# First structural characterisation of a 2,1,12-$MC_2B_9$ metallacarborane, [2,2,2-$(NMe_2)_3$-*closo*-2,1,12-$TaC_2B_9H_{11}$]. Trends in boron NMR shifts on replacing a {BH} vertex with a metal {$ML_n$} vertex in icosahedral carboranes

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FULL PAPER

**Andrei S. Batsanov, Pauline A. Eva, Mark A. Fox, Judith A. K. Howard, Andrew K. Hughes,* Andrew L. Johnson, Aileen M. Martin and Ken Wade**

*Department of Chemistry, Durham University Science Laboratories, South Road, Durham, UK DH1 3LE*

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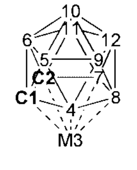
Reactions of $M(NMe_2)_5$ (M = Ta or Nb) with *nido*-2,9-$C_2B_9H_{13}$ and the salt [$Me_3NH$][*nido*-7,9-$C_2B_9H_{12}$] gave the isomeric dicarbollide complexes [2,2,2-$(NMe_2)_3$-*closo*-2,1,12-$MC_2B_9H_{11}$] (M = Ta **1**, Nb **4**) and [2,2,2-$(NMe_2)_3$-*closo*-2,1,7-$MC_2B_9H_{11}$] (M = Ta **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-$MC_2B_9$ metallacarborane. Comparison of $^{11}B$ NMR data of the tantalum complexes, along with the isomeric [3,3,3-$(NMe_2)_3$-*closo*-3,1,2-$TaC_2B_9H_{11}$] **3**, with that of 1,2-, 1,7- and 1,12-$C_2B_{10}H_{12}$, reveals that the metal vertex {$Ta(NMe_2)_3$}, 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 ($\eta^5$-$C_5H_5$)$CoC_2B_9H_{11}$ are tentatively predicted.

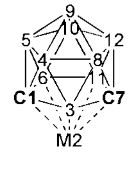
## Introduction

Hundreds of metallacarboranes have been synthesized since they were first reported by Hawthorne and co-workers in the 1960s.[1,2] The most commonly studied metallacarboranes are those with an icosahedral $MC_2B_9$ cage. The 3,1,2-, 2,1,7- and 2,1,12-$MC_2B_9$ (**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-$C_2B_{10}H_{12}$ respectively followed by addition of a metal fragment. Of these, metallacarboranes consisting of the 3,1,2-$MC_2B_9$ cage **A** are the most widely studied with over 300 structures determined by X-ray crystallography, followed by those containing 2,1,7-$MC_2B_9$ **B** geometries with some 30 structures known.[3] Dicarbollide complexes containing the 2,1,12-$MC_2B_9$ **C** type are limited to those containing cobalt, rhodium and nickel at the metal vertex and no structural characterisation has been reported.[4–12] Metallacarboranes with other $MC_2B_9$ 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-$MC_2B_9$ (**E**) cages have been structurally determined.[15,16]

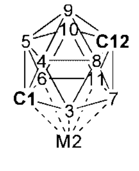
Despite the enormous number of icosahedral $MC_2B_9$ metallacarboranes known, $^{11}B$ NMR chemical shift assignments of these are sparse. Assignments determined by 2-D $^{11}B$–$^{11}B$ COSY spectroscopy have been reported for metallacarboranes with 3,1,2-$C_2B_9$ cages **A**, [$Cl_3TaC_2B_9H_{11}$] and [$X_2Ta(C_2B_9H_{11})_2$] (X = Me, F or Cl) derivatives,[17,18] [$(C_5H_5)CoC_2B_9H_{11}$],[19] [$(C_6Me_6)RuC_2B_9H_{11}$],[20] [$(C_5Me_5)RhC_2B_9H_{11}$] and derivatives,[19,21] [$(C_5Me_5)IrC_2B_9H_{11}$][19] and [$(C_5H_5)Mo(C_3H_3)C_2B_9H_9$].[22]



