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FULL PAPER

Synthesis of isomeric *B*-methylated tantalum carboranes, $(Me_2N)_3TaC_2B_9H_{10}Me$ †

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The cage-alkylated metallacarborane complex [4,4,4-$(NMe_2)_3$-3-Me-4,1,2-*closo*-$TaC_2B_9H_{10}$] **8**, is obtained as the only product from the reaction of $Ta(NMe_2)_5$ with *nido*-11-Me-2,7-$C_2B_9H_{12}$ **4**, which is prone to skeletal rearrangement under basic conditions. That no rearrangement occurs indicates that the hydroamminolysis reaction is a clean synthetic method. The isomeric metallacarboranes [3,3,3-$(NMe_2)_3$-4-Me-3,1,2-*closo*-$TaC_2B_9H_{10}$] **9** and [2,2,2-$(NMe_2)_3$-3-Me-2,1,7-*closo*-$TaC_2B_9H_{10}$] **10** are produced from the reaction of $Ta(NMe_2)_5$ with $[Me_3NH]$[*nido*-9-Me-7,8-$C_2B_9H_{11}$] **5** and $[Me_3NH]$[*nido*-8-Me-7,9-$C_2B_9H_{11}$] **6** respectively. Identities of the metallacarboranes **8**, **9** and **10** are deduced by detailed multinuclear (^{11}B, ^{13}C and ^1H) NMR spectroscopy. These geometries are supported by boron NMR shift predictions based on observed shifts of the known non-methylated analogues [3,3,3-$(NMe_2)_3$-*closo*-3,1,2-$TaC_2B_9H_{10}$] **1** and [3,3,3-$(NMe_2)_3$-*closo*-3,1,2-$TaC_2B_9H_{10}$] **2** and calculated shifts (GIAO-B3LYP/6-311G*//MP2/6-31G*) of the *B*-methyl carboranes, *closo*-3-Me-1,2-$C_2B_{10}H_{11}$ **11**, 4-Me-1,2-$C_2B_{10}H_{11}$ **12** and 2-Me-1,7-$C_2B_{10}H_{11}$ **13**. The molecular structure of **8** has been determined by X-ray diffraction.

Introduction

The coordination chemistry of the well known carborane ligand $C_2B_9H_{11}$ with middle and late transition metals has been established by a number of research groups,[1] typically by the reaction of alkali metal salts of *nido*-7,8-$C_2B_9H_{11}^{2-}$ with metal halides, leading to elimination of alkali metal halide. More recently the coordination chemistry of $C_2B_9H_{11}$ with early transition metals[2–4] has been explored, including their application to catalysis.[5] The amine-elimination reaction[6] of metal amides M–NR_2 with acidic ligand precursors has found use as a novel method for coordinating ligands,[7] and providing routes to thermodynamic product ratios.[8] Early transition metal metallacarborane complexes with M–NMe_2 groups have been prepared by the reaction of neutral carboranes or their mono-anionic ammonium salts with metal amides.[9] Metal amides have also found use in the synthesis of metal complexes of silaboranes,[10] and provide means to metallate ligands which are not stable as their alkali-metal salts.[11]

Recently we have reported the synthesis of a series of metallacarboranes $(C_2B_9H_{11})M(NMe_2)_3$ (M = Nb, Ta), from reactions of $M(NMe_2)_5$ with 11-vertex *nido*-carboranes, together with studies of their chemistry.[12–14] For example, [3,3,3-$(NMe_2)_3$-3,1,2-*closo*-$TaC_2B_9H_{11}$] **1**, [2,2,2-$(NMe_2)_3$-2,1,7-*closo*-$TaC_2B_9H_{11}$] **2** and [2,2,2-$(NMe_2)_3$-2,1,12-*closo*-$TaC_2B_9H_{11}$] **3** (Fig. 1) were formed from the hydroamminolysis of $Ta(NMe_2)_5$ with 7,8-$C_2B_9H_{13}$, $[NMe_3H^+][7,9\text{-}C_2B_9H_{12}^-]$ and 2,9-$C_2B_9H_{13}$ respectively.[12,13]

We were attracted to the neutral *B*-methylated carborane 11-Me-2,7-$C_2B_9H_{12}$ **4**,[15–18] prepared from the reaction of *nido*-7,8-$C_2B_9H_{11}^{2-}$ with MeI followed by acidification. The carborane can lead to three isomeric *B*-methylated *nido* carborane anions $MeC_2B_9H_{11}^-$ on deprotonation.[15,16] As shown in Scheme 1, the double deprotonation of **4** with two equivalents of a strong base, such as NaH, and subsequent mono-protonation results in the formation of 9-Me-7,8-$C_2B_9H_{11}^-$ **5**. The cage in **4** can be rearranged to 8-Me-7,9-$C_2B_9H_{11}^-$ **6** on mono-deprotonation by bases such as amines at temperatures above 20 °C. These *nido*-carborane anions **5** and **6** are formed from **4** *via* 11-Me-2,7-$C_2B_9H_{11}^-$ **7** which has been isolated at low temperatures in the mono-protonation of **4**. 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.

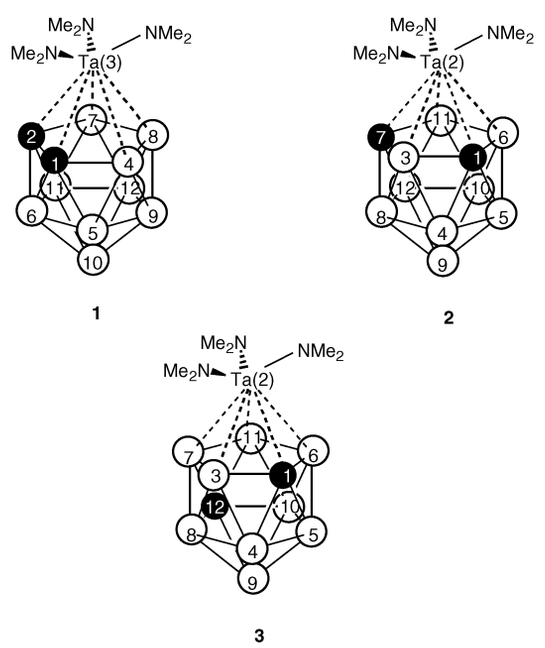

Fig. 1 The known isomers of $(NMe_2)_3TaC_2B_9H_{11}$ **1**–**3** (*exo*-hydrogens omitted for clarity).

