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Imide- and amide-supported Group 5 and 6 metallacarboranes

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Abstract

This account summarises recent results in the synthesis, reactivity and spectroscopic and structural characterisation of high oxidation state icosahedral *closo*-metallacarboranes of niobium, tantalum and tungsten, with an emphasis on the relationship between these metallacarboranes and analogous half-sandwich and metallocene complexes. Group 5 $M(NMe_2)_5$ reagents ($M = Nb$, Ta) react with *nido*-$C_2B_9H_{13}$ to yield 3,3,3-$(NMe_2)_3$-*closo*-3,1,2-$MC_2B_9H_{11}$. This reacts further by insertion of the metal–amide bonds with polar multiple bonds in CO_2 and CS_2, and with nitriles to give rare examples of the extensively delocalised strong π-donor *N*,*N*-dimethyl amidinate ligands. The amide bonds are cleaved by protic reagents. The isomeric 2,1,12, and 2,1,7 metallacarboranes are obtained from *nido*-2,9-$C_2B_9H_{13}$ and (Me_3NH)(*nido*-7,9-$C_2B_9H_{12}$). Comparison of ^{11}B-NMR data of the tantalum complexes reveals the influence on ^{11}B-NMR chemical shifts of the cluster on replacing a {BH} vertex by a $\{Ta(NMe_2)_3\}$ fragment. The base-sensitive cage-alkylated carborane *nido*-11-Me-2,7-$C_2B_9H_{12}$ is metallated to 4,4,4-$(NMe_2)_3$-3-Me-4,1,2-*closo*-$TaC_2B_9H_{10}$, and the isomeric metallacarboranes 3,3,3-$(NMe_2)_3$-4-Me-3,1,2-*closo*-$TaC_2B_9H_{10}$ and 2,2,2-$(NMe_2)_3$-3-Me-2,1,7-*closo*-$TaC_2B_9H_{10}$ can be obtained from (Me_3NH)(*nido*-9-Me-7,8-$C_2B_9H_{11}$) and (Me_3NH)(*nido*-8-Me-7,9-$C_2B_9H_{11}$). Amine elimination reaction from $W(N^tBu)_2(NH^tBu)_2$ yields 3-N^tBu-3,3-$(NH^tBu)_2$-*closo*-3,1,2-$WC_2B_9H_{11}$ of which one of the remaining amide ligands can be substituted by 2,6-dimethylphenol, water or Me_3SiCl. Acetonitrile inserts into the tungsten amide bond to give the *N*,*N*-dimethyl acetamidine adduct of $W(N^tBu)_2(C_2B_9H_{11})$, containing a hydrogen bond between the amidine and a bent imide. Structural studies reveal that the imide is the dominant π-donor in these complexes. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Metallacarboranes; Niobium; Tantalum

1. Introduction

Icosahedral MC_2B_9 metallacarborane [1] chemistry is well established for middle and late transition metals and has been extended to lanthanide [2] and early transition metals [3] in pursuit of metallocene analogues. A variety of ligands derived from smaller carboranes are also known and have been used as ligands to a wide range of transition metals [4]. The relationship between *closo*-3,1,2-$[MC_2B_9H_{11}]$ and cyclopentadienyl complexes, $M(\eta\text{-}C_5H_5)$, has been discussed in detail elsewhere [1]. The $C_2B_9H_{11}^{2-}$ ligand is a six-electron ligand, along with the imide, RN^{2-}, isolobal and isoelectronic with $C_5H_5^-$ and thus the fragment $[Ta(C_2B_9H_{11})]$ [5] has the same number of valence electrons as $[Hf(\eta\text{-}C_5H_5)]$, whilst $[W(C_2B_9H_{11})(RN)]$ is an electronic and structural mimic of a Group 4 bent metallocene. The cyclopentadienyl ligand has one low-lying σ and a degenerate pair of higher-energy π-donor orbitals and so is classed by Gibson as a Π_2 ligand [6]. By contrast, in the dicarbollide ligand the two π-donor orbitals are non-degenerate, so it is classified as Π_2', and this electronic difference results in an orientational preference, often described as a strong *trans* influence of the dicarbollide ligand, as observed in indenyl [7,8], pyrollyl [9] and carbonyl [10] complexes as well as the complexes described here.

In common with many other areas of organometallic chemistry, the most extensively used method for coordinating $C_2B_9H_{11}$ to a transition metal has been the elimination of halide salt between a metal halide and either an alkali-metal or thallium salt of (*nido*-$C_2B_9H_{11})^{2-}$. In recent years the amine elimination reaction [11] has found use as a novel method for coordinating anionic ligands [12], occasionally providing routes to otherwise inaccessible compounds [13], metallation of ligands which are not stable as alkali metal

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salts [14], or thermodynamic product ratios [15]. Metal amides have found use in the synthesis of metal complexes of silaboranes [16], and zirconium metallacarboranes [17].

Organometallic chemists are very familiar with the reactions of transition metal halides with reagents, such as alkyl lithium and Grignards, leading to metal carbon bonds. The reactions of metal amides are less familiar. The prototypical reactions of early transition metal M–NR_2 bonds are amine elimination with acids and the insertion of polar multiple bonds into the M–N bond [18].

2. First steps in Nb and Ta chemistry

Thermodynamically, a reaction will occur between $M(NR_2)_x$ and a Brønsted acid such as [*nido*-7,8-$C_2B_9H_{13}$] if the acid is more acidic than the eliminated HNR_2, $pK_a = 35–40$. We began our work in this area by reacting toluene solutions of the Group 5 homoleptic amides $M(NMe_2)_5$ (M = Nb and Ta) with one equivalent of *nido*-7,8-$C_2B_9H_{13}$ to cleave two metal–amide bonds (Scheme 1) and give 3,3,3-$(NMe_2)_3$-*closo*-3,1,2-$MC_2B_9H_{11}$ (M = Nb **1** and Ta **2**) [19]. The products, characterised by X-ray diffraction studies in both cases and NMR (^1H, ^{13}C and ^{11}B) spectroscopy, are considerably less reactive towards atmospheric moisture than the parent homoleptic amides, and slowly turn white on exposure to atmospheric moisture.