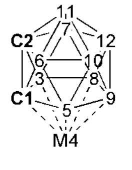
3,1,2-$MC_2B_9H_{11}$ **A**



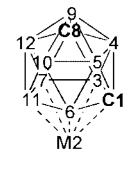
2,1,7-$MC_2B_9H_{11}$ **B**



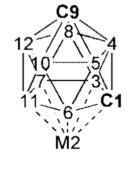
2,1,12-$MC_2B_9H_{11}$ **C**



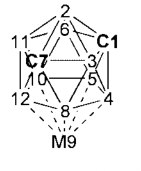
4,1,2-$MC_2B_9H_{11}$ **D**



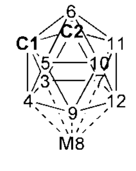
2,1,8-$MC_2B_9H_{11}$ **E**



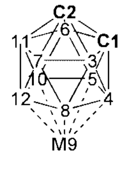
2,1,9-$MC_2B_9H_{11}$ **F**



9,1,7-$MC_2B_9H_{11}$ **G**



8,1,2-$MC_2B_9H_{11}$ **H**



9,1,2-$MC_2B_9H_{11}$ **I**

Here we report the syntheses and characterisation of the new tantalum compounds [2,2,2-$(NMe_2)_3$-*closo*-2,1,12-$TaC_2B_9H_{11}$] **1** and [2,2,2-$(NMe_2)_3$-*closo*-2,1,7-$TaC_2B_9H_{11}$] **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-$MC_2B_9$ metallacarborane; the structure of **2** has also been determined. Along with the recently reported isomer [3,3,3-$(NMe_2)_3$-*closo*-3,1,2-$TaC_2B_9H_{11}$] **3**,[23] this study demonstrates the first fully assigned $^{11}B$ and $^1H$ NMR data for a series of metallacarboranes incorporating 3,1,2-, 2,1,7- and 2,1,12-$MC_2B_9$ cages (**A**–**C**) and reveals clear trends in the $^{11}B$ NMR chemical shifts on replacing a {BH} vertex in the isomeric carboranes 1,2-, 1,7- and 1,12-$C_2B_{10}H_{12}$ by the metal vertex {$Ta(NMe_2)_3$}. These trends include data for the new niobium compounds [2,2,2-$(NMe_2)_3$-*closo*-2,1,12-$NbC_2B_9H_{11}$] **4** and [2,2,2-$(NMe_2)_3$-*closo*-2,1,7-$NbC_2B_9H_{11}$] **5** synthesized here, and the previously reported isomer [3,3,3-$(NMe_2)_3$-*closo*-3,1,2-$NbC_2B_9H_{11}$] **6**. From this study, the assignments of the reported

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**Table 1** $^{11}B$ NMR chemical shift data ($\delta$) for isomeric $MC_2B_9H_{11}$ complexes [M = BH, $Ta(NMe_2)_3$ or $Nb(NMe_2)_3$][a]

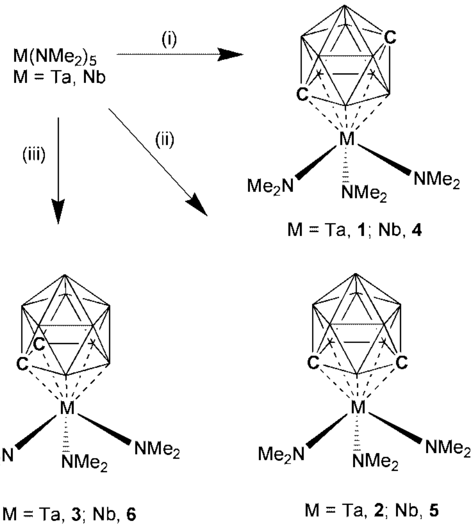
| 2,1,12-$MC_2B_9$ | B7,11 | B3,6 | B4,5 | B8,10 | B9 | | Average |
|---|---|---|---|---|---|---|---|
| M = BH | −14.7 | −14.7 | −14.7 | −14.7 | −14.7 | | −14.7 |
| $Ta(NMe_2)_3$ | −4.1 | −6.2 | −13.7 | −14.2 | −19.3 | | −10.6 |
| *difference* | *10.6* | *8.5* | *1.0* | *0.5* | *−4.6* | | |
| $Nb(NMe_2)_3$ | −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-$MC_2B_9$ | 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-$MC_2B_9$ | 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 metallacarborane and that of the same vertex in the parent $C_2B_{10}H_{12}$.

peaks in the $^{11}B$ NMR data for the seven isomers of $[(\eta^5\text{-}C_5H_5)CoC_2B_9H_{11}]$ are tentatively predicted.

