envelope is quoted. NMR spectra were recorded on the following instruments: Varian Unity-300 (^1H , ^{11}B , ^{13}C) and Bruker AMX500 (^1H , ^{11}B , 2D $^{11}\text{B}\{^1\text{H}\}$ - $^{11}\text{B}\{^1\text{H}\}$ COSY and $^{11}\text{B}\{^1\text{H}\}$ - $^1\text{H}\{^{11}\text{B}\}$ HETCOR (heteronuclear correlation)). All chemical shifts are reported in δ (ppm) and coupling constants in Hz. ^1H NMR spectra were referenced to residual proton impurity in the solvent (CHCl₃, δ 7.26), ^{13}C to the solvent resonance (CDCl₃, δ 77.0) and ^{11}B referenced externally to BF₃·Et₂O (δ 0). All spectra were recorded at ambient temperature. The neutral *nido*-carborane 2,9-C₂B₉H₁₃ and the salt [Me₃-NH][7,9-C₂B₉H₁₂] were made by methods similar to those described in the literature.^{34,35} Assigned NMR data²³ for [3,3,3-(NMe₂)₃-*closo*-3,1,2-TaC₂B₉H₁₁] **3**: ^{11}B , δ 1.7 (B8), −3.4 (B9,12), −5.7 (B4,7), −13.8 (B5,11,6) and −16.2 (B10); ^1H - $\{^{11}\text{B}\}$, 3.02 (B10H), 2.37 (B6H), 2.29 (B9,12H), 2.18 (B5,11H) and 1.62 (B4,7,8H).

Syntheses

[2,2,2-(NMe₂)₃-*closo*-2,1,12-TaC₂B₉H₁₁] 1. A solution of *nido*-2,9-C₂B₉H₁₃ (0.67 g, 5 mmol) in toluene (20 cm³) was treated dropwise with a toluene solution of Ta(NMe₂)₅ (2 g, 5 mmol). After stirring at 20 °C for 15 h the solution was filtered and the filtrate concentrated to about 5 cm³. The solution was layered with pentane and cooled to −40 °C. The resulting crystals were isolated by filtration. Yield 2.02 g, 91%. Crystals for structure determination were grown at −30 °C from a concentrated toluene solution layered with pentane. ^1H NMR (CDCl₃): δ 3.60 (18 H, CH₃), 2.87 (1 H, CH) and 2.30 (1 H, CH). Additional peaks in ^1H - $\{^{11}\text{B}\}$ NMR (CDCl₃): δ 3.10 (1 H; B9H), 2.38 (2 H; B8,10H), 2.30 (2 H; B4,5H), 1.70 (2 H; B7,11H) and 1.58 (2 H; B3,6H). ^{13}C - $\{^1\text{H}\}$ NMR (50 MHz, CDCl₃): δ 64.0 (C1), 62.3 (C12) and 49.5 (CH₃). ^{11}B NMR (CDCl₃): δ −4.1 (d, 2B, $J_{\text{B-H}}$ 189; B7,11), −6.2 (d, 2B, $J_{\text{B-H}}$ 158; B3,6), −14.2 (d, 2B; B4,5), −13.7 (d, 2B; B8,10) and −19.3 (d, 1B, $J_{\text{B-H}}$ 161 Hz; B9). Calc. for C₈H₂₉B₉N₃Ta: C, 21.5; H, 6.6; N, 9.4. Found: C, 21.1; H, 6.5; N, 7.9%.

[2,2,2-(NMe₂)₃-closo-2,1,7-TaC₂B₉H₁₁] 2. At room temperature, a stirred suspension of [Me₃NH][nido-7,9-C₂B₉H₁₂] (0.92 g, 5 mmol) in toluene (20 cm³) was treated dropwise with a toluene solution of Ta(NMe₂)₅ (2.0 g, 5 mmol). After refluxing for 15 h, the solution was cooled to 20 °C and concentrated to 5 cm³ under reduced pressure. The solution was layered with pentane and cooled to –40 °C. The resulting crystals were isolated by filtration. Yield 1.7 g, 76%. Crystals for structure determination were grown at –30 °C from a concentrated dichloromethane solution layered with toluene. ¹H NMR (CDCl₃): δ 3.64 (18 H, CH₃) and 2.22 (2 H, C7,9H). Additional peaks in ¹H-¹¹B NMR (CDCl₃): δ 3.03 (1 H; B9H), 2.46 (2 H; B6,11H), 2.35 (2 H; B4,8H), 2.22 (1 H; B10H), 1.99 (1 H; B3H) and 1.71 (2 H; B6,11). ¹³C-¹H NMR (CDCl₃): δ 57.7 (C7,9) and 49.4 (CH₃). ¹¹B-¹H NMR (CDCl₃): δ –5.2 (2B, d; B6,11), –5.9 (2B, d; B5,12), –11.1 (1B, d; B10), –11.8 (1B, d; B3), –13.1 (2B, d; B4,8) and –16.9 (1B, d; B9). Calc. for C₈H₂₉B₉N₃Ta: C, 21.6; H, 6.6; N, 9.4. Found: C, 21.0; H, 6.6; N, 7.4%. MS: *m/z* 446 [M⁺] and 313 [M⁺ – C₂B₉H₁₁].