† Electronic supplementary information (ESI) available: rotatable 3-D molecular structure diagram of **8** in CHIME format. See http://www.rsc.org/suppdata/dt/b1/b103353k/

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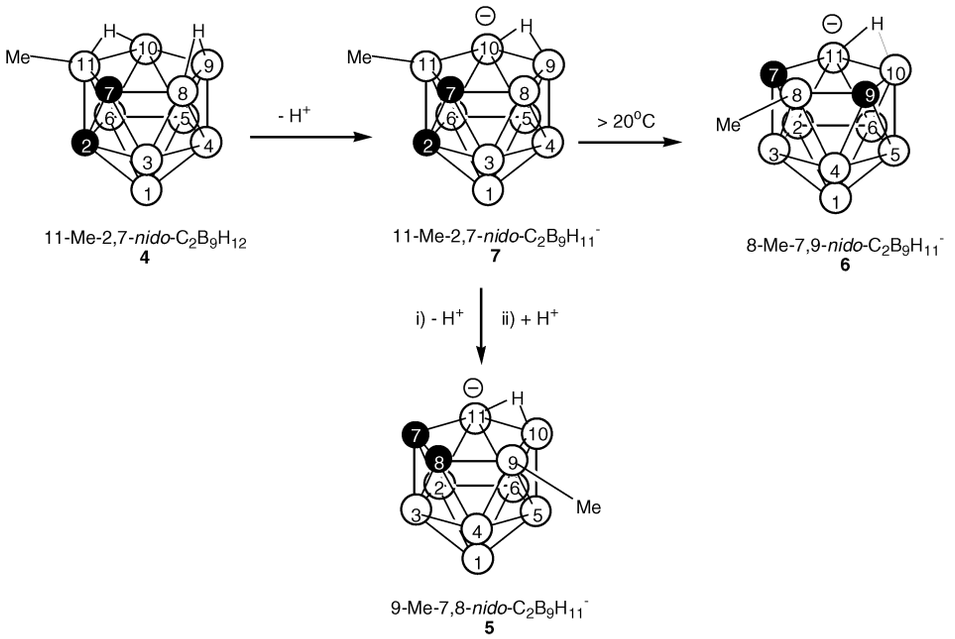


Scheme 1 The three isomeric *nido*-anions **5**–**7** obtained from 11-Me-2,7-*nido*-$C_2B_9H_{12}$ **4**.

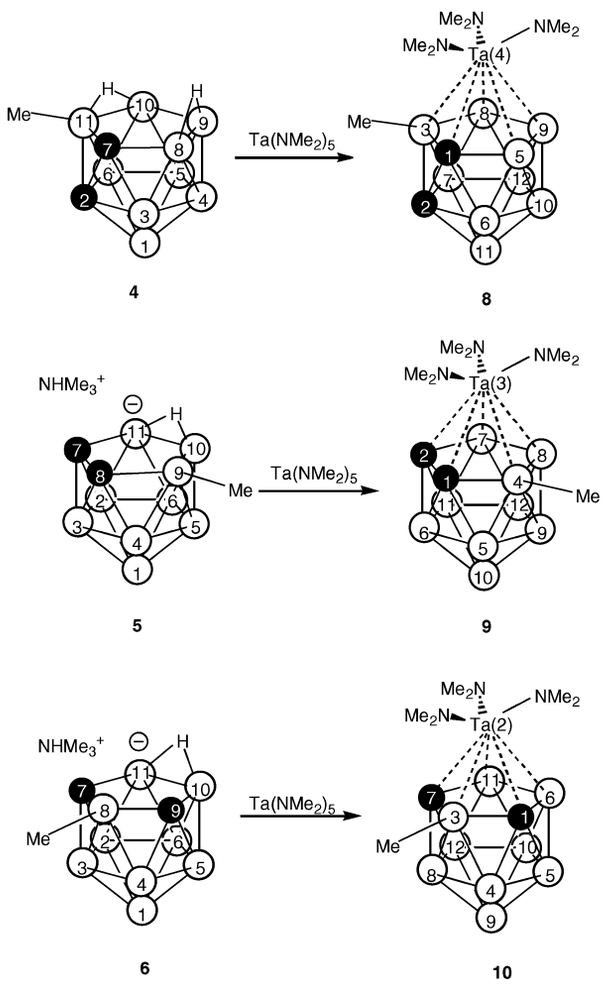
The reaction of the neutral *B*-methyl carborane **4** with transition metal amides has been explored to determine if it is possible to metallate **4** without skeletal rearrangement. The metallation of carborane precursors containing certain bulky substituents is well known to result in isomerisation during metathesis, or to give complexes which are subsequently prone to isomerisation, as a result of steric factors.[19–24] Here we report the reaction of $Ta(NMe_2)_5$ with carboranes **4**, **5** and **6**, and the characterisation of the metallacarborane products.

Results and discussion

Treating 11-Me-2,7-*nido*-$C_2B_9H_{12}$ **4** with $Ta(NMe_2)_5$ as a toluene solution at room temperature for 2 days affords only one product in high yield, identified as [4,4,4-$(NMe_2)_3$-3-Me-4,1,2-*closo*-$TaC_2B_9H_{10}$] **8**, Scheme 2. The reaction was repeated in benzene-d_6 in an NMR tube and found to be clean and quantitative. Since one aim of this work is to demonstrate that metallation occurs without skeletal rearrangement, we took great care to identify the metallacarborane **8** by detailed multinuclear NMR spectroscopy and X-ray crystallography which are discussed in detail later. Complex **8** 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 11-vertex *nido*-carboranes.[21]

Having demonstrated that **4** can be metallated without structural rearrangement, we investigated the reactions of the anions **5** and **6** with $Ta(NMe_2)_5$ with the aim of characterising the likely rearrangement products. We have previously observed that the reactions of neutral carborane precursors with metal amides proceed readily at room temperature, whilst the ammonium salts of carborane anions require elevated reaction temperatures, as in the case of [$NHMe_3$][7,9-*nido*-$C_2B_9H_{12}$].[13] Heating a toluene solution of [$NHMe_3$][9-Me-7,8-*nido*-$C_2B_9H_{11}$] **5** and $Ta(NMe_2)_5$ in a sealed ampoule at 120 °C for 18 hours results in the formation of [3,3,3-$(NMe_2)_3$-4-Me-3,1,2-*closo*-$TaC_2B_9H_{10}$] **9** identified by detailed NMR spectroscopy. This reaction is clean, and does not result in the production of side-products. Crystals of **9**, which were apparently suitable for X-ray diffraction studies, were obtained from toluene–pentane mixtures, but are systematically twinned, and a satisfactory structure solution has not been obtained.

Heating a solution of [$NHMe_3$][8-Me-7,9-*nido*-$C_2B_9H_{11}$] **6** and $Ta(NMe_2)_5$ in toluene to 120 °C in a sealed ampoule for 18 hours produces a successful reaction. The reaction is however not clean, and a number of unidentified borane products are obtained in addition to [2,2,2-$(NMe_2)_3$-3-Me-2,1,7-*closo*-$TaC_2B_9H_{10}$] **10**. The metallacarborane **10** can be isolated pure, albeit in low yield, by crystallisation and was characterised by multinuclear NMR spectroscopy.



Scheme 2 The synthesis of the isomeric tantalum carboranes **8**–**10** described in this work.

We are not aware of mechanistic studies of the hydroamminolysis or amine–elimination reaction of $M(NR_2)_x$ with acidic ligands (A–H = alcohols, primary or secondary amines, cyclopentadienes, carboranes), but it seems likely that the reaction involves a σ-bond metathesis type four-centred transition state, which may be assisted by prior coordination of A–H. Of relevance, the mechanism of metal–imido (M = R) ligand exchange with primary amines ($R'NH_2$) has been studied,[25] and we have previously noted that metal amides react faster with a secondary amine, able to pre-coordinate, than with a thermodynamically more acidic cyclopentadiene.[26] The double deprotonation and coordination reaction of **4** and other neutral di-basic carboranes with $Ta(NMe_2)_5$ may be concerted or involve two separate deprotonation steps. If it is the latter, the presumed non-isolable intermediate $[(NMe_2)_4TaC_2B_9H_{11}Me]$ must rapidly eject $HNMe_2$ to form the *closo*-metallacarborane and the skeletal rearrangement may be prevented by the $Ta(NMe_2)_4$ moiety in the intermediate. Furthermore, the eliminated $HNMe_2$ does not deprotonate, and hence rearrange, **4** under the reaction conditions. The reaction of $Ta(NMe_2)_5$ with trialkyl ammonium salts of carborane anions **5** and **6**, is presumed to proceed by deprotonation of the trialkyl ammonium cation followed by the slow reaction of $Ta(NMe_2)_4L$ (L = $HNMe_2$ or R_3N) with the carborane mono-anion.