## Results and discussion

The reactions of $Ta(NMe_2)_5$ with the neutral carborane *nido*-2,9-$C_2B_9H_{13}$ and the salt $[Me_3NH]$[*nido*-7,9-$C_2B_9H_{12}$] gave the isomeric dicarbollide complexes [2,2,2-$(NMe_2)_3$-*closo*-2,1,12-$TaC_2B_9H_{11}$] **1** and [2,2,2-$(NMe_2)_3$-*closo*-2,1,7-$TaC_2B_9H_{11}$] **2** respectively in high yields (Scheme 1). The new metallacarboranes 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.



**Scheme 1** The synthesis of the isomeric metallacarboranes [2,2,2-$(NMe_2)_3$-*closo*-2,1,12-$MC_2B_9H_{11}$] (M = Ta, **1**; Nb, **4**) and [2,2,2-$(NMe_2)_3$-*closo*-2,1,7-$MC_2B_9H_{11}$] (M = Ta, **2**; Nb, **5**) and the previously reported [3,3,3-$(NMe_2)_3$-*closo*-3,1,2-$MC_2B_9H_{11}$] (M = Ta, **3**; Nb, **6**). Reagents: (i) *nido*-2,9-$C_2B_9H_{13}$, (ii) $[Me_3NH]$[*nido*-7,9-$C_2B_9H_{12}$], (iii) *nido*-7,8-$C_2B_9H_{13}$.

Good quality 2-D $^{11}B$–$^{11}B$ COSY and $^{11}B$–$^1H$ correlation NMR spectra were obtained from these compounds, along with [3,3,3-$(NMe_2)_3$-*closo*-3,1,2-$TaC_2B_9H_{11}$] **3** synthesized from $Ta(NMe_2)_5$ and *nido*-7,8-$C_2B_9H_{13}$,[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 metallacarborane, *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*-$C_2B_{10}H_{12}$ 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 {BH} vertex with a $\{(Me_2N)_3Ta\}$ vertex in all cases.

Syntheses of the new niobium complexes [2,2,2-$(NMe_2)_3$-*closo*-2,1,12-$NbC_2B_9H_{11}$] **4** and [2,2,2-$(NMe_2)_3$-*closo*-2,1,7-$NbC_2B_9H_{11}$] **5** were achieved by the same route as for **1** and **2** respectively, using $Nb(NMe_2)_5$ in place of $Ta(NMe_2)_5$ (Scheme 1). The niobium derivatives **4**, **5** and the recently reported isomer [3,3,3-$(NMe_2)_3$-*closo*-3,1,2-$NbC_2B_9H_{11}$] **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 $d(Ta) \leftarrow p_\pi(N)$ 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 $\tau$ 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

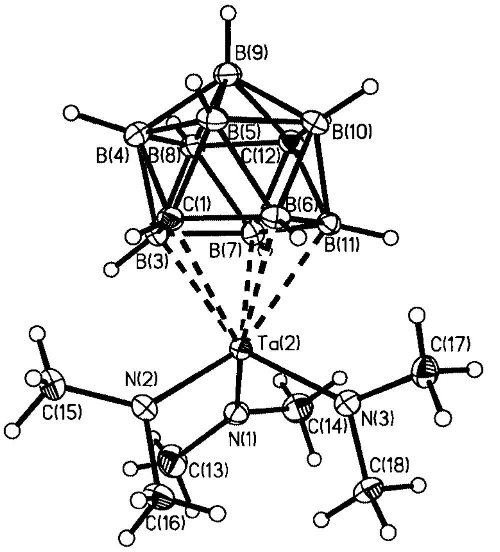


**Fig. 1** The molecular structure of [2,2,2-$(NMe_2)_3$-*closo*-2,1,12-$TaC_2B_9H_{11}$] **1**, showing 50% displacement ellipsoids.