The molecular structure of **1** (Fig. 1) reveals that the metal atom is co-ordinated by the open C_2B_3 face of the dicarbollide ligand (in a nearly symmetrical η^5 fashion) and by three trigonal planar dimethylamide ligands acting as 3-electron LX ligands. Together with the 4-electron LX_2 dicarbollide, this completes an 18-electron ML_4X_5 configuration of the Nb or Ta atom. The most notable structural feature is the orientation of the NMe_2 ligands with respect to the pentagonal face of the dicarbollide ligand. The amide can be described as ‘vertical’ if the Cb–M–N–C torsion angle (where Cb is the centroid of the C_2B_3 ring), τ is 0 or 180°, or ‘horizontal’ for the perpendicular orientation. In **1** and **2**, two NMe_2 ligands are ‘vertical’ while the third is ‘horizontal’. In each molecule, the ‘horizontal’ ligand lies opposite the polyhedral carbon–carbon bond and forms a M–N bond appreciably shorter than the ‘vertical’ ligands. Such a geometry for a (η-C_5H_5)MX_3 complex would be described as a three-legged piano stool, although, since the convention in metallacarborane chemistry is for the metal vertex to appear at the top of the figure, the geometry is best described as an upside-down piano stool.

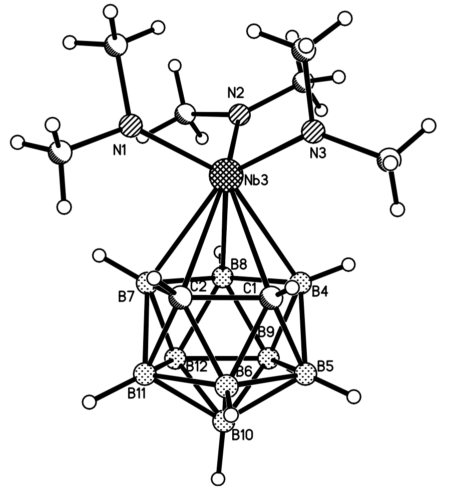
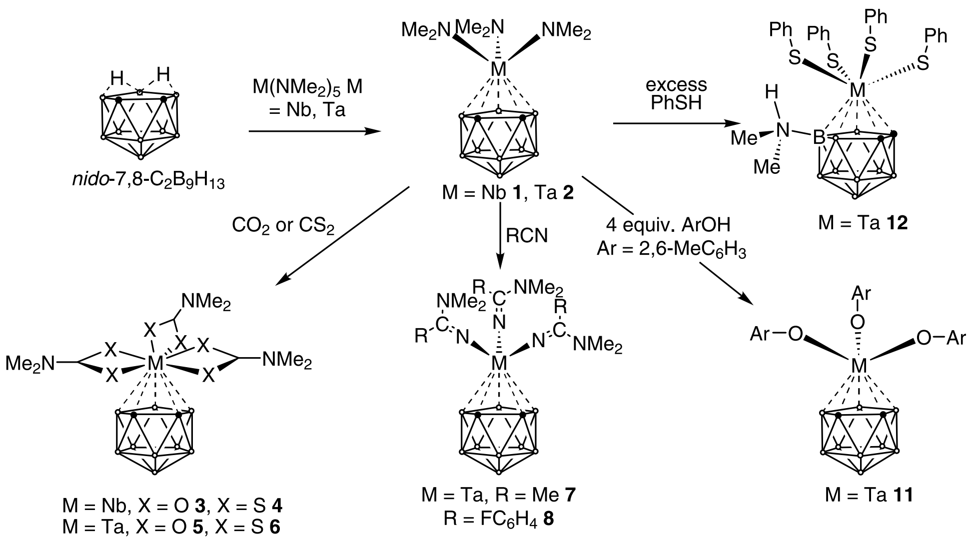


Fig. 1. Structure of 3,3,3-$(NMe_2)_3$-*closo*-3,1,2-$NbC_2B_9H_{11}$ (**1**).

If they persist in solution, these solid-state structures would give rise to three environments for the methyl



Scheme 1. The synthesis and reactivity of 3,3,3-$(NMe_2)_3$-*closo*-3,1,2-$MC_2B_9H_{11}$ (M = Nb, Ta).

groups. The observation of a singlet for the NMe_2 groups in ^1H- and ^{13}C-NMR indicates either rapid fluxional processes or that the chemical shift difference between the methyl groups is small in the ground state.

3. Nb and Ta insertion chemistry with CX_2 and nitriles

The dicarbollide amide complexes **1** and **2** undergo insertion reactions with CO_2 and CS_2 to give carbamate and dithiocarbamate 3,3,3-$(X_2CNMe_2)_3$-*closo*-3,1,2-$MC_2B_9H_{11}$ (M = Nb, X = O **3**, S **4**; M = Ta, X = O **5**, S **6**) complexes, respectively (Scheme 1). The ^1H and ^{13}C spectra of these are consistent with the presence of “vertical” and “horizontal” X_2C-NMe_2 ligands in these complexes, and rotation about the M-(thio)carbamate axis being slow on the NMR timescale at room temperature, by contrast with the fast rotation of the NMe_2 ligands in **1** and **2**. The spectra are qualitatively similar to those observed for the *iso*-numeral Group 4 cyclopentadienyl complexes $(\eta\text{-}C_5R_5)M(X_2CNR_2)_3$ [20], and we assume that the same mechanisms of ligand fluxionality apply. The structures of **4** (Fig. 2) and **5** show bidentate planar (thio)carbamate ligands, two of which are ‘horizontal’ and one ‘vertical’.

Nitriles insert into the metal nitrogen bond of early transition metal amides to form *N*,*N*-dialkylamidinate ligands (Fig. 4), M-NC(Me)NR_2 [21], much less familiar [22] than the isomeric *N*,*N*′-dialkylamidinates [23]. Thus, acetonitrile and *p*-fluorobenzonitrile readily insert into the amide bonds of 3,3,3-$(NMe_2)_3$-*closo*-3,1,2-$TaC_2B_9H_{11}$ to give the tris-insertion products 3,3,3-$(N{=}C(Me)NMe_2)_3$-*closo*-3,1,2-$TaC_2B_9H_{11}$ (**7**) (Fig. 3), and 3,3,3-$[N{=}C(C_6H_4F)NMe_2]_3$-*closo*-3,1,2-$TaC_2B_9H_{11}$ (**8**) [24]. The NMR spectra of **7** are complicated by dynamic exchange processes that are close to coalescence at ambient temperature due to restricted rotation about the Ta–N and C–NMe_2 bonds. Dehydrochlorination occurs on attempted recrystallisation of **8** from pentane–dichloromethane resulting in 3-Cl-3,3-$[N{=}C(C_6H_4F)NMe_2]_2$-*closo*-3,1,2-$TaC_2B_9H_{11}$ (**9**), where one amidinate ligand has been replaced by a chloride.