In a reaction analogous to those reported by Wesemann for metallasilaboranes,[27] the tris(amide) metallacarboranes **8**, **9** and **10** react slowly with CD_2Cl_2 to replace the NMe_2 units stepwise by Cl units. The same reaction is observed for the previously reported metallacarboranes **1**, **2** and **3**; these reactions and the characterisation of the resulting mixed amide chloride substituted metallacarboranes will be reported on separately.

NMR spectroscopy

Proton NMR data for **8**, **9** and **10** reveal a single resonance (δ 3.55–3.53) for the Ta–NMe_2 units in each compound, all six amide methyl groups being equivalent on the NMR timescale. These observations must indicate fluxional processes in solution, as widely observed for other early transition metal amide species such as **1**, **2** and **3**.[12,13] The single peak corresponding to the methyl group attached to boron in the region δ 0.45–0.31 in compounds **8**, **9** and **10** sharpens on broad-band boron decoupling.

The ^1H, ^{11}B and ^{13}C NMR spectra of **8** are entirely consistent with a *closo*-metallacarborane of formula $(NMe_2)_3TaC_2B_9H_{10}Me$ with no plane of symmetry. Two dimensional ^{11}B–$^{11}B\{^1H\}$ COSY NMR spectroscopy is a very useful tool for assignments of boron peaks in compounds such as the carboranes and metallacarboranes discussed here.[4,13,28] In the 2D ^{11}B–$^{11}B\{^1H\}$ COSY spectrum of **8** the peak corresponding to the methylated boron has two cross-peaks implying that this boron is linked to only two neighbouring boron atoms. The only isomer consistent with this NMR observation is [4,4,4-$(NMe_2)_3$-3-Me-4,1,2-*closo*-$TaC_2B_9H_{10}$]. Further support for this configuration is the presence of a sharp peak and a broad peak corresponding to the cage carbons in the $^{13}C\{^1H\}$ NMR spectrum. Similar peak shapes are observed in the $^{13}C\{^1H\}$ NMR spectrum of [2,2,2-$(NMe_2)_3$-2,1,12-*closo*-$TaC_2B_9H_{10}$] **3** where one cage carbon is next to the metal atom whereas the other cage carbon is not.[13] Only broad resonances corresponding to cage carbons are observed in [3,3,3-$(NMe_2)_3$-3,1,2-*closo*-$TaC_2B_9H_{10}$] **1** and [2,2,2-$(NMe_2)_3$-2,1,7-*closo*-$TaC_2B_9H_{10}$] **2** where the cage carbons are next to the tantalum atom.

Proton, boron and carbon NMR data for **9** are also in agreement with a *closo*-$(Me_2N)_3TaC_2B_9H_{10}Me$ isomer without a plane of symmetry. In the 2D ^{11}B–$^{11}B\{^1H\}$ COSY spectrum for **9**, the peak corresponding to the methylated boron has three cross-peaks indicating that this atom has three neighbouring boron atoms. The two peaks assigned to the cage carbons in the ^{13}C spectrum of **9** are broad like those found for **1** and **2** where the cage carbons are linked to the metal atom. These observations are consistent with the formulation of **9** as [3,3,3-$(Me_2N)_3$-4-Me-3,1,2-*closo*-$TaC_2B_9H_{10}$].

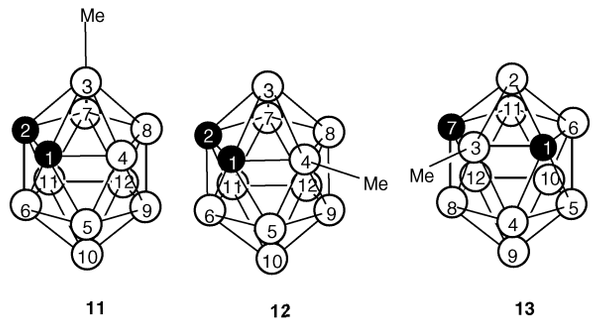


Fig. 2 The *B*-methyl-*closo*-carboranes **11**–**13** related to metallacarboranes **8**–**10** by replacing the $Ta(NMe_2)_3$ vertex by a BH vertex.

For **10**, the ^{11}B, ^1H and ^{13}C NMR data are consistent with a *closo*-metallacarborane of formula $(Me_2N)_3TaC_2B_9H_{10}Me$ with a mirror plane of symmetry. The broad peak assigned to the cage carbons in the ^{13}C NMR spectrum shows that the cage carbons are next to the metal atom. Based on this observation only two isomers [3,3,3-$(Me_2N)_3$-8-Me-3,1,2-$TaC_2B_9H_{10}$] and [2,2,2-$(Me_2N)_3$-3-Me-2,1,7-$TaC_2B_9H_{10}$] are possible for **10**. Comparison of the proton and carbon NMR data for **10** with that for the non-alkylated metallacarborane **2** shows similarities, so that compound **10** is assigned as [2,2,2-$(Me_2N)_3$-3-Me-2,1,7-*closo*-$TaC_2B_9H_{10}$].

Missing cross-peaks are however not unusual in 2D ^{11}B–$^{11}B\{^1H\}$ COSY spectra so to support the spectroscopic identification of the three isomeric metallacarboranes **8**, **9** and **10**, boron chemical shift predictions for these compounds were carried out.

Whilst reliable results are obtained from *ab initio* calculations of the structures and ^{11}B NMR chemical shifts of boranes and carboranes, it is not possible to perform reliable calculations on metallacarboranes. Our approach therefore is to calculate at the highest possible level of theory for the parent *closo*-carboranes 3-Me-1,2-$C_2B_{10}H_{11}$ **11**,[29] 4-Me-1,2-$C_2B_{10}H_{11}$ **12**[30] and 3-Me-1,7-$C_2B_{10}H_{11}$ **13**[31] which are analogues of **8**, **9** and **10** respectively on replacing the $\{(NMe_2)_3Ta\}$ vertex with a {BH} vertex, Fig. 2. We then investigate the chemical shift differences caused by methylating one boron atom, or by replacing a {BH} vertex with $\{(NMe_2)_3Ta\}$. Experimentally assigned boron chemical shifts are not known for **11**, **12** and **13**. The carborane 3-Me-1,7-$C_2B_{10}H_{11}$ should be correctly numbered as 2-Me-1,7-$C_2B_{10}H_{11}$ but the former numbering is used here to correspond with the numbering in **10**.

