HALOGENATION OF TRIS(AMIDO)TANTALACARBORANES WITH DIHALOMETHANES CH_2X_2 (X = Cl, Br)

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Dedicated to Professor Jaromír Plešek on the occasion of his 75th birthday in recognition of his outstanding contributions to boron chemistry.

Slow reactions of isomeric metallacarboranes of general formulae $[(NMe_2)_3TaC_2B_9H_{11}]$ (3 isomers) and $[(NMe_2)_3TaC_2B_9H_{10}Me]$ (3 isomers) with CD_2Cl_2 afford quantitative yields of monochloro complexes $[Cl(NMe_2)_2TaC_2B_9H_{11}]$ and $[Cl(NMe_2)_2TaC_2B_9H_{10}Me]$. Exposure to CD_2Cl_2 for months leads to solutions containing about 70% of the dichlorides in three cases. More prolonged exposure of these and the other monochlorides leads to a mixture of boron-substituted complexes. Hydrolysis of [3,3,3-$(NMe_2)_3$-3,1,2-$TaC_2B_9H_{11}$] by moist toluene results in the formation of the oxo-bridged complex 3,3′-[3,3-$(NMe_2)_2$-3,1,2-$TaC_2B_9H_{11}]_2$(μ-O), characterised by single-crystal X-ray crystallography. The limited solubility of the latter complex in CD_2Cl_2 eliminates the presence of this compound in the reaction of [3,3,3-$(NMe_2)_3$-3,1,2-$TaC_2B_9H_{11}$] with CD_2Cl_2. The reaction of [2,2,2-$(NMe_2)_3$-2,1,12-$TaC_2B_9H_{11}$] with CH_2Br_2 in C_6D_6 quantitatively yields the monobromide [2-Br-2,2-$(NMe_2)_2$-2,1,12-$TaC_2B_9H_{11}$]. Prolonged reaction with CH_2Br_2 leads directly to isomeric boron-substituted complexes with no evidence for dibromides. The influence on ^{11}B, ^{13}C and ^1H NMR chemical shifts of replacing an amide group in $[(NMe_2)_3TaC_2B_9H_{11}]$ with chloride to give $[Cl(NMe_2)_2TaC_2B_9H_{11}]$ is also discussed.

Keywords: Tantalum; Carboranes; Metallacarboranes; Tantalacarboranes; Halogenations; Isoelectronic analogues.

We have been exploring the synthesis of a range of complexes from the metallacarborane[1] [3,3,3-$(NMe_2)_3$-3,1,2-$TaC_2B_9H_{11}$] (**1a**) by replacing or converting the reactive amido groups, using either the amine-elimination reaction with acidic reagents or insertion of polar multiple bonds into the Ta–NMe_2 bonds[2]. Most reactions involve all three amido groups, with the exception of the mono-insertion with cyclohexyl isocyanide. The related

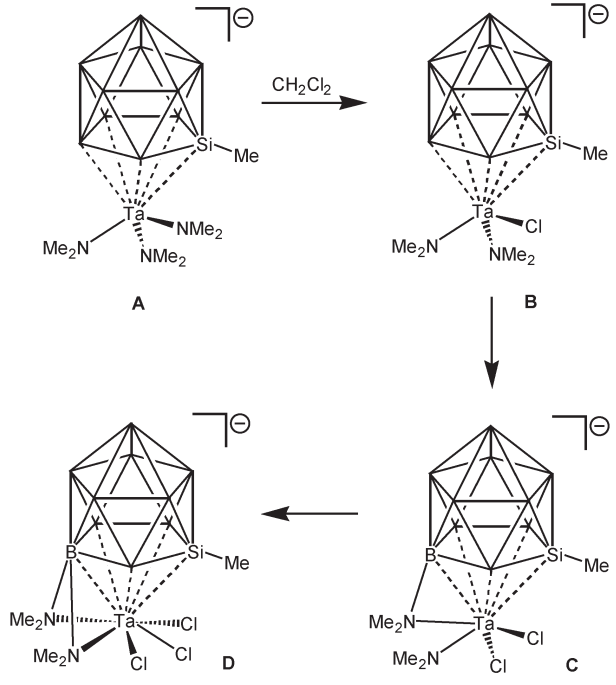
tantalacarboranes [2,2,2-$(NMe_2)_3$-*closo*-2,1,7-$TaC_2B_9H_{11}$] (**1b**), [2,2,2-$(NMe_2)_3$-*closo*-2,1,12-$TaC_2B_9H_{11}$] (**1c**), [3-Me-4,4,4-$(NMe_2)_3$-*closo*-4,1,2-$TaC_2B_9H_{10}$] (**1d**), [4-Me-3,3,3-$(NMe_2)_3$-*closo*-3,1,2-$TaC_2B_9H_{10}$] (**1e**) and [3-Me-2,2,2-$(NMe_2)_3$-*closo*-2,1,7-$TaC_2B_9H_{10}$] (**1f**) are expected to have similar derivative chemistry as for **1a**, but until now this has not been demonstrated[1,3,4].