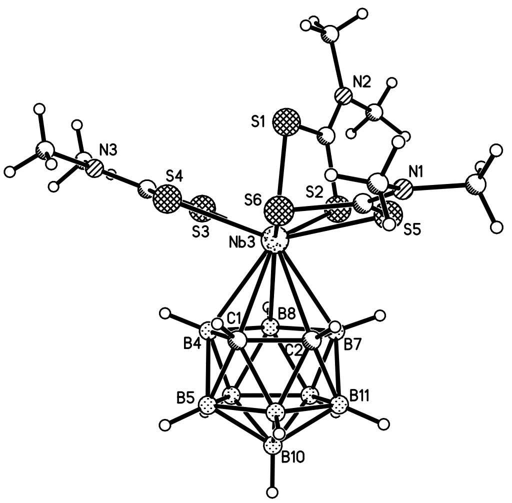


Fig. 2. Structure of 3,3,3-$(S_2C\text{-}NMe_2)_3$-*closo*-3,1,2-$NbC_2B_9H_{11}$ (**4**).

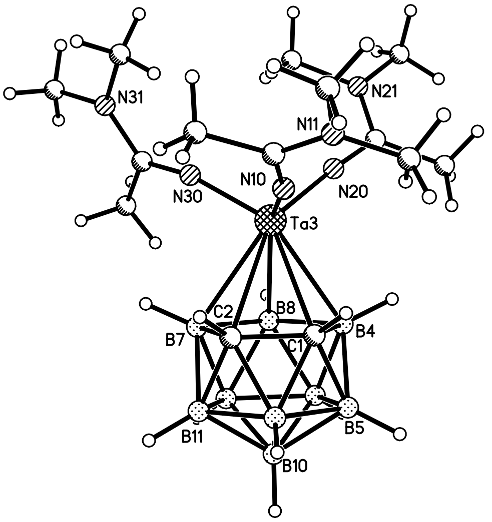


Fig. 3. Structure of 3,3,3-$(N{=}C(Me)NMe_2)_3$-*closo*-3,1,2-$TaC_2B_9H_{11}$ (**7**).

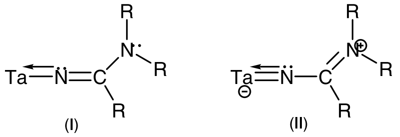


Fig. 4. The amide and imide canonical forms of an *N*,*N*-dialkyl amidinate ligand.

The molecular structure of the acetonitrile insertion product, **7**, reveals three close to planar *N*,*N*-dimethyl amidinate ligands coordinated in a monodentate fashion, giving an approximate propeller-like geometry to the TaL_3 unit, with one ligand localised *cis* to the C_2 unit of the $C_2B_9H_{11}$ ligand. The Ta–N distances are intermediate between typical amide, Ta–NR_2, and tantalum imide, Ta–NR, distances, and the unique acetamidinate ligand shows the longest Ta–N bond. These structural features reflect a delocalised π-bonding framework over the entire amidinate ligand and a balance between the two canonical forms, (I) tantalum amide and (II) tantalum imide.

The strong π-donation to the metal atom from three amidinate ligands results in a competitive weakening of the carborane to metal π-donation, and these complexes show long ring centroid–metal distances.

By contrast with the unreactive secondary amide M–NR_2 bonds of **1** and **2**, the primary amide bonds of these amidinate complexes are much more reactive towards moisture and other acidic reagents. During our attempts to prepare crystals of **7** and **8**, we also obtained good quality crystals of the hydrolysis product from **7**, namely

3-{3,3-[N=C(Me)NMe$_2$]$_2$-*closo*-3,1,2-TaC$_2$B$_9$H$_{11}$}$_2$(μ-O) (**10**) [25]. The structural features of this molecule again reflect a delocalised π-bonding framework over the entire amidinate ligand and a balance between tantalum amide and tantalum imide canonical forms. The strong π-donation to the metal atom from the amidinate ligands results in a competitive weakening of the carborane to metal π-donation, and the C$_2$B$_3$ ring centroid–metal distance is intermediate between those of 3,3,3-(NMe$_2$)$_3$-*closo*-3,1,2-TaC$_2$B$_9$H$_{11}$ with moderate π-donor amide ligands, and the tris(acetamidinate), 3,3,3-[N=C(Me)NMe$_2$]$_3$-*closo*-3,1,2-TaC$_2$B$_9$H$_{11}$.

4. Nb and Ta acid/base chemistry

Only starting materials were recovered from refluxing toluene solutions of **2** with the carbon-based acids C$_5$H$_6$, C$_5$H$_5$Me or phenyl acetylene, so we explored the reactions of **2** with coordinating acids such as amines, alcohols and thiols which are kinetically more active in their reactions with metal amides than are carbon acids.

The reaction of **2** with four equivalents of 2,6-dimethylphenol yields 3,3,3-(OC$_6$H$_3$Me$_2$-2,6)$_3$-*closo*-3,1,2-TaC$_2$B$_9$H$_{11}$ (**11**) (Scheme 1), although attempts to react **2** with stoichiometric quantities of methanol or ethanol resulted in the formation of (NH$_2$Me$_2$)(*nido*-7,8-C$_2$B$_9$H$_{12}$). The solid state structure of **11**, exhibits evidence of the *trans*-influence of the dicarbollide ligand, with two phenoxide ligands lying nearly parallel to the C$_2$B$_3$ face, and one perpendicular, in a fashion which should now be familiar (Fig. 5). One carbon atom of the C$_2$B$_3$ face lies almost directly *trans* to the unique phenoxide ligand.

The reaction of four equivalents of thiophenol with **2** is more complicated and produces a 53% yield of 3,3,3,3-(SC$_6$H$_5$)$_4$-9-NHMe$_2$-*closo*-3,1,2-TaC$_2$B$_9$H$_{10}$ (**12**), where the β-boron of the C$_2$B$_3$ face bears a NHMe$_2^+$ substituent. In the solid state, the Ta(SPh)$_4$ fragment of **12** has a distorted four-legged piano-stool structure (Fig. 6), with two thiolate ligands bent away from the dicarbollide ligand, and two displaced towards the dicarbollide ligand.

5. *meta* and *para* Carborane as precursors to metallacarboranes

Of the hundreds of known metallacarboranes, the most commonly studied are those with an icosahedral 3,1,2-MC$_2$B$_9$ cage. This, and the isomeric 2,1,7- and 2,1,12-MC$_2$B$_9$ (**A**, **B** and **C**) cages (Fig. 7), are generated by base removal of the most positive boron atom of the three icosahedral carboranes, 1,2-, 1,7- and 1,12-C$_2$B$_{10}$H$_{12}$, respectively, followed by addition of a metal fragment. Structural reports describe over 300 structures of type **A**, with some 30 structures of 2,1,7-MC$_2$B$_9$ **B** known [26]. Prior to our work [27], complexes containing the 2,1,12-MC$_2$B$_9$ **C** type were limited to those containing cobalt, rhodium and nickel, and no structural characterisation had been reported. Metallacarboranes with other MC$_2$B$_9$ cage conformations (**D**–**I**) are synthesised via cage rearrangements and compounds with 4,1,2- (**D**) and 2,1,8-MC$_2$B$_9$ (**E**) cages having been structurally determined [28,29].