Optimised geometry determinations for the *B*-methyl-*closo*-carboranes **11**, **12** and **13** were carried out at the MP2/6-31G* level of theory and boron chemical shifts were computed from these geometries at the GIAO-B3LYP/6-311G* level. The good accuracy of boron chemical shifts at these levels of theory for carboranes has already been demonstrated elsewhere,[32] and is demonstrated here by comparison of experimental and calculated shifts listed in Table 1 for the well known *ortho*-carborane, 1,2-$C_2B_{10}H_{12}$, and *meta*-carborane 1,7-$C_2B_{10}H_{12}$ which reveals the largest shift difference to be only 1.6 ppm.

As listed in Table 1, on replacing an exo-hydrogen of a boron atom with a methyl group, *e.g.* from 1,2-$C_2B_{10}H_{12}$ to **11** or **12** (entries **A** and **B**) and from 1,7-$C_2B_{10}H_{12}$ to **13** (entry **C**), only the shifts of the methylated and the antipodal boron atoms are significantly influenced. Similar effects are noted in the assigned experimental chemical shifts for 9-Et-1,7-$C_2B_9H_{11}$.[33] By adding the shift differences caused by the methyl group to the assigned boron shifts of the known complexes **1** and **2**, the boron shifts generated differ from observed shifts of **9** and **10** by 3.0 to −1.3

Table 1 Experimental (in **bold**), *ab initio* calculated and empirically predicted ^{11}B NMR chemical shifts (δ) for compounds discussed in this study

	Vertex									
	3	4	5	6	7	8	9	10	11	12
1,2-$C_2B_{10}H_{12}$ experimental	**−15.1**	**−14.0**	**−14.0**	**−15.1**	**−14.0**	**−9.6**	**−2.9**	**−9.6**	**−14.0**	**−2.9**
1,2-$C_2B_{10}H_{12}$ *ab initio*	−16.7	−14.7	−14.7	−16.7	−14.7	−9.3	−2.0	−9.3	−14.7	−2.0
Difference	*1.6*	*0.7*	*0.7*	*1.6*	*0.7*	*−0.3*	*−0.9*	*−0.3*	*0.7*	*−0.9*
3-Me-1,2-$C_2B_{10}H_{11}$ **11** *ab initio*	−6.8	−12.7	−15.1	−15.1	−12.7	−9.3	−1.7	−13.1	−15.2	−1.7
A = *difference between* **11** *and ab initio 1,2-*$C_2B_{10}H_{12}$	*9.9*	*2.0*	*−0.4*	*1.6*	*2.0*	*0.0*	*0.3*	*−3.8*	*−0.5*	*0.3*
4-Me-1,2-$C_2B_{10}H_{11}$ **12** *ab initio*	−15.9	−4.5	−14.1	−16.4	−14.3	−8.5	−0.3	−9.2	−18.4	−2.6
B = *difference between* **12** *and ab initio 1,2-*$C_2B_{10}H_{12}$	*0.8*	*10.2*	*0.6*	*0.3*	*0.4*	*0.8*	*1.7*	*0.1*	*−3.7*	*−0.6*
[4,4,4-$(NMe_2)_3$-3-Me-4,1,2-$TaC_2B_9H_{10}$] **8**	**−0.5**		**−6.8**	**−12.6**	**−11.0**	**1.0**	**7.6**	**−12.1**	**−19.9**	**−1.5**
Replace $(NMe_2)_3$Ta for BH at vertex 4 in **11**	−5.9		−4.1	−15.4	−13.3	1.5	9.7	−8.2	−22.9	−1.6
Difference between predicted and observed for **8**	*5.4*		*−2.7*	*2.8*	*2.3*	*−0.5*	*−2.1*	*−3.9*	*3.5*	*0.1*
[3,3,3-$(NMe_2)_3$-3,1,2-$TaC_2B_9H_{11}$] **1**		**−5.7**	**−13.8**	**−13.8**	**−5.7**	**1.8**	**−3.4**	**−16.2**	**−13.8**	**−3.4**
[3,3,3-$(NMe_2)_3$-4-Me-3,1,2-$TaC_2B_9H_{10}$] **9**		**3.2**	**−10.2**	**−13.1**	**−6.2**	**2.4**	**−1.2**	**−16.6**	**−16.6**	**−2.3**
Predicted for **9** (**1** + **B**)		4.5	−13.2	−13.5	−5.3	2.6	−1.7	−16.1	−17.5	−4.0
Difference between predicted and observed for **9**		*−1.3*	*3.0*	*0.4*	*−0.9*	*−0.2*	*0.5*	*−0.5*	*0.9*	*1.7*
1,7-$C_2B_{10}H_{12}$ experimental	**−17.1**	**−17.1**	**−13.6**	**−7.0**	**−13.6**	**−13.6**	**−10.9**	**−10.9**	**−13.6**	**−7.0**
1,7-$C_2B_{10}H_{12}$ *ab initio*	−18.6	−18.6	−14.3	−7.3	−14.3	−14.3	−10.5	−10.5	−14.3	−7.3
Difference	*1.5*	*1.5*	*0.7*	*0.3*	*0.7*	*0.7*	*−0.4*	*−0.4*	*0.7*	*0.3*
3-Me-1,7-$C_2B_9H_{11}$ **13**	−17.4	−9.4	−13.1	−7.1	−13.8	−13.1	−9.9	−14.1	−13.8	−7.1
C = *difference between* **13** *and ab initio 1,7-*$C_2B_{10}H_{12}$	*1.2*	*9.2*	*1.2*	*0.2*	*0.5*	*1.2*	*0.6*	*−3.6*	*0.5*	*0.2*
[2,2,2-$(NMe_2)_3$-2,1,7-$TaC_2B_9H_{11}$] **2**		**−11.8**	**−13.1**	**−5.9**	**−5.2**	**−13.1**	**−16.9**	**−11.1**	**−5.2**	**−5.9**
[2,2,2-$(NMe_2)_3$-3-Me-2,1,7-$TaC_2B_9H_{10}$] **10**		**−6.0**	**−11.6**	**−6.6**	**−6.6**	**−11.6**	**−19.2**	**−15.5**	**−6.6**	**−6.6**
Predicted for **10** (**2** + **C**)		−2.6	−11.9	−5.7	−4.7	−11.9	−16.3	−14.7	−4.7	−5.7
Difference between predicted and observed for **10**		*−3.4*	*0.3*	*−1.7*	*−1.9*	*0.3*	*−2.9*	*−0.8*	*−1.9*	*−0.9*

ppm and −3.4 to 0.3 ppm, respectively. These results confirm the identities of **9** and **10**.

What about predicted boron chemical shifts for **8**? Since the complex 4,4,4-$(NMe_2)_3$-4,1,2-*closo*-$TaC_2B_9H_{11}$ is not known experimentally, we cannot apply the chemical shift differences caused by *B*-methylation. In our previous report on the synthesis of the 2,1,7 and 2,1,12 isomers of {[$(NMe_2)_3$Ta]-$C_2B_9H_{11}$},[13] and comparison of their NMR data with that of the 3,1,2 isomer,[12] we noted that replacing a BH vertex in the appropriate isomer of $C_2B_{10}H_{12}$ by a Ta$(NMe_2)_3$ vertex results in a consistent change in the ^{11}B shielding of remaining boron vertices which are neighbouring (NE), butterfly (BE) or antipodal (AE) with respect to the Ta$(NMe_2)_3$ vertex. Thus using the typical values of NE = 10 ppm, BE = 1 and AE = −5, the boron shifts generated from 3-Me-1,2-$C_2B_{10}H_{11}$ by replacing a {BH} unit at vertex 4 with a {Ta$(NMe_2)_3$} unit differ from observed boron shifts for **8** by 5.4 to −3.9 ppm. The larger error range in the chemical shifts for **8** calculated by this empirical method is not surprising in view of the crude prediction method used. Nevertheless this result supports the identity of **8** as [4,4,4-$(NMe_2)_3$-3-Me-4,1,2-*closo*-$TaC_2B_9H_{10}$].