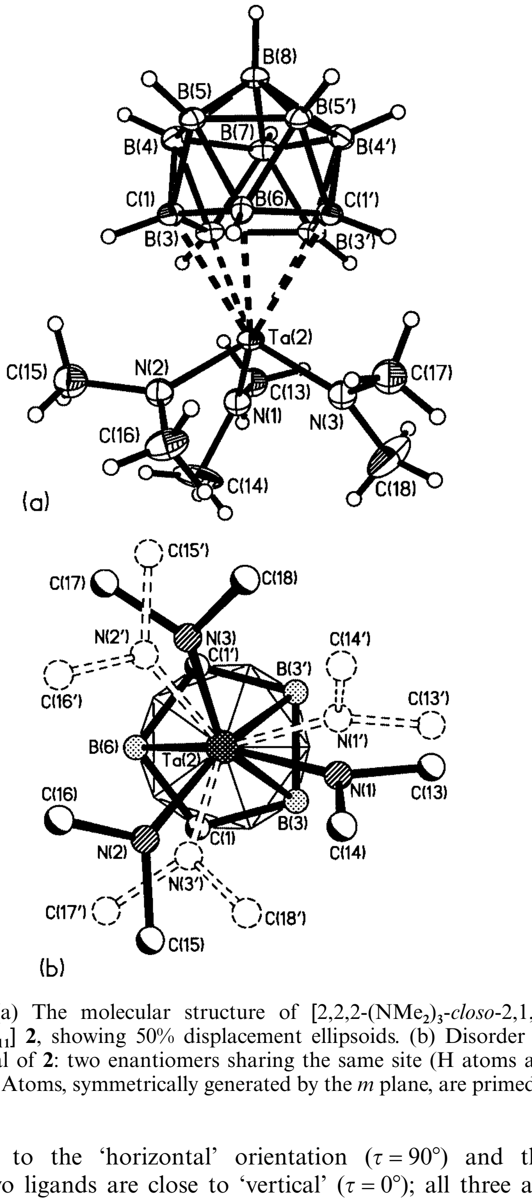


**Fig. 2** (a) The molecular structure of [2,2,2-$(NMe_2)_3$-*closo*-2,1,7-$TaC_2B_9H_{11}$] **2**, showing 50% displacement ellipsoids. (b) Disorder in the crystal of **2**: two enantiomers sharing the same site (H atoms are omitted). Atoms, symmetrically generated by the *m* plane, are primed.

**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 $\eta^5$-co-ordinated ring.

is close to the ‘horizontal’ orientation ($\tau = 90°$) and the other two ligands are close to ‘vertical’ ($\tau = 0°$); 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[$(CyN)_2C(NCy)$]$(NMe_2)_3$}[24] and [Nb(2,6-$^iPr_2C_6H_3N$)$(NMe_2)_3$],[25] and can be explained by non-degeneracy of the two orthogonal π-donor orbitals of the imide and the $C_2B_9H_{11}$ or guanidinide ligands. The horizontal $NMe_2$ 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-$MC_2B_9$ 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] pyrrolyl[28] and carbonyl[29] complexes. Similar orientational preferences in the isomeric metallacarboranes are less well documented.[7]

Molecules of [2,2,2-$(NMe_2)_3$-*closo*-2,1,7-$TaC_2B_9H_{11}$] **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, $N(1)Me_2$, closer to the vertical and two others to the horizontal conformation. Surprisingly, the Ta(2)–N(1) bond to the unique vertical $NMe_2$ ligand is shorter than the rest (although the precision is low due to the disorder).

The co-ordinated $CB_4$ face in complex **1** has an envelope-like distortion, typical for icosahedral metallacarboranes with a metal-$CB_4$ face bonding (*i.e.* with 4,1,2-$MC_2B_9$ (**D**),[15] 2,1,8-$MC_2B_9$ (**E**)[15] and 2,1-$MCB_{10}$ cages[30]): the C(1) atom lies 0.08 Å further from Ta(2) than the $B_4$ plane. In **2** both metal-co-ordinated carbon atoms, C(1) and C(1′), are similarly shifted by 0.09 Å out of the $B_3$ 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-$C_2B_{10}H_{12}$ and four 3,1,2-$MC_2B_9$ cage (**A**) complexes have been compared and