Having developed some understanding of the synthesis, structures and reactivity of *closo*-3,1,2-tantalacarboranes, we sought to explore the synthesis and properties of isomeric tantalacarboranes, and so set ourselves on the route of preparing some examples of these.

The same metal amide plus acidic carborane precursor method was used. Whilst neutral *nido*-7,8-C$_2$B$_9$H$_{13}$ and *nido*-2,9-C$_2$B$_9$H$_{13}$ are known, for the analogous 7,9-

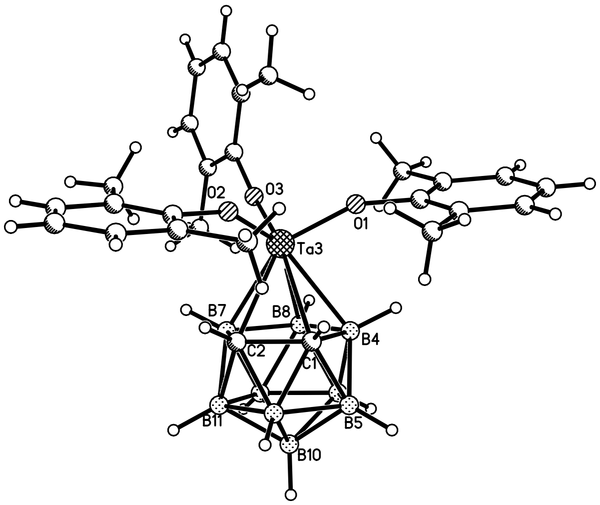


Fig. 5. Structure of 3,3,3-(OC$_6$H$_3$Me$_2$-2,6)$_3$-*closo*-3,1,2-TaC$_2$B$_9$H$_{11}$ (**11**).

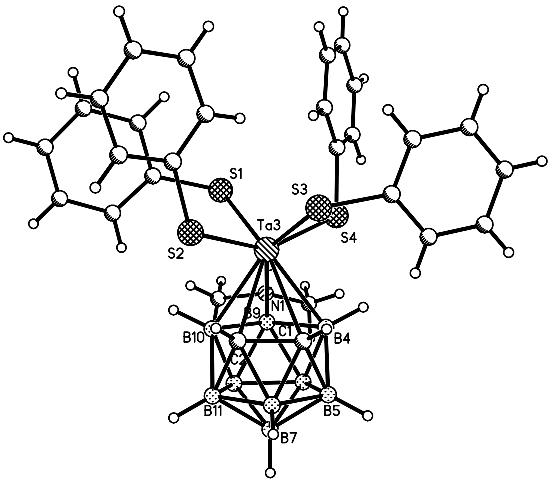
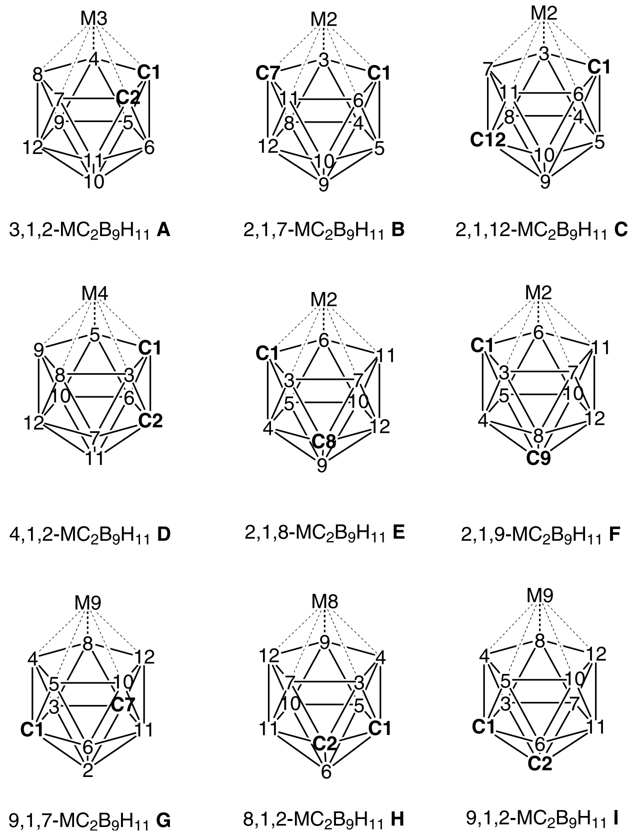


Fig. 6. Structure of 3,3,3,3-(SC$_6$H$_5$)$_4$-9-NHMe$_2$-*closo*-3,1,2-TaC$_2$B$_9$H$_{10}$ (**12**).


3,1,2-$MC_2B_9H_{11}$ **A** 2,1,7-$MC_2B_9H_{11}$ **B** 2,1,12-$MC_2B_9H_{11}$ **C**

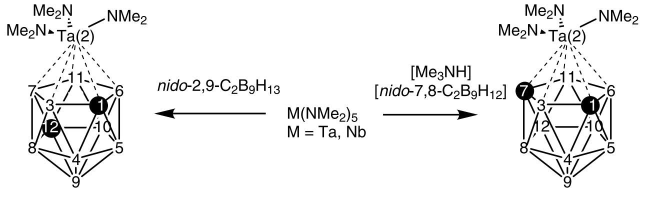
4,1,2-$MC_2B_9H_{11}$ **D** 2,1,8-$MC_2B_9H_{11}$ **E** 2,1,9-$MC_2B_9H_{11}$ **F**

9,1,7-$MC_2B_9H_{11}$ **G** 8,1,2-$MC_2B_9H_{11}$ **H** 9,1,2-$MC_2B_9H_{11}$ **I**

Fig. 7. Structures of the nine possible isomers of *closo*-MC_2B_9 metallacarboranes.

carborane the salt (Me_3NH)(*nido*-7,9-$C_2B_9H_{12}$) is a more convenient starting material. The reactions of $M(NMe_2)_5$ (M = Ta, Nb) with *nido*-2,9-$C_2B_9H_{13}$ and (Me_3NH)(*nido*-7,9-$C_2B_9H_{12}$) do indeed yield the isomeric dicarbollide complexes 2,2,2-$(NMe_2)_3$-*closo*-2,1,12-$MC_2B_9H_{11}$ (**13**) and 2,2,2-$(Me_2N)_3$-*closo*-2,1,7-$MC_2B_9H_{11}$ (**14**) in high yields. The neutral carborane reacts at ambient temperatures, but the ammonium salt requires toluene reflux for complete reaction (Scheme 2).