X-Ray crystallography

To further confirm the identity of [4,4,4-$(NMe_2)_3$-3-Me-4,1,2-*closo*-$TaC_2B_9H_{10}$] **8**, its structure was determined by X-ray diffraction. The molecular structure appears in Fig. 3 and selected bond lengths and angles are given in Table 2. The structure consists of a 12 vertex *closo*-metallacarborane, and confirms the assignment of a 3-Me-4,1,2-*closo*-$TaC_2B_9H_{10}$ structure made from the spectroscopic data. Details of how the carbon and boron atoms were distinguished are given in the experimental section. The Ta–Cb (= CB_4 centroid) distance of 1.982 Å is comparable with those observed in other Ta(carborane)$(NMe_2)_3$ complexes,[13] and the Ta–C and Ta–B distances are essentially equal, with no folding of the CB_4 face. The

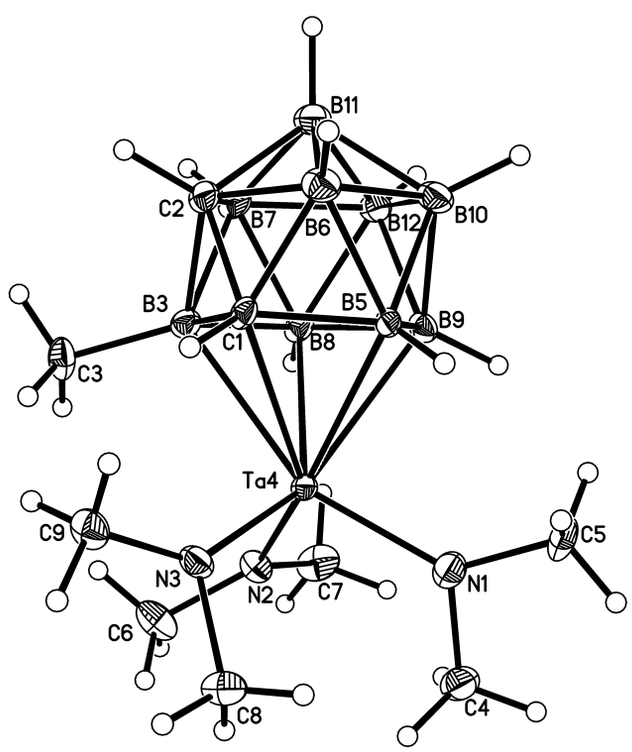


Fig. 3 The molecular structure of [4,4,4-$(NMe_2)_3$-3-Me-4,1,2-*closo*-$TaC_2B_9H_{10}$] **8**, showing 40% displacement ellipsoids, with hydrogen atoms as arbitrary sized spheres.

Ta$(NMe_2)_3$ fragment adopts a propeller-like configuration, although the blades are not inclined at the same angle, the dihedral angles between the Cb–Ta–N and C–N–C planes are 21.5° for N(3), 22.8° for N(1) and 71.8° for N(2). The more horizontal amide ligand, that containing N(2), displays the

Table 2 Selected bond lengths (Å) and angles (°) for **8**[a]

Ta(4)–N(2)	1.967(4)	Ta(4)–Cb	1.982
Ta(4)–N(3)	1.988(4)	C(1)–C(2)	1.625(6)
Ta(4)–N(1)	2.000(5)	C(3)–B(3)	1.600(7)
Ta(4)–C(1)	2.475(4)	C(1)–B(5)	1.673(6)
Ta(4)–B(5)	2.475(5)	C(1)–B(3)	1.712(7)
Ta(4)–B(3)	2.479(6)	B(3)–B(8)	1.798(7)
Ta(4)–B(9)	2.488(5)	B(5)–B(9)	1.792(7)
Ta(4)–B(8)	2.491(5)	B(8)–B(9)	1.804(7)
N(2)–Ta(4)–N(3)	96.63(16)	N(3)–Ta(4)–N(1)	105.35(16)
N(2)–Ta(4)–N(1)	95.46(18)		

[a] Cb = centroid of the CB_4 face of the ligand.

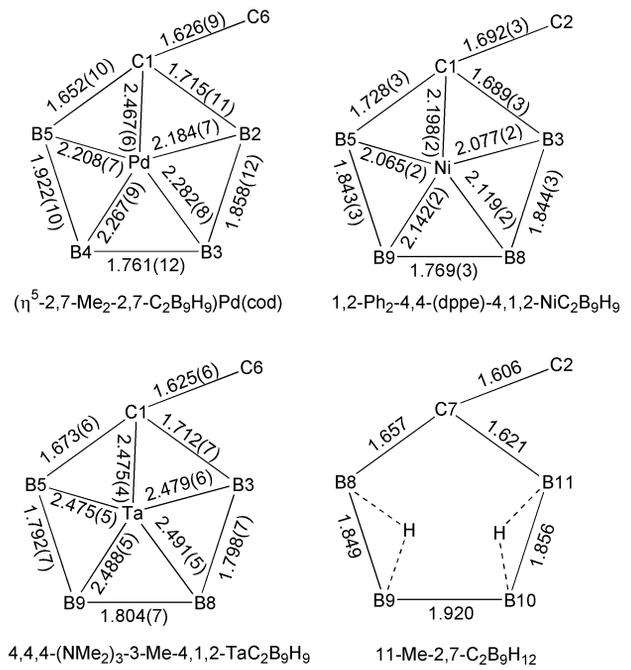


Fig. 4 Bond lengths in structurally characterised carboranes and metallacarboranes.

shortest Ta–N distance, 1.988(4) Å, suggesting that this is the strongest π-donor of the three amides, a feature previously observed in **1** and **3**.[12,13] The $MeC_2B_9H_{10}$ ligand, by analogy with $C_2B_9H_{11}$, will offer one σ- and two π-donor orbitals to tantalum, with the π-orbitals non-degenerate, resulting in an orientational preference for the carborane ligand, and accounting for the two vertical one horizontal arrangement of the amide ligands. The Ta–NMe_2 groups are planar with the sum of angles at nitrogen being 360° in each case within experimental error.

It is instructive to compare the geometry of the CB_4 face of **8** with those of the non-metallated precursor 11-Me-2,7-$C_2B_9H_{12}$, **4**,[15] and two late transition-metal products of sterically induced rearrangement, 1,2-Ph_2-4,4-(dppe)-4,1,2-*closo*-$NiC_2B_9H_9$,[21] and (η5-2,7-Me_2-2,7-$C_2B_9H_9$)Pd(cod).[24] The relevant data are illustrated in Fig. 4 and demonstrate that the tantalum atom in **8** is centred over the CB_4 face which is almost a regular pentagon. By contrast the nickel and palladium complexes display a significant slip away from the carbon atom and a lengthening of the two non-contiguous boron–boron edges; such ring slips in 18-electron late transition metallacarboranes are well documented.[34] The C–C bond length is longest in the diphenyl substituted metallacarborane. The most notable features of **4** are two B–H–B bridges on the open face, and a long unbridged B–B edge.