Since organometallic chemists are most familiar with the reactions of metal–halogen bonds with reagents such as alkyllithiums and Grignards, the replacement of an amide ligand by a chloride appears to be an ideal route to mixed amido-chloro tantalacarboranes which would be versatile reagents. One merit of employing metal amides is that many reactions are higher-yielding, thus [3,3,3-$(NMe_2)_3$-3,1,2-$TaC_2B_9H_{11}$] is prepared from $Ta(NMe_2)_5$ in higher yield than is the chloride analogue [3,3,3-Cl_3-3,1,2-$TaC_2B_9H_{11}$] prepared from $TaCl_5$ [5]. A number of reagents have been utilised for the conversion of M–NR_2 groups to M–Cl, Me_2NH_2Cl will convert M–NMe_2 into M–Cl and two equivalents of volatile Me_2NH [6]. Similar reactions have been reported using 2,6-dimethylpyridinium chloride[7], and Me_3SiCl [8] which reacts with $Ta(NMe_2)_5$ to form $Ta(NMe_2)_3Cl_2$ [9]. More recently, dichloromethane has been shown to replace an amido[10], amidinato[2] or imido[11] group in tantalum complexes with a chloride. By direct analogy with the work reported here, the metallasilaborane anion [1-Me-2,2,2-$(NMe_2)_3$-2,1-$TaSiB_{10}H_{10}$] (**A**) reacts with dichloromethane to yield initially the monochloride anion [1-Me-2-Cl-2,2-$(NMe_2)_2$-2,1-$TaSiB_{10}H_{10}$] (**B**) and Me_2NCH_2Cl (Scheme 1)[10]. The monochloride is subsequently converted to a dichloride anion **C** with an amido bridge and finally to a trichloride anion **D** with two amido bridges. Using the more reactive dibromomethane, instead of dichloromethane, yields only the tribromo analogue of **D**.

We have previously reported the NMR data of the tantalacarboranes **1a**–**1f** in a variety of solvents including benzene-d_6, CD_2Cl_2 and $CDCl_3$. The samples in chlorinated solvents change their appearance over prolonged periods and here we report the products from reaction with CD_2Cl_2, which in all cases led to quantitative monochlorination. We also discuss the bromination of [2,2,2-$(NMe_2)_3$-*closo*-2,1,12-$TaC_2B_9H_{11}$] (**1c**) with dibromomethane and the crystal structure of the oxo-bridged 3,3′-[3,3-$(NMe_2)_2$-3,1,2-$TaC_2B_9H_{11}$]$_2$O (**4**) generated from hydrolysis of [3,3,3-$(NMe_2)_3$-*closo*-3,1,2-$TaC_2B_9H_{11}$] (**1a**). The profound influence of the ligand composition at the metal vertex on ^{11}B, ^{13}C and ^{1}H NMR chemical shifts is also discussed.