Good quality 2D $^{11}B-^{11}B$ COSY and $^{11}B-^{1}H$ correlation NMR spectra from the tantalum compounds, along with 3,3,3-$(Me_2N)_3$-*closo*-3,1,2-$TaC_2B_9H_{11}$ allowed their ^{11}B and ^{1}H chemical shifts to be assigned, representing the first complete NMR assignments for more than one isomer of a MC_2B_9-type metallacarborane (Fig. 7).



Scheme 2. The syntheses of the isomeric metallacarboranes 2,2,2-$(NMe_2)_3$-*closo*-2,1,12-$MC_2B_9H_{11}$ (**13**) and 2,2,2-$(Me_2N)_3$-*closo*-2,1,7-$MC_2B_9H_{11}$ (**14**).

Given that we had prepared three of the nine possible isomeric MC_2B_9 metallacarboranes, it was instructive to explore the differences in the ^{11}B-NMR chemical shifts caused by replacing a BH vertex with a metal fragment (Fig. 8). Average shift differences of +8.9 ppm (max/min 12.3 to 5.0) for the neighbouring boron atoms, −5.6 (−4.6 to −6.6) for antipodal and +0.6 (2.3 to −0.8) for other (butterfly) boron atoms were found. Clearly there are strong neighbouring and antipodal effects on the boron chemical shifts when a {BH} vertex is replaced by a $\{(Me_2N)_3Ta\}$ group. 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 [30]. An increase in the electron density in these orbitals is believed to cause a shielding effect on the chemical shift of the antipodal boron atom. On this basis, the electron density is low in the surface orbitals for the $\{(Me_2N)_3Ta\}$ vertex.

Detailed examination of the molecular structures reveals significant differences between the isomers. In **13** (Fig. 9), as in **1** and **2**, one NMe_2 ligand is close to 'horizontal', and the other two ligands are close to 'vertical', with all three inclined in the same direction to form a chiral propeller conformation. The horizontal NMe_2 ligand forms a shorter stronger Ta–N bond than the vertical ligands.

Molecules of 2,2,2-$(Me_2N)_3$-*closo*-2,1,7-$TaC_2B_9H_{11}$ (**14**) (Fig. 10) are disordered across a crystallographic mirror plane, resulting in two sets of three dimethylamide ligands, each of which corresponds to one enantiomer of a chiral propeller conformation with one ligand closer to the vertical and two others to the horizontal conformation.

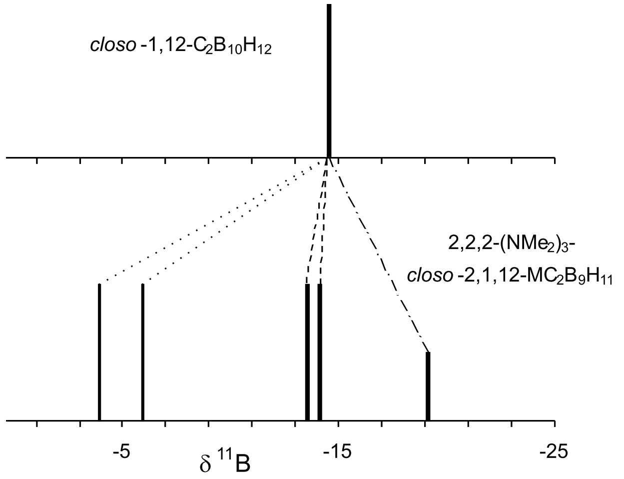


Fig. 8. Histogram representation of the ^{11}B-NMR spectra of *closo*-1,12-$C_2B_{10}H_{12}$ and **13** showing the influence of the $Ta(NMe_2)_3$ vertex on the ^{11}B-NMR chemical shift of the neighbouring (B3,6,7,11), butterfly (B4,5,8,10) and antipodal (B9) boron atoms.

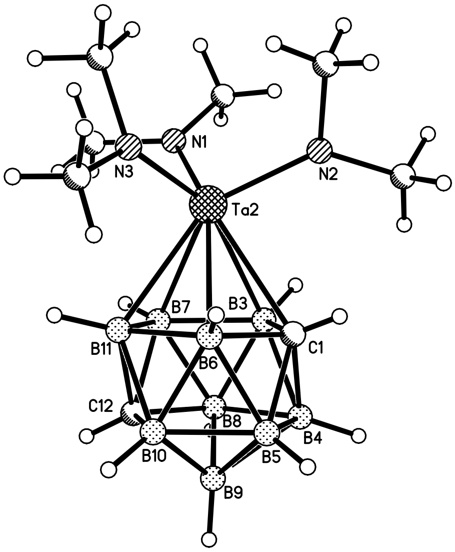


Fig. 9. Structure of 2,2,2-$(NMe_2)_3$-*closo*-2,1,12-$MC_2B_9H_{11}$ (**13**).

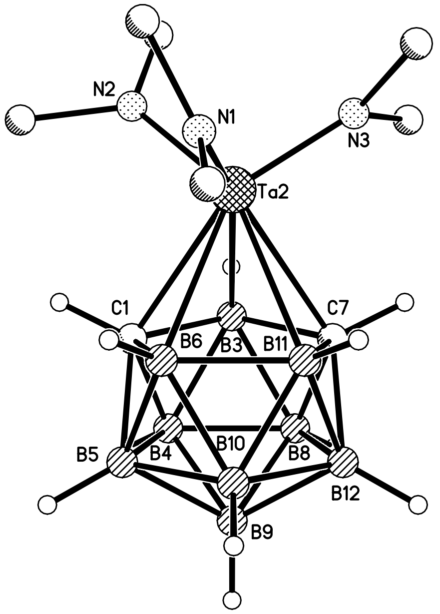


Fig. 10. Structure of 2,2,2-$(Me_2N)_3$-*closo*-2,1,7-$TaC_2B_9H_{11}$ (**14**).