In conclusion, we have demonstrated that $Ta(NMe_2)_5$ reacts with a carborane, **4**, which is prone to undergo skeletal rearrangement under basic conditions. The reaction proceeds in high yield without such rearrangement, and the structure of the product has been determined by spectroscopic and diffraction methods. The higher temperature reaction of $Ta(NMe_2)_5$ with **5** and **6**, the trialkylammonium salts of the carborane anions obtained by skeletal rearrangement of **4**, also gives rise to the respective metallacarboranes, characterised by spectroscopic methods. The structures of the metallacarboranes are in accord with their predicted ^{11}B NMR chemical shifts.

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. Toluene and pentane were dried by prolonged reflux over the appropriate drying agent, prior to distillation and deoxygenation by freeze–pump–thaw processes where appropriate. CD_2Cl_2 was vacuum-distilled from CaH_2 and stored under a dry nitrogen atmosphere. Elemental analysis was performed by the micro-analytical service within this department. NMR spectra were recorded on the following instruments: Varian Unity-300 (^1H, ^{11}B, ^{13}C), Bruker AM250 (^1H, ^{13}C) and Varian 500 (^1H, ^{11}B NMR). 2D ^{11}B–^{11}B COSY spectra were recorded on the 500 whereas $^1H\{^{11}B\}$ and $^1H\{^{11}B$-selective$\}$ spectra were recorded on the Unity, and used to fully assign the ^1H spectra. All chemical shifts are reported in δ (ppm) and coupling constants in Hz. ^1H NMR spectra were referenced to residual protio impurity in the solvent ($CDHCl_2$, δ 5.32). ^{13}C NMR spectra were referenced to the solvent resonance (CD_2Cl_2 δ 53.5). ^{11}B NMR were referenced externally to $Et_2O{\cdot}BF_3$, $\delta = 0.0$ ppm and are given as chemical shift (multiplicity in proton coupled spectrum, $^1J(^1H–^{11}B)$, assignment). Peaks corresponding to the B–Me group are not observed in $^{13}C\{^1H\}$ NMR spectra here, usually they can only be seen with neat or highly concentrated NMR samples, with very long acquisition times, with broad-band boron decoupling or at low temperatures.

Microanalyses were consistently low in carbon, even for crystalline samples used for X-ray diffraction studies, presumably due to the formation of incombustible TaN, TaC and BN. The reported values are the best of four independent determinations. The preparation of $Ta(NMe_2)_5$ followed a literature procedure.[35] Preparations (which are modifications of literature methods[16,17]) of **4**, **5** and **6** will be described elsewhere.

Syntheses

[4,4,4-(NMe_2)$_3$-3-Me-4,1,2-*closo*-$TaC_2B_9H_{10}$] 8. A toluene solution (5 ml) of freshly prepared **4** (0.30 g, 2 mmol) was added dropwise to a toluene solution (10 ml) of $Ta(NMe_2)_5$ (0.80 g, 2 mmol) and left to stir at room temperature for 2 days. The bright yellow solution was then layered with pentane (*ca.* 50 ml) whereupon interdiffusion of the two solvents afforded bright yellow crystals. 0.48 g, 52%. Calc. for $C_9H_{31}B_9N_3Ta$: C, 23.5; H, 6.8; N, 9.1. Found: C, 20.6; H, 6.9; N, 8.3%. NMR data: ^{11}B, δ 7.6 (d, 124, B9), 1.0 (d, 126, B8), −0.5 (s, B3), −1.5 (d, 141, B12), −6.8 (d, 132, B5), −11.0 (d, 155, B7), −12.1 (d, B10), −12.6 (d, B6), −19.9 (d, 156, B11); ^{13}C δ 59.5 (C2), 56.7 (C1), 49.5 (NMe_2); ^1H δ 3.62 (NMe_2), 3.53 (C2-H), 3.00 (B11-H), 2.84 (C1-H), 2.63 (B12-H), 2.63 (B6-H), 2.16 (B7-H), 2.12 (B10-H), 1.93 (B8-H), 1.93 (B9-H), 1.52 (B5-H), 0.44 (B-Me); ^{11}B–$^{11}B\{^1H\}$ COSY, observed cross peaks B9–B8 (s), B9–B12 (m), B9–B5 (s), B9–B10 (m), B8–B3 (m), B8–B12 (w), B8–B7 (m), B3–B7 (w), B12–B7 (m), B12–B10 (m), B12–B11 (m), B5–B10/6 (m), B7–B11 (w), B10/6–B11 (m).

[3,3,3-(NMe_2)$_3$-4-Me-3,1,2-*closo*-$TaC_2B_9H_{10}$] 9. A toluene solution (5 ml) of freshly prepared **5** (0.10 g, 0.47 mmol) was added dropwise to a stirred toluene solution (10 ml) of $Ta(NMe_2)_5$ (0.22 g, 0.55 mmol). The ampoule was then placed

in an oil-bath and the temperature slowly raised to 120 °C and heating continued for 18 h. The volatiles were removed *in vacuo* and the residues washed with pentane (2 × 25 ml) to afford a crude bright yellow solid. Crystallisation from a toluene–pentane solution afforded a bright yellow crystalline solid 0.064 g, 30%. Calc. for $C_9H_{31}B_9N_3Ta$: C, 23.5; H, 6.8; N, 9.1. Found: C, 20.4; H, 6.8; N, 7.9%. NMR data: ^{11}B δ 3.2 (s, B4), 2.4 (d, 129, B8), −1.2 (d, 141, B9), −2.3 (d, 169, B12), −6.2 (d, 133, B7), −10.2 (d, 161, B5), −13.1 (d, 160, B6), −16.6 (d, B10 and B11); ^{13}C δ 53.2 (partially obscured by CD_2Cl_2, cage C), 51.4 (cage C), 49.3 (NMe_2); ^1H δ 3.55 (NMe_2), 2.89 (B10-H), 2.88 (C2-H), 2.64 (C1-H), 2.31 (B12-H), 2.26 (B9-H), 2.23 (B6-H), 2.04 (B5-H), 1.96 (B11-H), 1.64 (B8-H), 1.55 (B7-H), 0.31 (B4-Me); ^{11}B–$^{11}B\{^1H\}$ COSY, observed cross peaks B4–B8 (w), B4–B9 (w), B4–B5 (w), B8–B9 (w), B8–B12 (w), B8–B7 (s), B9–B12 (w), B9–B5 (m), B9–B10 (m), B12–B7 (m), B12–B10/11 (m), B5–B10 (m), B5–B6 (w), B6–B10/11 (w).