**Table 3** Assigned $^{11}B$ chemical shifts for 3,1,2-$MC_2B_9H_{11}$ 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 | 1.7 | −3.4 | −13.8 | −13.8 | −16.2 | −8.2 |
| | | *9.3* | *12.3* | *0.4* | *1.2* | *2.3* | *−5.6* | |
| $Nb(NMe_2)_3$ | 23 | −6.1 | 3.3 | −2.9 | −13.2 | −13.2 | −14.4 | −7.4 |
| | | *9.9* | *13.9* | *0.9* | *1.8* | *2.9* | *−3.8* | |
| $Ir(C_5Me_5)$ | 19 | −8.7 | −0.8 | −11.9 | −21.8 | −26.4 | −1.7 | −12.6 |
| | | *6.3* | *9.8* | *−8.1* | *−6.8* | *−10.3* | *8.9* | |
| $Ru(C_6Me_6)$ | 20 | −5.4 | 4.2 | −9.5 | −19.8 | −24.0 | −2.3 | −10.2 |
| | | *9.6* | *14.8* | *−5.7* | *−4.8* | *−7.9* | *8.3* | |
| $Co(C_5H_5)$ | 19 | −4.9 | 6.8 | −5.9 | −16.1 | −22.4 | 3.5 | −7.3 |
| | | *10.1* | *17.4* | *−2.1* | *−1.1* | *−6.3* | *14.1* | |
| $Rh(C_5Me_5)$ | 19 | −3.5 | 8.6 | −8.3 | −18.6 | −23.4 | −1.8 | −8.6 |
| | | *11.5* | *19.2* | *−4.5* | *−3.6* | *−7.3* | *8.8* | |
| $TaMe_2(C_2B_9H_{11})^-$ | 18 | 0.1 | 12.9 | 0.1 | −11.1 | −14.4 | −8.7 | −3.6 |
| | | *15.1* | *23.5* | *3.9* | *3.9* | *1.7* | *1.9* | |
| $TaF_2(C_2B_9H_{11})^-$ | 18 | 0.4 | 13.2 | 1.5 | −7.6 | −10.5 | −10.6 | −2.1 |
| | | *15.4* | *23.8* | *5.3* | *7.4* | *5.6* | *0.0* | |
| $TaCl_2(C_2B_9H_{11})^-$ | 18 | −5.6 | 26.7 | 2.9 | −4.7 | −11.8 | −14.4 | −1.6 |
| | | *9.4* | *37.3* | *6.7* | *10.3* | *4.3* | *−3.8* | |
| $TaCl_3$ | 17 | 2.6 | 15.8 | 7.3 | −3.2 | −5.7 | −5.7 | 2.0 |
| | | *17.6* | *26.4* | *11.1* | *11.8* | *10.4* | *4.9* | |

[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-$C_2B_{10}H_{12}$.

**Table 4** Predicted and observed $^{11}B$ NMR chemical shifts for the isomeric (η-$C_5H_5$)Co($C_2B_9H_{11}$) 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) |
| | −15.7 (B4,8) | −16.8 (2) | | | |
| 2,1,12 **C** | −2.4 (B9) | −2.8 (1) | 9,1,7 **G** | 5.1 (B5,12) | 0.8 (2) |
| | −3.2 (B7,11,3,6) | −4.6 (2) | | 1.2 (B10) | −3.6 (1) |
| | | −6.4 (2) | | −1.6 (B4,8) | −5.8 (2) |
| | −17.3 (B4,5,8,10) | −16.1 (2) | | −4.5 (B2) | −6.8 (1) |
| | | −19.3 (2) | | −15.7 (B6,11) | −15.7 (2) |
| | | | | −19.4 (B3) | −19.8 (1) |
| 4,1,2 **D** | 7.7 (B9) | 9.5 | 8,1,2 **H**[c] | 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 | | | |
| | −17.6 (B7) | −18.0 | | | |
| | −18.7 (B6) | −19.1 | | | |
| 2,1,8 **E** | 5.1 (B6) | 0.4 | 9,1,12 **I**[c] | 7.7 (B12) | 4.2 (1) |
| | 1.2 (B11) | −0.2 | | 0.9 (B8,10) | 0.5 (2) |
| | −0.8 (B9) | −1.9 | | −3.5 (B4,5) | −1.8 (2) |
| | −1.6 (B7) | −3.0 | | −17.6 (B7,11) | −9.6 (2) |
| | −5.3 (B3) | −8.3 | | −18.7 (B3,6) | −12.4 (2) |
| | −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 $C_2B_{10}H_{12}$ on replacing a BH vertex with a $Co(C_5H_5)$ vertex. [b] Data taken from ref. 5. [c] For these isomers, the observed data are for a derivative of [$(C_5H_5)CoC_2B_9H_{11}$], *i.e.* [$(C_5H_5)Co(C_3H_6)C_2B_9H_9$].