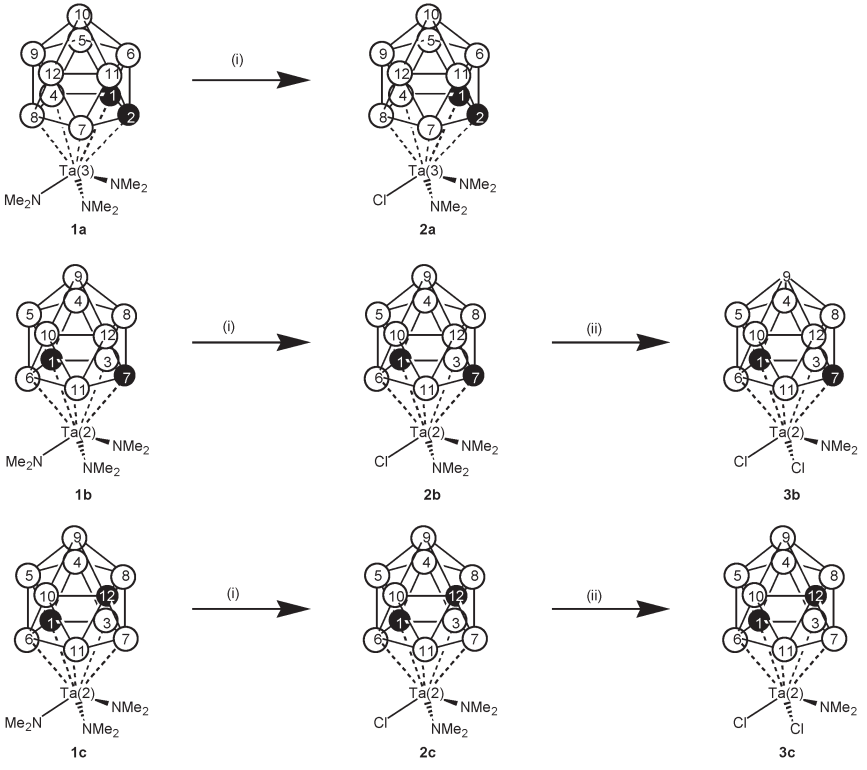
RESULTS AND DISCUSSION

Crystalline samples of the complexes [3,3,3-$(NMe_2)_3$-*closo*-3,1,2-$TaC_2B_9H_{11}$] (**1a**)[1], [2,2,2-$(NMe_2)_3$-*closo*-2,1,7-$TaC_2B_9H_{11}$] (**1b**)[3], [2,2,2-$(NMe_2)_3$-*closo*-2,1,12-$TaC_2B_9H_{11}$] (**1c**), [3-Me-4,4,4-$(NMe_2)_3$-*closo*-4,1,2-$TaC_2B_9H_{10}$] (**1d**)[4], [4-Me-3,3,3-$(NMe_2)_3$-*closo*-3,1,2-$TaC_2B_9H_{10}$] (**1e**) and [3-Me-2,2,2-$(NMe_2)_3$-*closo*-2,1,7-$TaC_2B_9H_{10}$] (**1f**) were sealed in NMR tubes with CD_2Cl_2. In each case, the initial reaction causes one Ta–NMe_2 ligand to be replaced by a Ta–Cl, and by careful monitoring of the reaction mixture by ^{11}B NMR spectroscopy it was possible to obtain NMR data for the monochlorides [3-Cl-3,3-$(NMe_2)_2$-*closo*-3,1,2-$TaC_2B_9H_{11}$] (**2a**), [2-Cl-2,2-$(NMe_2)_2$-*closo*-2,1,7-$TaC_2B_9H_{11}$] (**2b**), [2-Cl-2,2-$(NMe_2)_2$-*closo*-2,1,12-$TaC_2B_9H_{11}$] (**2c**), [3-Me-4-Cl-4,4-$(NMe_2)_2$-*closo*-4,1,2-$TaC_2B_9H_{10}$] (**2d**), [4-Me-3-Cl-3,3-$(NMe_2)_2$-*closo*-3,1,2-$TaC_2B_9H_{10}$] (**2e**) and [3-Me-2-Cl-2,2-$(NMe_2)_2$-*closo*-2,1,7-$TaC_2B_9H_{10}$]



SCHEME 1
Reactions of amidotantalaboranes with dichloromethane reported by Wesemann[10]. All unlabelled vertices contain BH moieties