[2,2,2-$(NMe_2)_3$-3-Me-2,1,7-*closo*-$TaC_2B_9H_{10}$] 10. A toluene solution (5 ml) of freshly prepared **6** (0.10 g, 0.47 mmol) was added dropwise to a stirred toluene solution (10 ml) of $Ta(NMe_2)_5$ (0.22 g, 0.55 mmol). The ampoule was then placed in an oil-bath and the temperature slowly raised to 120 °C for 18 h. The volatiles were removed *in vacuo* and the residues washed with pentane (2 × 20 ml) to afford a crude bright yellow solid. Crystallisation from a toluene–pentane solution gave a bright yellow crystalline solid 0.032 g, 15%. NMR data ^{11}B δ −6.0 (s, B3), −6.6 (d, B5, B6, B11 and B12), −11.6 (d, 155, B4 and B8), −15.5 (d, 138, B10), −19.2 (d, 155, B8); ^{13}C δ 59.1 (C1 and C7), 49.1 (NMe_2); ^1H δ 3.55 (NMe_2), 2.74 (B9-H), 2.38 (B5-H and B12-H), 2.19 (C1-H, B4-H, C7-H and B8-H), 1.58 (B6-H and B11-H), 0.45 (B3-Me).

Computational section

All *ab initio* computations here were carried out with the Gaussian 94 package.[36] The geometries of 1,2-$C_2B_{10}H_{12}$, 1,7-$C_2B_{10}H_{12}$ and the *B*-methyl carboranes $MeC_2B_{10}H_{11}$ **11**, **12** and **13** were optimised at the HF/6-31G* level with no symmetry constraints. No imaginary frequencies were found from frequency calculations on these optimised geometries at the HF/6-31G* level. The HF-optimised geometries were then determined at the computationally intensive MP2/6-31G* level. NMR shifts at the GIAO-B3LYP/6-311G* level were then calculated for the MP2-optimised geometries. Theoretical ^{11}B chemical shifts at the GIAO-B3LYP/6-311G*//MP2/6-31G* level listed in Table 1 have been referenced to B_2H_6 (δ 16.6[38]) and converted to the usual $BF_3{\cdot}OEt_2$ scale; $\delta(^{11}B) = 102.83 - \sigma(^{11}B)$.

X-Ray crystallography

The single-crystal diffraction study of **8** was carried out with a SMART 1K CCD area detector, using graphite-monochromated Mo-*Kα* radiation ($\bar{\lambda} = 0.71073$ Å). The reflection intensities were corrected for by a semi-empirical method based on multiple scans of identical reflections and Laue equivalents using SHELXTL software.[38] The structure was solved by direct methods and refined by full-matrix least squares against F^2 of all data, using SHELXTL programs. Crystal data and experimental details are listed in Table 3. The cage carbon atoms 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 factors (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.

CCDC reference number 163356.

See http://www.rsc.org/suppdata/dt/b1/b103353k/ for crystallographic data in CIF or other electronic format.

Table 3 Crystallographic data for compound **8**

Empirical formula	$C_9H_{31}B_9N_3Ta$
Temperature/K	100.0(2)
Crystal system	Monoclinic
Space group	*Cc*
a/Å	7.614(2)
b/Å	18.192(4)
c/Å	13.584(3)
β/°	98.89(3)
U/Å^3	1859.1(6)
Z	4
μ(Mo-Kα)/mm^{-1}	5.904
Reflections collected	11038
Independent reflections	4708
R(int)	0.0372
Data	4708
$R\,[I > 2\sigma(I)]$	0.0220
$wR(F^2)$ (all data)	0.0510

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References

1 R. N. Grimes, *Coord. Chem. Rev.*, 2000, **200**, 773; R. N. Grimes, in *Comprehensive Organometallic Chemistry II*, ed. E. W. Abel, F. G. A. Stone and G. Wilkinson, Pergamon Press, Oxford, 1995, vol. 1, ch. 9; M. F. Hawthorne, *Acc. Chem. Res.*, 1968, **1**, 281; A. K. Saxena and N. S. Hosmane, *Chem. Rev.*, 1993, **93**, 1081.

2 G. C. Bazan, W. P. Schaefer and J. E. Bercaw, *Organometallics*, 1993, **12**, 2126.

3 X. H. Bei, V. G. Young and R. F. Jordan, *Organometallics*, 2001, **20**, 355; X. H. Bei, C. Kreuder, D. C. Swenson, R. F. Jordan and V. G. Young, *Organometallics*, 1998, **17**, 355; M. Yoshida, D. J. Crowther and R. F. Jordan, *Organometallics*, 1997, **16**, 1349; D. J. Crowther, D. C. Swenson and R. F. Jordan, *J. Am. Chem. Soc.*, 1995, **117**, 10403; D. E. Bowen, R. F. Jordan and R. D. Rogers, *Organometallics*, 1995, **14**, 3630; R. Uhrhammer, Y. X. Su, D. C. Swenson and R. F. Jordan, *Inorg. Chem.*, 1994, **33**, 4398.

4 R. Uhrhammer, D. J. Crowther, J. D. Olson, D. C. Swenson and R. F. Jordan, *Organometallics*, 1992, **11**, 3098; D. J. Crowther, R. A. Fisher, A. M. Canich, G. G. Hlatky and H. W. Turner, *US Pat.*, 5502124, 1996; D. J. Crowther, S. L. Borkowsky, D. Swenson, T. Y. Meyer and R. F. Jordan, *Organometallics*, 1993, **12**, 2897; D. J. Crowther, D. C. Swenson and R. F. Jordan, *J. Am. Chem. Soc.*, 1995, **117**, 10403; Y. X. Su, S. E. Reck, I. A. Guzei and R. F. Jordan, *Organometallics*, 2000, **19**, 4858.

5 S. Saccheo, G. Gioia, A. Grassi, D. E. Bowen and R. F. Jordan, *J. Mol. Catal. A*, 1998, **128**, 111; M. Yoshida and R. F. Jordan, *Organometallics*, 1997, **16**, 4508.

6 G. Chandra and M. F. Lappert, *J. Chem. Soc. A*, 1968, 1940; M. F. Lappert, P. P. Power, A. R. Sanger and R. C. Srivastava, *Metal and Metalloid Amides*, Ellis Horwood Publishers, Chichester, 1980; M. H. Chisholm and I. P. Rothwell, in *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, vol. 2, ch. 13.4, Pergamon Press, Oxford, 1987.

7 A. K. Hughes, A. Meetsma and J. H. Teuben, *Organometallics*, 1993, **12**, 1936; W. A. Hermann and W. Baratta, *J. Organomet. Chem.*, 1996, **506**, 357; Y. Mu, W. E. Piers, M. A. MacDonald and M. J. Zaworotko, *Can. J. Chem.*, 1995, **73**, 2233; Y. Mu, W. E. Piers, D. C. MacQuarrie, M. J. Zaworotko and V. G. Young, *Organometallics*, 1996, **15**, 2720; Z. Ziniuk, I. Goldberg and M. Kol, *J. Organomet. Chem.*, 1997, **546**, 441; M. K. T. Tin, N. Thirupathi, G. P. A. Yap and D. S. Richeson, *J. Chem. Soc., Dalton Trans.*, 1999, 2947.

8 G. M. Diamond, R. F. Jordan and J. L. Petersen, *Organometallics*, 1996, **15**, 4045; J. N. Christopher, G. M. Diamond, R. F. Jordan and J. L. Petersen, *Organometallics*, 1996, **15**, 4038; G. M. Diamond, R. F. Jordan and J. L. Petersen, *J. Am. Chem. Soc.*, 1996, **118**, 8024.