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-$C_2B_{10}H_{12}$ are listed in Table 3. In all cases, except for the $[Cl_2Ta(C_2B_9H_{11})_2]^-$ 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 $[Cl_2Ta(C_2B_9H_{11})_2]^-$ anion differ significantly from the related tantalum anions, $[F_2Ta(C_2B_9H_{11})_2]^-$ and $[Me_2Ta(C_2B_9H_{11})_2]^-$.[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-$CoC_2B_9H_{11}$ 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-$MC_2B_9H_{11}$ 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 |
| *difference* | | *10.6* | *8.5* | *1.0* | *0.5* | *−4.6* | |
| $Nb(NMe_2)_3$ | This work | −4.5 | −5.9 | −13.4 | −14.2 | −17.6 | −10.4 |
| *difference* | | *10.2* | *8.8* | *1.3* | *0.5* | *−2.9* | |
| $Co(C_5H_5)$ | 12 | −4.4 | −6.5 | −15.6 | −18.8 | −2.7 | −10.4 |
| *difference* | | *10.3* | *8.2* | *−0.9* | *−4.1* | *12.0* | |
| $Rh(PPh_3)_2H$ | 38 | −6.2 | −8.7 | −19.4 | −19.4 | −1.1 | −12.1 |
| *difference* | | *8.5* | *6.0* | *−4.7* | *−4.7* | *13.6* | |
| $Rh(PPh_3)(MeCO_2)$ | 10 | 3.9 | −9.4 | −18.6 | −20.1 | 3.9 | −9.4 |
| *difference* | | *18.6* | *5.3* | *−3.9* | *−5.4* | *18.6* | |
| $Rh(PPh_3)(CO)^-$ | 7 | −23.9 | −25.1 | −10.9 | −17.1 | −14.6 | −18.7 |
| *difference* | | *−9.2* | *−10.4* | *3.8* | *−2.4* | *0.1* | |
| $Ni(PPh_3)_2$ | 11 | −20.0 | −20.0 | −10.1 | −14.9 | −8.1 | −15.3 |
| *difference* | | *−5.3* | *−5.3* | *4.6* | *−0.2* | *6.6* | |

[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-$C_2B_{10}H_{12}$.

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 computations[31] on the *static* geometry of 3-($C_5Me_5$)-3,1,2-$RhC_2B_9H_{11}$ obtained by single crystal X-ray diffraction[19] 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-$MC_2B_9$ (**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-$C_2B_{10}H_{12}$ ($\delta_B$ −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-$MC_2B_9$ derivatives and clearly those complexes with a $\{ML_2\}$ type vertex such as $\{Ni(PPh_3)_2\}$ and $\{Rh(PPh_3)(CO)^-\}$ do not follow the trend observed for the other complexes. These observations are in agreement with the observation that $\{L_3M\}$, $\{L_5M\}$ and $\{L_6M\}$ vertices in metallacarboranes listed in Tables 3–5 are isolobal to the {BH} vertex whereas the non-conical $\{ML_2\}$ vertices, $\{(Ph_3P)_2Ni\}$ and $\{(Ph_3P)_2Rh^-\}$, 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 $\{(C_5H_5)Co\}$ vertex and low for the $\{(Me_2N)_3Ta\}$ vertex.