(**2f**) (Scheme 2). The reactions are exceptionally clean, the only other species present in the ^{1}H NMR spectrum was identified as NMe_2CD_2Cl. In all cases the ^{1}H NMR resonance attributed to Me_2NCD_2Cl (δ 2.16) increased in intensity as that associated with M–NMe_2 decreased. When the monoamminolysis reaction was complete in 14–18 days, integration of the ^{1}H NMR signals gave 12 (Ta–NMe_2) to 6 (NMe_2CD_2Cl) in all cases. The transformation was associated with a shift to higher frequency for the remaining M–NMe_2 ligands, consistent with the replacement of the amido with a more electronegative halide ligand. For the monochlorides **2d** and **2e**, where no molecular symmetry plane exists, two peaks corresponding to the non-equivalent NMe_2 groups are observed in their ^{1}H NMR spectra.

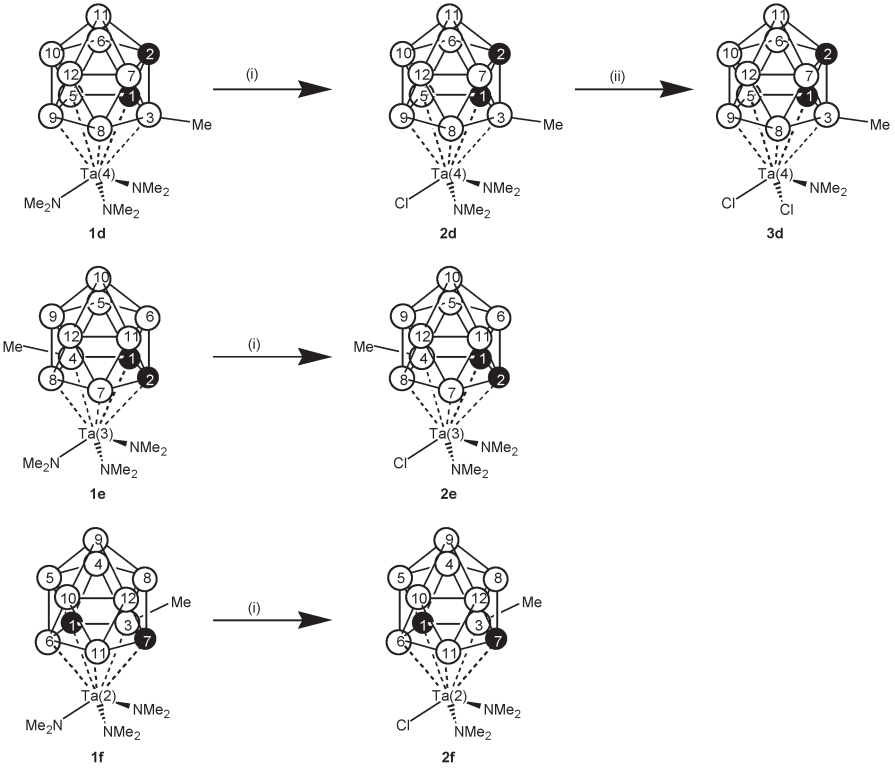


SCHEME 2

The reactions of **1a**–**1f** with CD_2Cl_2 to generate **2a**–**2f** and **3c**–**3e** on prolonged reactions. Reaction conditions: (i) CD_2Cl_2 14–18 days; (ii) CD_2Cl_2 3 months

By contrast with the clean monochlorination reaction, further chlorination was evident only for three complexes and required several months to give solutions containing about 30% of the starting monochloride together with the dichlorides [2,2-Cl_2-2-(NMe_2)-*closo*-2,1,7-$TaC_2B_9H_{11}$] (**3b**), [2,2-Cl_2-2-(NMe_2)-*closo*-2,1,12-$TaC_2B_9H_{11}$] (**3c**) and [3-Me-4,4-Cl_2-4-(NMe_2)-*closo*-4,1,2-$TaC_2B_9H_{10}$] (**3d**). Prolonged reaction, in an attempt to increase the conversion of the mono- to dichlorides, results in a mixture of products, none of which can be uniquely identified by NMR, although it is clear that B–H units have been replaced by B–Cl or B–N units.