[2,2,2-(NMe₂)₃-closo-2,1,12-NbC₂B₉H₁₁] 4. A solution of nido-2,9-C₂B₉H₁₃ (0.67 g, 5 mmol) in toluene (20 cm³) was treated dropwise with a toluene solution of Nb(NMe₂)₅ (2 g, 5 mmol). After stirring at 20 °C for 15 h the solution was refluxed for 2 h. The volatiles were removed under reduced pressure and the residue was extracted with hexanes to give an orange solution. This solution was filtered and the solvent removed under reduced pressure to give crude product which was purified by crystallisation from hexanes at –40 °C. ¹H NMR (CDCl₃): δ 3.49 (18 H, CH₃), 2.74 (1 H, CH) and 2.43 (1 H, CH). Additional peaks in ¹H-¹¹B NMR (CDCl₃): δ 3.10 (1 H), 2.38 (2 H), 2.30 (2 H), 1.70 (2 H) and 1.58 (2 H). ¹³C-¹H NMR (50 MHz, CDCl₃): δ 65.3 (C1), 62.5 (C12) and 50.9 (CH₃). ¹¹B NMR (CDCl₃): δ –4.5 (d, 2B), –5.9 (d, 2B), –13.4 (d, 2B), –14.2 (d, 2B) and –17.6 (d, 1B). Calc. for C₈H₂₉B₉N₃Nb: C, 26.9; H, 8.2; N, 11.7. Found: C, 27.3; H, 8.2; N, 11.7%.

[2,2,2-(NMe₂)₃-closo-2,1,7-NbC₂B₉H₁₁] 5. At room temperature, a stirred suspension of [Me₃NH][nido-7,9-C₂B₉H₁₂] (0.92 g, 5 mmol) in toluene (20 cm³) was treated dropwise with a toluene solution of Nb(NMe₂)₅ (1.6 g, 5 mmol). After refluxing for 15 h, the solution was cooled to 20 °C and concentrated to 5 cm³ under reduced pressure. The solution was layered with pentane and slowly cooled to –40 °C. The resulting crystals were isolated by filtration. Yield 1.29 g, 72%. ¹H NMR (CDCl₃): δ 3.46 (18 H, CH₃) and 2.35 (2 H, C7,9H). Additional peaks in ¹H-¹¹B NMR (CDCl₃): δ 3.68 (1 H), 2.39 (2 H), 2.08 (2 H), 2.04 (1 H), 1.94 (1 H) and 1.87 (2 H). ¹³C-¹H NMR (CDCl₃): δ 59.3 (C7,9) and 50.7 (CH₃). ¹¹B-¹H NMR (CDCl₃): δ –4.7 (2B), –5.8 (2B), –11.4 (2B), –12.9 (2B) and –15.6 (1B). Calc. for C₈H₂₉B₉N₃Nb: C, 26.9; H, 8.2; N, 11.7. Found: C, 26.5; H, 8.7; N, 9.9%.

X-Ray crystallography

Single-crystal diffraction experiments at *T* = 120 K were carried out with a SMART 1K CCD area detector, using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). A combination of 4 sets of ω scans, each scan at different 2θ and/or ϕ angles, nominally covered *ca.* 75% of full sphere of the reciprocal space up to 2θ = 58°. Reflection intensities were corrected for absorption by numerical integration (based on crystal face indexing) for complex **1** and by semi-empirical method (comparison of Laue equivalents)³⁶ for **2**. The structures were solved by a combination of direct and Patterson methods and refined by full-matrix least squares against *F*² of all data, using SHELXTL programs.³⁷ The cage carbon atoms in **1** and **2** were identified as follows: (a) these atoms form the shortest bonds to the other atoms of the cage;

Table 6 Crystal data for compounds **1** and **2** at 120 K

	1	2
Formula	C ₈ H ₂₉ B ₉ N ₃ Ta	
<i>M</i>	445.58	
Crystal system	Monoclinic	Orthorhombic
Space group	<i>P</i> 2 ₁ / <i>n</i> (no. 14)	<i>Pnma</i> (no. 62)
<i>a</i> /Å	9.758(1)	10.538(1)
<i>b</i> /Å	17.658(3)	12.001(1)
<i>c</i> /Å	10.326(1)	14.136(2)
β /°	96.04(1)	
<i>U</i> /Å ³	1769.4(4)	1787.7(5)
<i>Z</i>	4	4
μ (Mo-Kα)/mm ^{–1}	6.20	6.14
Reflections measured	17446	16808
Unique reflections	4719	2517
<i>R</i> (int)	0.021	0.057
Reflections with <i>I</i> ≥ 2σ(<i>I</i>)	4071	2353
<i>R</i> [<i>I</i> ≥ 2σ(<i>I</i>)]	0.016	0.052
<i>wR</i> (<i>F</i> ²), all data	0.037	0.138

(b) if all atoms of the cage are refined as boron, these atoms display unreasonably small anisotropic displacement parameters (ADPs); (c) of a variety of least-squares refinements with the C atoms in different positions, the present assignments give the smallest dispersion of the equivalent isotropic *U* of the cage atoms. The disorder of the NMe₂ groups in **2** is 50:50, and in space group *Pnma* the two positions are related *via* the *m* plane. An alternative refinement in space group *Pn*2₁*a* was attempted and proved unstable; anisotropic ADPs of *all* atoms (except Ta) were non-positive definite; isotropic refinement produced large (3 to 4 times) differences between the ADPs of chemically equivalent atoms. Crystal data and experimental details are listed in Table 6.

CCDC reference number 186/2156.

See <http://www.rsc.org/suppdata/dt/b0/b005294i/> for crystallographic files in .cif format.

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