The averaged boron shifts of the metallacarboranes in Tables 3 and 5 are similar to $C_2B_{10}H_{12}$ in many cases, which suggest similarities in the cage electronics between these compounds. Averaged shifts significantly to high frequency ($\delta$ 2.0 to −3.6) are found for tantalum derivatives containing the 3,1,2-$MC_2B_9$ cage, $[Cl_3Ta(C_2B_9H_{11})]$, $[Cl_2Ta(C_2B_9H_{11})_2]^-$, $[F_2Ta(C_2B_9H_{11})_2]^-$ and $[Me_2Ta(C_2B_9H_{11})_2]^-$, 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 $C_2B_{10}H_{12}$ 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 microanalytical 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 ($^1$H, $^{11}$B, $^{13}$C) and Bruker AMX500 ($^1$H, $^{11}$B, 2D $^{11}$B{$^1$H}–$^{11}$B{$^1$H} COSY and $^{11}$B{$^1$H}–$^1$H{$^{11}$B} HETCOR (heteronuclear correlation)). All chemical shifts are reported in $\delta$ (ppm) and coupling constants in Hz. $^1$H NMR spectra were referenced to residual proton impurity in the solvent ($CHCl_3$, $\delta$ 7.26), $^{13}$C to the solvent resonance ($CDCl_3$, $\delta$ 77.0) and $^{11}$B referenced externally to $BF_3 \cdot Et_2O$ ($\delta$ 0). All spectra were recorded at ambient temperature. The neutral *nido*-carborane 2,9-$C_2B_9H_{13}$ and the salt $[Me_3NH][7,9\text{-}C_2B_9H_{12}]$ were made by methods similar to those described in the literature.[34,35] Assigned NMR data[23] for [3,3,3-$(NMe_2)_3$-*closo*-3,1,2-$TaC_2B_9H_{11}$] **3**: $^{11}$B, $\delta$ 1.7 (B8), −3.4 (B9,12), −5.7 (B4,7), −13.8 (B5,11,6) and −16.2 (B10); $^1$H-{$^{11}$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-$(NMe_2)_3$-*closo*-2,1,12-$TaC_2B_9H_{11}$] 1.** A solution of *nido*-2,9-$C_2B_9H_{13}$ (0.67 g, 5 mmol) in toluene (20 cm$^3$) was treated dropwise with a toluene solution of $Ta(NMe_2)_5$ (2 g, 5 mmol). After stirring at 20 °C for 15 h the solution was filtered and the filtrate concentrated to about 5 cm$^3$. 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. $^1$H NMR ($CDCl_3$): $\delta$ 3.60 (18 H, $CH_3$), 2.87 (1 H, CH) and 2.30 (1 H, CH). Additional peaks in $^1$H-{$^{11}$B} NMR ($CDCl_3$): $\delta$ 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-{$^1$H} NMR (50 MHz, $CDCl_3$): $\delta$ 64.0 (C1), 62.3 (C12) and 49.5 ($CH_3$). $^{11}$B NMR ($CDCl_3$): $\delta$ −4.1 (d, 2B, $J_{B\text{-}H}$ 189; B7,11), −6.2 (d, 2B, $J_{B\text{-}H}$ 158; B3,6), −14.2 (d, 2B; B4,5), −13.7 (d, 2B; B8,10) and −19.3 (d, 1B, $J_{B\text{-}H}$ 161 Hz; B9). Calc. for $C_8H_{29}B_9N_3Ta$: C, 21.5; H, 6.6; N, 9.4. Found: C, 21.1; H, 6.5; N, 7.9%.

**[2,2,2-($NMe_2$)$_3$-*closo*-2,1,7-$TaC_2B_9H_{11}$] 2.** At room temperature, a stirred suspension of [$Me_3NH$][*nido*-7,9-$C_2B_9H_{12}$] (0.92 g, 5 mmol) in toluene (20 cm$^3$) was treated dropwise with a toluene solution of Ta($NMe_2$)$_5$ (2.0 g, 5 mmol). After refluxing for 15 h, the solution was cooled to 20 °C and concentrated to 5 cm$^3$ 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. $^1$H NMR ($CDCl_3$): $\delta$ 3.64 (18 H, $CH_3$) and 2.22 (2 H, C7,9H). Additional peaks in $^1$H-{$^{11}$B} NMR ($CDCl_3$): $\delta$ 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). $^{13}$C-{$^1$H} NMR ($CDCl_3$): $\delta$ 57.7 (C7,9) and 49.4 ($CH_3$). $^{11}$B-{$^1$H} NMR ($CDCl_3$): $\delta$ −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 $C_8H_{29}B_9N_3Ta$: 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$^+$ − $C_2B_9H_{11}$].