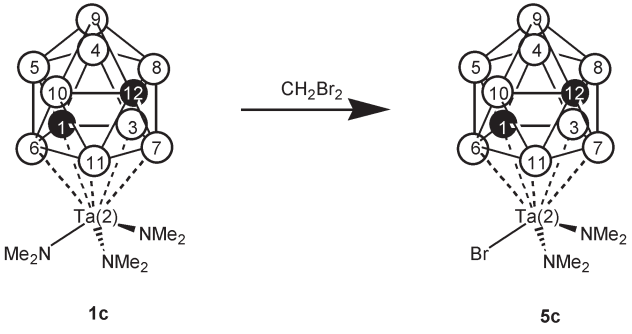
On prolonged reaction, the NMe_2CD_2Cl by-product reacts further with CD_2Cl_2 to give a product tentatively identified by mass spectrometry as $[Me_2N(CD_2Cl)(CD_2NMe_2)]^+Cl^-$. We have also obtained crystals, a partial structure of which reveals $Me_2N(CD_2X)_2$ units, but the extensive disorder cannot be successfully modelled, nor the X groups identified.



SCHEME 2
(*Continued*)

The reactions with CH_2Cl_2 described above result in the replacement of one NMe_2 ligand by an NMR-silent chloride ligand, together with the generation of NMe_2CD_2Cl. It is well established that the hydrolysis of tantalum chloro, amido and alkyl complexes may generate oxo-bridged Ta–O–Ta species[9,12–16]. The hydrolysis of **1a**–**1f** would generate species whose NMR spectra would be indistinguishable in terms of peak multiplicities from the chlorides that **2a**–**2f** are identified as. To discount this possibility the rational synthesis and characterisation of 3,3′-[3,3-$(NMe_2)_2$-3,1,2-$TaC_2B_9H_{11}]_2$(μ-O) (**4**) was addressed. Treating [3,3,3-$(NMe_2)_3$-3,1,2-$TaC_2B_9H_{11}$] (**1a**) with toluene (deoxygenated but not dried) afforded 3,3′-[3,3-$(NMe_2)_2$-3,1,2-$TaC_2B_9H_{11}]_2$-(μ-O) (**4**) directly as a pale yellow powder in low yield together with significant amounts of $[Me_2NH_2][nido\text{-}7,8\text{-}C_2B_9H_{12}]$. Crystals suitable for a X-ray diffraction study were obtained from a very dilute CH_2Cl_2 solution overlayered with pentane. The crystalline material displayed poor solubility in all common laboratory solvents, hampering spectroscopic characterisation, although demonstrating that **4** and **2a** are not the same compound.

To further confirm that the reaction occurring in CD_2Cl_2 is not a hydrolysis reaction, but replacement of NMe_2 by Cl we examined the reaction with CH_2Br_2 (Scheme 3). It might be reasonably expected that the rate of reaction would increase for the Br leaving group. Reaction of [2,2,2-$(NMe_2)_3$-*closo*-2,1,12-$TaC_2B_9H_{11}$] (**1c**) with neat CH_2Br_2 is at least an order of magnitude faster than with CH_2Cl_2 and in the absence of a definitive structural study lends further credence to the proposed formulations. To permit us to obtain full spectroscopic data for [2-Br-2,2-$(NMe_2)_2$-*closo*-2,1,12-$TaC_2B_9H_{11}$] (**5c**) the reaction was repeated with a C_6D_6 solution of CH_2Br_2, corresponding to approximately 4 equivalents of CH_2Br_2 per com-



1c **5c**

SCHEME 3
The reaction of **1c** with dibromomethane

plex **1c**. The NMR spectrum showed that CH_2Br_2 was consumed during the course of the reaction.

NMR Spectroscopy

^{11}B and ^{1}H NMR resonances for the monochlorides **2a**–**2f** were assigned with the aid of 2D ^{11}B-^{11}B COSY and $^{1}H\{^{11}B$ selective$\}$ spectra, and assignments are listed in Tables I and II along with the data for the previously reported tris(amido)tantalacarboranes **1a**–**1f** in CD_2Cl_2 for comparison.