9 D. E. Bowen, R. F. Jordan and R. D. Rogers, *Organometallics*, 1995, **14**, 3630.

10 L. Wesemann, M. Trinkaus and M. Ruck, *Angew. Chem., Int. Ed.*, 1999, **38**, 2375.

11 I. A. Guzei, A. G. Baboul, G. P. A. Yap, A. L. Rheingold, H. B. Schlegel and C. H. Winter, *J. Am. Chem. Soc.*, 1997, **119**, 3387; I. A. Guzei, G. P. A. Yap and C. H. Winter, *Inorg. Chem.*, 1997, **36**, 1738; Y. Mu, W. E. Piers, L. R. Macgillivray and M. J. Zaworotko, *Polyhedron*, 1995, **14**, 1.

12 A. S. Batsanov, A. V. Churakov, J. A. K. Howard, A. K. Hughes, A. L. Johnson, A. J. Kingsley, I. S. Neretin and K. Wade, *J. Chem. Soc., Dalton Trans.*, 1999, 3867.

13 A. S. Batsanov, P. A. Eva, M. A. Fox, J. A. K. Howard, A. K. Hughes, A. L. Johnson, A. M. Martin and K. Wade, *J. Chem. Soc., Dalton Trans.*, 2000, 3519.

14 C. K. Broder, A. E. Goeta, J. A. K. Howard, A. K. Hughes, A. L. Johnson, J. M. Malget and K. Wade, *J. Chem. Soc., Dalton Trans.*, 2000, 3526; A. E. Goeta, A. K. Hughes and J. M. Malget, *Acta Crystallogr., Sect. C*, 2001, **57**, 702.

15 S. P. Knyazev, V. A. Brattsev and V. I. Stanko, *Doklady (Engl. Transl.)*, 1977, **234**, 299; S. P. Knyazev, V. A. Brattsev and V. I. Stanko, *Doklady (Engl. Transl.)*, 1977, **234**, 323; V. Brattsev, *Spec. Publ. R. Soc. Chem.*, 2000, **253**, 205.

16 L. I. Zakharkin, G. G. Zhigareva, V. A. Antonovich, A. I. Yanovskii and Yu. T. Struchkov, *J. Gen. Chem. USSR (Engl. Transl.)*, 1986, 1823.

17 L. I. Leites, S. S. Bukalov, L. E. Vinogradova, S. P. Knyazev and Yu. A. Strelenko, *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)*, 1986, 1633.

18 Yu. T. Struchkov, M. Yu. Antipin, V. I. Stanko, V. A. Brattsev, N. I. Kirillova and S. P. Knyazev, *J. Organomet. Chem.*, 1977, **141**, 133.

19 D. R. Baghurst, R. C. B. Copley, H. Fleischer, D. M. P. Mingos, G. O. Kyd, L. J. Yellowlees, A. J. Welch, T. R. Spalding and D. O'Connell, *J. Organomet. Chem.*, 1993, **447**, C14; B. E. Hodson, D. Ellis, T. D. McGrath, J. J. Monaghan, G. M. Rosair and A. J. Welch, *Angew. Chem., Int. Ed.*, 2001, **40**, 715; S. Dunn, R. M. Garrioch, G. M. Rosair, L. Smith and A. J. Welch, *Coll. Czech. Chem. Commun.*, 1999, **64**, 1013; S. Dunn, G. M. Rosair, A. S. Weller and A. J. Welch, *Chem. Commun.*, 1998, 1065; S. Dunn, G. M. Rosair, R. L. Thomas, A. S. Weller and A. J. Welch, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 645; G. Barbera, S. Dunn, M. A. Fox, R. M. Garrioch, B. E. Hodson, K. S. Low, G. M. Rosair, F. Teixidor, C. Viñas, A. J. Welch and A. S. Weller, *Spec. Publ. R. Soc. Chem.*, 2000, **253**, 329.

20 L. F. Warren and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1970, **92**, 1157; J. A. Long, T. B. Marder, P. E. Behnken and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1984, **106**, 2979; D. O'Connell, T. R. Spalding, G. Ferguson, J. F. Gallagher and J. D. Kennedy, *J. Organomet. Chem.*, 1995, **503**, C12.

21 R. M. Garrioch, P. Kuballa, K. S. Low, G. M. Rosair and A. J. Welch, *J. Organomet. Chem.*, 1999, **575**, 57.

22 N. Carr, D. F. Mullica, E. L. Sappenfield and F. G. A. Stone, *Inorg. Chem.*, 1994, **33**, 1666.

23 M. R. Churchill and K. Gold, *J. Am. Chem. Soc.*, 1970, **92**, 1180.

24 K. A. Fallis, D. F. Mullica, E. L. Sappenfield and F. G. A. Stone, *Inorg. Chem.*, 1994, **33**, 4927.

25 R. I. Michelman, R. G. Bergman and R. A. Andersen, *Organometallics*, 1993, **12**, 2741.

26 A. K. Hughes and A. J. Kingsley, *J. Chem. Soc., Dalton Trans.*, 1997, 4139.

27 L. Wesemann, *Spec. Publ. R. Soc. Chem.*, 2000, **253**, 353.

28 X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy, K. Nestor, M. Thornton-Pett, S. Heřmánek, T. Jelínek and B. Štíbr, *J. Chem. Soc., Dalton Trans.*, 1990, 681; M. Bown, J. Plesek, K. Base, B. Štíbr, X. L. R. Fontaine, N. N. Greenwood and J. D. Kennedy, *Magn. Reson. Chem.*, 1989, **27**, 947.

29 J. Li, D. J. Caparrelli and M. Jones, *J. Am. Chem. Soc.*, 1993, **115**, 408; V. N. Kalinin, N. I. Kobel'kova and L. I. Zakharkin, *J. Gen. Chem. (USSR)*, 1977, **47**, 879.

30 D. D. Sung, J. D. Lee and S. K. Choi, *Bull. Korean Chem. Soc.*, 1987, **8**, 63.

31 K. Yuan and M. Jones Jr., *Tetrahedron Lett.*, 1992, **33**, 7481.

32 M. A. Fox, R. Greatrex, M. Hofmann and P. v. R. Schleyer, *J. Organomet. Chem.*, 2000, **614–615**, 262.

33 S. Heřmánek, *Chem. Rev.*, 1992, **92**, 325.

34 M. F. Hawthorne, *J. Organomet. Chem.*, 1975, **100**, 97; H. M. Colquhoun, T. J. Greenhough and M. G. H. Wallbridge, *J. Chem. Soc., Dalton Trans.*, 1979, 619; D. M. P. Mingos, M. I. Forsyth and A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 1978, 1363; M. J. Calhorda, D. M. P. Mingos and A. J. Welch, *J. Organomet. Chem.*, 1982, **228**, 309; E. J. M. Hamilton and A. J. Welch, *Polyhedron*, 1990, **9**, 2407.

35 D. C. Bradley and I. M. Thomas, *Can. J. Chem.*, 1962, **40**, 1355.

36 Gaussian 94, Revision E.2, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1995.

37 T. P. Onak, H. L. Landesman and R. E. Williams, *J. Phys. Chem.*, 1959, **63**, 1533.

38 SHELXTL-NT, Version 5.1, Bruker Analytical X-Ray Instruments Inc., Madison, WI, USA, 1998.