**[2,2,2-($NMe_2$)$_3$-*closo*-2,1,12-$NbC_2B_9H_{11}$] 4.** A solution of *nido*-2,9-$C_2B_9H_{13}$ (0.67 g, 5 mmol) in toluene (20 cm$^3$) was treated dropwise with a toluene solution of Nb($NMe_2$)$_5$ (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. $^1$H NMR ($CDCl_3$): $\delta$ 3.49 (18 H, $CH_3$), 2.74 (1 H, CH) and 2.43 (1 H, CH). Additional peaks in $^1$H-{$^{11}$B} NMR ($CDCl_3$): $\delta$ 3.10 (1 H), 2.38 (2 H), 2.30 (2 H), 1.70 (2 H) and 1.58 (2 H). $^{13}$C-{$^1$H} NMR (50 MHz, $CDCl_3$): $\delta$ 65.3 (C1), 62.5 (C12) and 50.9 ($CH_3$). $^{11}$B NMR ($CDCl_3$): $\delta$ −4.5 (d, 2B), −5.9 (d, 2B), −13.4 (d, 2B), −14.2 (d, 2B) and −17.6 (d, 1B). Calc. for $C_8H_{29}B_9N_3Nb$: C, 26.9; H, 8.2; N, 11.7. Found: C, 27.3; H, 8.2; N, 11.7%.

**[2,2,2-($NMe_2$)$_3$-*closo*-2,1,7-$NbC_2B_9H_{11}$] 5.** At room temperature, a stirred suspension of [$Me_3NH$][*nido*-7,9-$C_2B_9H_{12}$] (0.92 g, 5 mmol) in toluene (20 cm$^3$) was treated dropwise with a toluene solution of Nb($NMe_2$)$_5$ (1.6 g, 5 mmol). After refluxing for 15 h, the solution was cooled to 20 °C and concentrated to 5 cm$^3$ 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%. $^1$H NMR ($CDCl_3$): $\delta$ 3.46 (18 H, $CH_3$) and 2.35 (2 H, C7,9H). Additional peaks in $^1$H-{$^{11}$B} NMR ($CDCl_3$): $\delta$ 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). $^{13}$C-{$^1$H} NMR ($CDCl_3$): $\delta$ 59.3 (C7,9) and 50.7 ($CH_3$). $^{11}$B-{$^1$H} NMR ($CDCl_3$): $\delta$ −4.7 (2B), −5.8 (2B), −11.4 (2B), −12.9 (2B) and −15.6 (1B). Calc. for $C_8H_{29}B_9N_3Nb$: 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 ($\bar{\lambda}$ = 0.71073 Å). A combination of 4 sets of $\omega$ scans, each scan at different 2$\theta$ and/or $\varphi$ angles, nominally covered *ca.* 75% of full sphere of the reciprocal space up to 2$\theta$ = 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; (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 $NMe_2$ 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*2$_1$*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.

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

| | **1** | **2** |
|---|---|---|
| Formula | $C_8H_{29}B_9N_3Ta$ | |
| $M$ | 445.58 | |
| Crystal system | Monoclinic | Orthorhombic |
| Space group | $P2_1/n$ (no. 14) | *Pnma* (no. 62) |
| $a$/Å | 9.758(1) | 10.538(1) |
| $b$/Å | 17.658(3) | 12.001(1) |
| $c$/Å | 10.326(1) | 14.136(2) |
| $\beta$/° | 96.04(1) | |
| $U$/Å$^3$ | 1769.4(4) | 1787.7(5) |
| $Z$ | 4 | 4 |
| $\mu$(Mo-Kα)/mm$^{-1}$ | 6.20 | 6.14 |
| Reflections measured | 17446 | 16808 |
| Unique reflections | 4719 | 2517 |
| $R$(int) | 0.021 | 0.057 |
| Reflections with $I \geq 2\sigma(I)$ | 4071 | 2353 |
| $R$ [$I \geq 2\sigma(I)$] | 0.016 | 0.052 |
| $wR(F^2)$, all data | 0.037 | 0.138 |

CCDC reference number 186/2156.

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

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