We have previously reported that trends in ^{11}B chemical shifts for neighbouring (NE), antipodal (AE) and butterfly (BE) vertices on replacing a {BH} vertex with a metal $\{ML_n\}$ vertex indicate that NE and AE boron atoms are most affected by the substitution[3]. Similar trends were observed on replacing a {BH} vertex with a {BMe} vertex[4]. The spectroscopic data for complexes **1** and **2** listed in Table I reveal the changes in the ^{11}B NMR chemical shifts on the replacement of an amido ligand by a more electronegative chloride. Average chemical shift differences were to higher frequency, +3.5 ppm for NE, +4 ppm for AE and +2 ppm for BE boron atoms. For the methyl-substituted boron atoms in **2d**–**2f** the chemical shift differences are more pronounced. The ^{13}C NMR chemical shifts for the cage carbons are also influenced by ligand replacement and move approximately 6 ppm to higher frequency for NE carbons and 3 ppm for the BE carbons.

No such clear trends are observed for the ^{1}H NMR chemical shifts listed in Table II, the peaks are shifted to higher frequency in the range between 0.09 and 0.49 ppm for the hydrogens attached to boron and methyl groups. More pronounced effects are shown in chemical shifts for the protons attached to the NE cage carbons, moving to higher frequency in the region of 0.6 ppm.

A simple addition method to predict the ^{11}B NMR chemical shifts for the dichlorides and trichlorides based on the known shift differences between the monochlorides **2a**–**2f** and the tris(amido) complexes **1a**–**1f** is attractive. As shown in Table I, the differences in the ^{11}B NMR chemical shifts on going from the monochlorides, **2b**–**2d**, to the presumed dichlorides, **3b**–**3d**, do not correspond to those on going from the starting tris(amido) complexes, **1b**–**1d**, to these monochlorides. Thus the simple addition method fails for these complexes and clearly the influence of the ligands on the ^{11}B NMR chemical shifts of these metallacarboranes is complex.

Comparison of the ^{11}B NMR chemical shifts for the monobromide **5c** with the analogous monochloride **2c** reveals that the influence of the bro-

TABLE I

^{11}B and ^{13}C NMR chemical shift data for the tris(amido)- **1a–1f**, mono(chloro)bis(amido)- **2a–2f**, and di(chloro)mono(amido)tantaladicarbaboranes **3b–3d** in CD_2Cl_2

Compound	NE		BE			AE	^{13}C		
	B4,7	B8	B5,11	B9,12	B6	B10	C1,2		NMe_2
3,3,3-$(NMe_2)_3$-3,1,2-$TaC_2B_9H_{11}$ (**1a**)	–5.7	1.7	–13.8	–3.4	–13.8	–16.2	52.4		49.4
3-Cl-3,3$(NMe_2)_2$-3,1,2-$TaC_2B_9H_{11}$ (**2a**)	–2.0	4.9	–10.9	–0.7	–12.3	–12.3	57.0		46.6
Difference	*3.7*	*3.2*	*2.9*	*2.7*	*1.5*	*3.9*	*4.6*		*–2.8*
	B3	B6,11	B4,8	B5,12	B10	B9	C1,7		NMe_2
2,2,2-$(NMe_2)_3$-2,1,7-$TaC_2B_9H_{11}$ (**1b**)	–12.1	–5.6	–13.4	–6.3	–11.5	–17.4	57.6		49.3
2-Cl-2,2-$(NMe_2)_2$-2,1,7-$TaC_2B_9H_{11}$ (**2b**)	–7.6	–2.0	–11.1	–4.1	–9.0	–12.8	62.2		48.3
Difference	*4.5*	*3.6*	*2.3*	*2.2*	*2.5*	*4.6*	*4.6*		*–1.0*
2,2-Cl_2-2-NMe_2-2,1,7-$TaC_2B_9H_{11}$ (**3b**)	–2.1	1.1	–8.9	–2.1	–6.9	–8.9			
Difference	*4.5*	*3.1*	*2.2*	*2.0*	*2.1*	*3.9*			
	B3,6	B7,11	B4,5		B8,10	B9	C1	C12	NMe_2
2,2,2-$(NMe_2)_3$-2,1,12-$TaC_2B_9H_{11}$ (**1c**)	–6.5	–4.4	–13.9		–14.3	–19.4	64.1	62.4	49.7
2-Cl-2,2-$(NMe_2)_2$-2,1,12-$TaC_2B_9H_{11}$ (**2c**)	–2.6	–2.2	–11.7		–12.7	–15.9	73.5	65.9	48.0
Difference	*3.9*	*2.2*	*2.2*		*1.6*	*3.5*	*9.4*	*3.5*	*–1.7*
2,2-Cl_2-2-NMe_2-2,1,12-$TaC_2B_9H_{11}$ (**3c**)	0.4	0.0	–10.8		–10.8	–11.7			
Difference	*3.0*	*2.2*	*0.9*		*1.9*	*4.2*			