6. Let's alkylate the ring. Does the ligand rearrange?

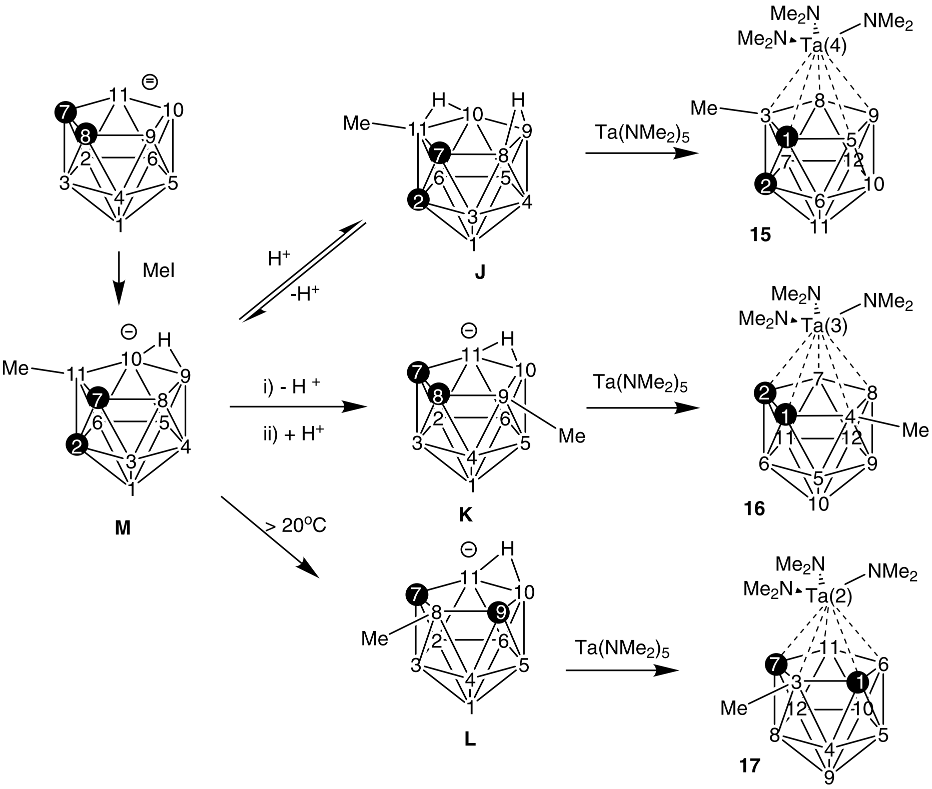
Having demonstrated that amine elimination between M−NR_2 and an acidic carborane occurs for the *nido*-carboranes derived from *ortho*, *meta* and *para*-carborane, we decided to investigate other carboranes as ligands. One of our long-term targets is to metallate carboranes bearing a second functional group attached to the cluster through an alkyl chain. Whilst exploring synthetic routes to these ligands [31], we established the principles of metallating alkylated carboranes.

We were attracted to the neutral B-methylated carborane 11-Me-2,7-$C_2B_9H_{12}$ (**J**) [32], prepared from the reaction of *nido*-7,8-$C_2B_9H_{11}^{2-}$ with MeI followed by acidification of intermediate **M** (Scheme 3). Interestingly, carborane **J** can lead to three isomeric B-methylated *nido* carborane anions $MeC_2B_9H_{11}^-$ on deprotonation. Double deprotonation by two equivalents of a strong base, such as NaH, and subsequent mono-protonation results in the formation of 9-Me-7,8-$C_2B_9H_{11}^-$ (**K**). Mono-deprotonation of 11-Me-2,7-$C_2B_9H_{12}$ (**J**), by bases such as amines at temperatures above 20 °C results in rearrangement to 8-Me-7,9-$C_2B_9H_{11}^-$ (**L**). Both of these rearrangements take place via 11-Me-2,7-$C_2B_9H_{11}^-$ (**M**) which has been isolated at low temperatures in the mono-deprotonation of **J**. These isomerisation reactions are driven by electronic factors, including the preference for a methyl group to be terminal rather than bridging in the initial methylation, and for hydrogen atoms to bridge B−B rather than B−C bonds on the open face in the subsequent protonation steps.

The reaction of **J** with transition metal amides was explored to determine if it is possible to metallate **J** without skeletal rearrangement. Treating 11-Me-2,7-*nido*-$C_2B_9H_{12}$ (**J**) with $Ta(NMe_2)_5$ affords only 4,4,4-$(NMe_2)_3$-3-Me-4,1,2-*closo*-$TaC_2B_9H_{10}$ (**15**), in high yield [33]. Complex **15** is the first 4,1,2-MC_2B_9 type metallacarborane to be directly formed from a *nido* carborane with a 2,7-C_2B_9 cage and *not* produced by skeletal rearrangement on metallation of an 11-vertex *nido*-carborane [34].

The reactions of the anions **K** and **L** with $Ta(NMe_2)_5$ provide access to the likely rearrangement products from **J**. Whilst the reactions of neutral carboranes with metal amides proceed readily at room temperature, the ammonium salts of carborane anions require elevated reaction temperatures, as in the case of (Me_3NH)(7,9-*nido*-$C_2B_9H_{11}$) discussed earlier. Heating a toluene solution of $(NHMe_3)$(9-Me-7,8-*nido*-$C_2B_9H_{11}$) (**K**) and $Ta(NMe_2)_5$ in a sealed ampoule at 120 °C for 18 h results in the formation of 3,3,3-$(NMe_2)_3$-4-Me-3,1,2-*closo*-$TaC_2B_9H_{10}$ (**16**), identified by detailed NMR spectroscopy. This reaction is clean, and does not result in the production of side-products. Heating a solution of $(NHMe_3)$(8-Me-7,9-*nido*-$C_2B_9H_{11}$) (**L**) and $Ta(NMe_2)_5$ in toluene to 120 °C in a sealed ampoule for 18 h produces a number of unidentified borane products in addition to 2,2,2-$(NMe_2)_3$-3-Me-2,1,7-*closo*-$TaC_2B_9H_{10}$ (**17**), which was isolated pure, albeit in low yield.

All three clusters, **15**, **16** and **17** were characterised by ^{1}H-, ^{13}C- and ^{11}B-NMR data. In seeking to confirm these spectra, we looked to a computational method, but it is not possible to perform calculations at the highest level on metallacarboranes, although reliable results are obtained from ab initio calculations of the structures and ^{11}B-NMR chemical shifts of boranes and carboranes [35]. We chose to explore the alternative approach of calculating at the highest possible level of theory for the parent *closo*-carborane $MeC_2B_{10}H_{11}$



Scheme 3. The synthesis and inter-conversion of the isomeric *nido*-MeC$_2$B$_9$ carboranes and their metallation reactions with Ta(NMe$_2$)$_5$.

analogues of **15**, **16** and **17**, respectively, on replacing the {(NMe$_2$)$_3$Ta} vertex by a {BH} vertex. The chemical shift differences caused by methylating one boron atom, or by replacing a {BH} vertex with {(NMe$_2$)$_3$Ta}, were then explored (Fig. 11). These results confirm the identities of **15**, **16** and **17**.

The identity of 4,4,4-(NMe$_2$)$_3$-3-Me-4,1,2-*closo*-TaC$_2$B$_9$H$_{10}$ (**15**) was confirmed by X-ray diffraction (Fig. 12), which reveals a familiar three-legged piano-stool Ta(carborane)(NMe$_2$)$_3$ geometry, where the Ta–C and Ta–B distances are essentially equal, with no folding of the CB$_4$ cluster face. The Ta(NMe$_2$)$_3$ fragment adopts a propeller-like configuration, although the blades are not inclined at the same angle, with one horizontal and two vertical in inclination, and the horizontal ligand displaying the shortest Ta–N distance.