	B3	B5	B8	B9	B6	B7	B10	B12	B11	C1	C2	NMe_2
3-Me-4,4,4-$(NMe_2)_3$-4,1,2-$TaC_2B_9H_{10}$ (**1d**)	–0.5	–6.8	1.0	7.6	–12.6	–11.0	–12.1	–1.5	–19.9	56.7	59.5	49.5
3-Me-4-Cl-4,4-$(NMe_2)_2$-4,1,2-$TaC_2B_9H_{10}$ (**2d**)	2.4	–2.2	4.4	10.2	–11.1	–8.9	–9.5	0.8	–15.9	63.2	62.7	48.0,47.3
Difference	*2.9*	*4.6*	*3.4*	*2.6*	*1.5*	*2.1*	*2.6*	*2.3*	*4.0*	*6.5*	*3.2*	*–1.5,–1.8*
3-Me-4,4-Cl_2-4-NMe_2-4,1,2-$TaC_2B_9H_{10}$ (**3d**)	8.1	–1.7	5.6	15.2	–9.8	–7.3	–8.6	2.2	–12.1			
Difference	*5.7*	*0.5*	*1.2*	*5.0*	*1.3*	*1.6*	*0.9*	*1.6*	*3.8*			

TABLE I
(*Continued*)

Compound	NE			BE					AE	^{13}C		
	B4	B7	B8	B5	B11	B9	B12	B6	B10	C1	C2	NMe_2
4-Me-3,3,3-$(NMe_2)_3$-3,1,2-$TaC_2B_9H_{10}$ (**1e**)	3.2	–6.2	2.4	–10.2	–16.6	–1.2	–2.3	–13.1	–16.6	53.2	51.4	49.3
4-Me-3-Cl-3,3-$(NMe_2)_2$-3,1,2-$TaC_2B_9H_{10}$ (**2e**)	8.6	–2.9	4.9	–7.4	–14.0	1.7	–0.2	–12.4	–12.4	59.2	57.4	49.2
Difference	*5.4*	3.3	*2.5*	*2.8*	*2.6*	*2.9*	*2.1*	*0.7*	*4.2*	*6.0*	*6.0*	*–0.1*
	B3		B6,11	B4,8		B5,12	B10		B9	C1,7		NMe_2
3-Me-2,2,2-$(NMe_2)_3$-2,1,7-$TaC_2B_9H_{10}$ (**1f**)	–6.0		–6.6	–11.6		–6.6	–15.5		–19.2	59.1		49.1
3-Me-2-Cl-2,2-$(NMe_2)_2$-2,1,7-$TaC_2B_9H_{10}$ (**2f**)	–1.5		–3.4	–10.7		–5.2	–13.7		–15.1	64.0		49.4
Difference	*4.5*		*3.2*	*0.9*		*1.4*	*1.8*		*4.1*	*4.9*		*0.3*
	B3,6		B7,11	B4,5			B8,10		B9	C1	C12	NMe_2
2,2,2-$(NMe_2)_3$-2,1,12-$TaC_2B_9H_{11}$ (**1c**)	–6.0		–4.7	–12.3			–12.3		–17.2			
2-Br-2,2-$(NMe_2)_2$-2,1,12-$TaC_2B_9H_{11}$ (**5c**)	–2.1		–2.1	–11.0			–12.3		–14.7			
Difference	*3.9*		*2.6*	*1.3*			*0.0*		*3.5*			

TABLE II

^{1}H NMR data for the tris(amido)- **1a–1f**, mono(chloro)bis(amido)- **2a–2f**, and di(chloro)mono(amido)tantaladicarbaboranes **3b–3d** in CD_2Cl_2