7. High oxidation state tungstenacarboranes

Following our work on amide-supported niobium and tantalum metallacarboranes, electronic and structural analogues of half sandwich complexes, we decided to explore high oxidation state tungsten mimics of metallocenes. There is a well-established metallacarborane chemistry of low oxidation-state Group 6 dominated by the work of Stone and co-workers [36]. The few

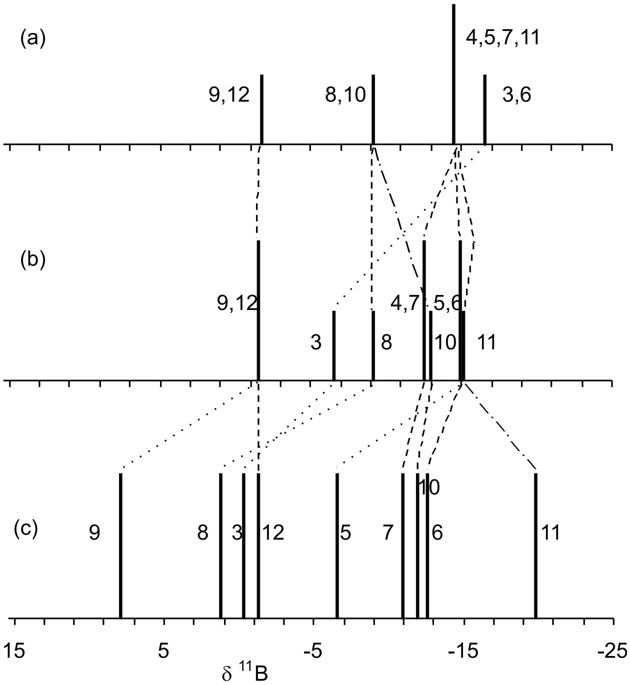


Fig. 11. Histogram plots of the ^{11}B-NMR spectra of (a) *closo*-1,2-C$_2$B$_{10}$H$_{12}$ calculated ab initio, (b) *closo*-3-Me-1,2-C$_2$B$_{10}$H$_{11}$ calculated ab initio showing the effect of cage methylation, (c) 4,4,4-(NMe$_2$)$_3$-3-Me-4,1,2-*closo*-TaC$_2$B$_9$H$_{10}$ showing the neighbouring and antipodal effects.

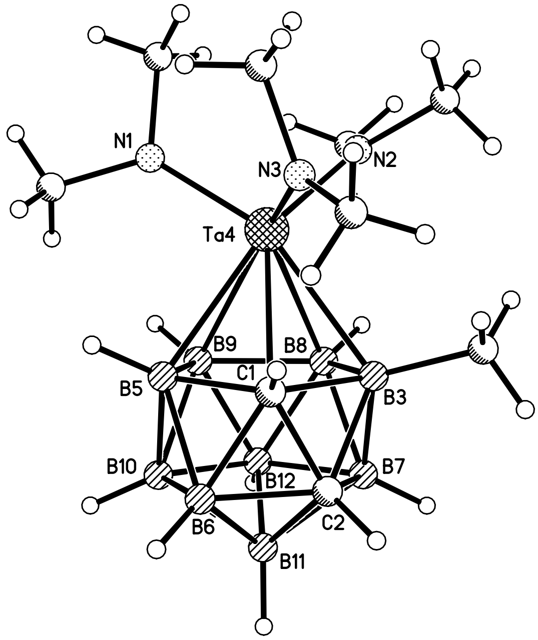


Fig. 12. Structure of the B-methyl complex 4,4,4-$(NMe_2)_3$-3-Me-4,1,2-*closo*-$TaC_2B_9H_{10}$ (**15**).

examples of W(VI) or Mo(VI) [37] include $\{[MoO_2(\eta^5\text{-}C_2B_9H_{11})]_2(\mu\text{-}O)\}^{2-}$ and $[MoO_3(\eta^1\text{-}C_2B_9H_{11})]^{2-}$ from the oxidation of the dithiolate complex $[NMe_4]_2$[3,3-$(CO)_2$-3,3-$(SPh)_2$-*closo*-3,1,2-$MoC_2B_9H_{11}$] [38], and the amine elimination of *nido*-7,8-$C_2B_9H_{13}$ and W(NAr)Me_3Cl to give 3-NAr-3-Me-3-Cl-*closo*-3,1,2-$WC_2B_9H_{11}$ (Ar = 2,6-dimethylphenyl) [39].

The readily synthesised [40] organo-imide complex [41] $W(N^tBu)_2(NH^tBu)_2$ is a W(VI) starting material that we and others have previously exploited [42–44]. This imide amide complex reacts with *nido*-7,8-$C_2B_9H_{13}$ to yield highly air- and moisture-sensitive 3-N^tBu-3,3-$(NH^tBu)_2$-*closo*-3,1,2-$WC_2B_9H_{11}$ (**18**) and one equivalent of $^tBuNH_2$ (Scheme 4) [45]. This is an apparently 20-electron compound with a large number of π-donor ligands competing for the available π-acceptor orbitals of the metal.

The difference between the ^{13}C-NMR chemical shifts of α and β carbon atoms ($\Delta\delta$)is typical of a mono(*tert*-butylimido)tungsten(VI) complex [46]. Following numerous attempts (many of which produced the hydrolysis product described below) we were able to obtain crystals suitable for a structural study (Fig. 13), which revealed that the imide ligand is close to linear, with a short M–N bond, suggesting that this is the dominant π-donor ligand. The amido ligands are both planar and orientated such that their alkyl groups are pointing away from the dicarbollide ligand. The arrangement of the amide ligands indicates that they are not both offering their maximum number of π-electrons to the metal centre, so that an 18-electron count is achieved. The W–Cb distance is considerably longer than in the π-

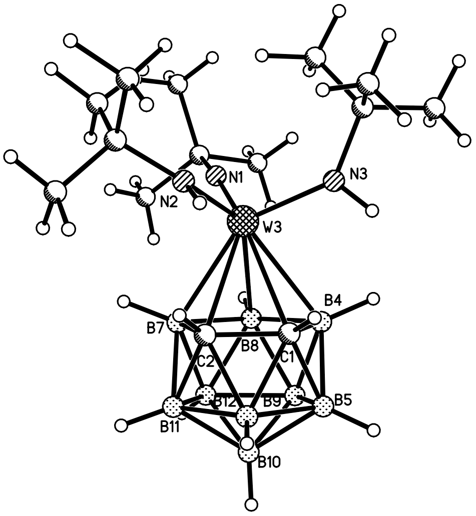
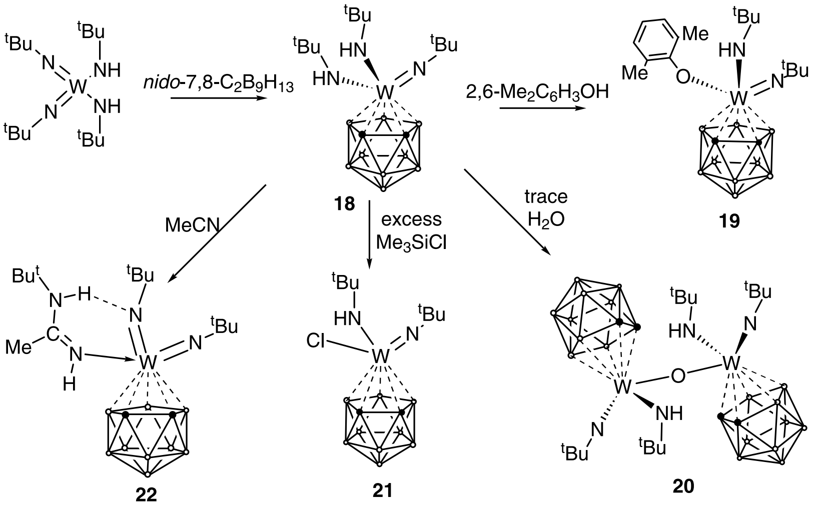


Fig. 13. Structure of 3-N^tBu-3,3-$(NH^tBu)_2$-*closo*-3,1,2-$WC_2B_9H_{11}$ (**18**).



Scheme 4. The synthesis and reactions of 3-N^tBu-3,3-$(NH^tBu)_2$-*closo*-3,1,2-$WC_2B_9H_{11}$.

acceptor ligand supported low oxidation-state complexes of Stone, but comparable with the high oxidation state molybdenum complex $\{[(C_2B_9H_{11})MoO_2]_2(\mu\text{-}O)\}^{2-}$, containing π-donor oxide ligands. The carborane cage is orientated with the C_2 unit of the C_2B_3 pentagon approximately *trans* to the imido ligand.

3-N^tBu-3,3-$(NH^tBu)_2$-*closo*-3,1,2-$WC_2B_9H_{11}$ is a useful starting material for a range of other tungsten carborane complexes by amine-elimination of one of the W-amide bonds. Thus reaction with an excess of 2,6-dimethyl phenol gives 3-N^tBu-3-NH^tBu-3-$(OC_6H_3Me_2)$-*closo*-3,1,2-$WC_2B_9H_{11}$ (**19**) and with water (adventitious or deliberately added) gives the hydrolysis product, 3-[3-N^tBu-3-NH^tBu-*closo*-3,1,2-$WC_2B_9H_{11}]_2$-(μ-O)] (**20**). Both of these complexes were structurally characterised, although the structure of the μ-oxo complex suffers from unresolved disorder, probably as a result of co-crystallisation of the *rac*- and *meso*-diastereomers.

The molecular structure of **19** shows a linear imide ligand and the dicarbollide is orientated with the C_2 unit of the C_2B_3 face *trans* to the imide. Replacement of one amide ligand in **18** by a weaker π-donor phenoxide results in a significant shortening of the remaining W–amide bond and a shortening of the W–Cb centroid distance. The metal–imide distance is unaltered, suggesting that this is the dominant π-donor, providing maximum π-bonding in both complexes.

The exclusive formation of **19** from the reaction of **18** with an excess of 2,6-dimethyl phenol implies that the replacement of one of the amide ligands by a weaker π-donor alkoxide ligand reduces the susceptibility of the complex to further electrophilic attack. This is further exemplified by the exclusive formation of the monochloride 3-N^tBu-3-NH^tBu-3-Cl-*closo*-3,1,2-$WC_2B_9H_{11}$ (**21**) in the reaction of **18** with an excess of Me_3SiCl.

Following on from studies of the insertion chemistry with CO_2, CS_2 and nitriles with tantalum metallacarboranes, we investigated the insertion chemistry of the amide and imide ligands in **18**. Stirring in acetonitrile gives 3,3-$(N^tBu)_2$-3-$[N(H)C(Me)NH^tBu]$-*closo*-3,1,2-$WC_2B_9H_{11}$ (**22**), the amidine adduct [23] of the hypothetical $M(1\sigma 2\pi)_3$ complex 3,3-$(N^tBu)_2$-*closo*-3,1,2-$WC_2B_9H_{11}$. Other examples of 18-electron $M(1\sigma 2\pi)_3$ complexes readily coordinate a neutral [47] or anionic [48] donor ligand, to give formally 20-electron d^0 complexes.

The molecular structure of **22** (Fig. 14) reveals one short linear imide ligand, comparable to those seen in compounds **18** and **19**, and a second longer and bent imide. The coordination sphere is completed by the neutral *N-tert*-butyl acetamidine ligand. The long tungsten–dicarbollide centroid distance, 2.065 Å, reflects the electronic saturation and the dicarbollide ligand is orientated with the C_2 unit approximately *trans* to the bent imide ligand. The amidine is involved in a novel N···H–N hydrogen bond to the bent imide nitrogen, which represents a functional model for imide exchange at a metal centre.

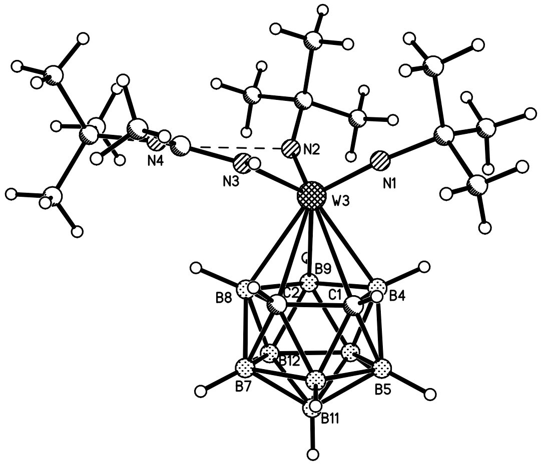


Fig. 14. Structure of 3,3-$(N^tBu)_2$-3-$[N(H)C(Me)NH^tBu]$-*closo*-3,1,2-$WC_2B_9H_{11}$ (**22**).

In conclusion, we have demonstrated the application of the amine–elimination reaction of metal amide complexes with acidic neutral and anionic carboranes, and the potential chemistry of the resulting metallacarboranes. For neutral carboranes, amine elimination is often a high yield, low temperature reaction, and allows base-sensitive clusters to be metallated. Our studies of high oxidation-state Group 5 and 6 metallacarboranes have also prompted wider structural and NMR spectroscopic studies in our research group, where metallacarborane chemistry is on-going, and recent studies include the behaviour of metal amides in reactive halogenated solvents, which will be reported soon.

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