Compound	NE		BE			AE	Cage and amide protons	
	B4,7H	B8H	B5,11H	B9,12H	B6H	B10H	C1,2H	NMe_2
3,3,3-$(NMe_2)_3$-3,1,2-$TaC_2B_9H_{11}$ (**1a**)	1.65	1.65	2.21	2.32	2.41	3.05	2.76	3.66
3-Cl-3,3-$(NMe_2)_2$-3,1,2-$TaC_2B_9H_{11}$ (**2a**)	1.92	2.03	2.47	2.58	2.50	3.18	3.43	3.87
Difference	*0.27*	*0.38*	*0.26*	*0.26*	*0.09*	*0.13*	*0.67*	*0.21*
	B3H	B6,11H	B4,8H	B5,12H	B10H	B9H	C1,7H	NMe_2
2,2,2-$(NMe_2)_3$-2,1,7-$TaC_2B_9H_{11}$ (**1b**)	1.90	1.59	2.17	2.29	2.05	2.82	2.14	3.56
2-Cl-2,2-$(NMe_2)_2$-2,1,7-$TaC_2B_9H_{11}$ (**2b**)	2.43	1.98	2.53	2.56	2.43	3.09	2.69	3.88
Difference	*0.53*	*0.39*	*0.36*	*0.27*	*0.38*	*0.27*	*0.55*	*0.32*
2,2-Cl_2-2-NMe_2-2,1,7-$TaC_2B_9H_{11}$ (**3b**)	2.76	2.33	2.76	2.76	2.80	3.32	3.34	4.46
Difference	*0.33*	*0.35*	*0.23*	*0.20*	*0.37*	*0.23*	*0.65*	*0.58*
	B3,6H	B7,11H	B4,5H	B8,10H		B9H	C1H C12H	NMe_2
2,2,2-$(NMe_2)_3$-2,1,12-$TaC_2B_9H_{11}$ (**1c**)	1.58	1.70	2.34	2.34		3.05	2.34 2.89	3.62
2-Cl-2,2-$(NMe_2)_2$-2,1,12-$TaC_2B_9H_{11}$ (**2c**)	2.07	1.90	2.52	2.52		3.15	2.88 3.15	3.86
Difference	*0.49*	*0.20*	*0.18*	*0.18*		*0.10*	*0.54 0.26*	*0.24*
2,2-Cl_2-2-NMe_2-2,1,12-$TaC_2B_9H_{11}$ (**3c**)	2.43	2.25	2.73	2.66		3.31	3.31 3.41	4.45
Difference	*0.36*	*0.35*	*0.21*	*0.14*		*0.16*	*0.43 0.26*	*0.59*
	B3Me B5H	B8H B9H	B6H	B7H	B10H B12H	B11H	C1H C2H	NMe_2
3-Me-4,4,4-$(NMe_2)_3$-4,1,2-$TaC_2B_9H_{10}$ (**1d**)	0.44 1.52	1.93 1.93	2.63	2.16	2.12 2.63	3.00	2.84 3.53	3.62
3-Me-4-Cl-4,4-$(NMe_2)_2$-4,1,2-$TaC_2B_9H_{10}$ (**2d**)	0.61 1.94	2.20 2.09	2.79	2.40	2.40 2.71	3.08	3.42 3.76	3.81, 3.76
Difference	*0.17 0.42*	*0.27 0.16*	*0.16*	*0.24*	*0.28 0.08*	*0.08*	*0.58 0.23*	*0.19, 0.14*
3-Me-4,4-Cl_2-4-NMe_2-4,1,2-$TaC_2B_9H_{10}$ (**3d**)[a]	0.86						4.11 3.96	4.35
Difference	*0.15*						0.69 0.20	*0.54, 0.59*

TABLE II
(*Continued*)

Compound	NE			BE					AE	Cage and amide protons		
	B4Me	B7H	B8H	B5H	B11H	B9H	B12H	B6H	B10H	C1H	C2H	NMe_2
4-Me-3,3,3-$(NMe_2)_3$-3,1,2-$TaC_2B_9H_{10}$ (**1e**)	0.31	1.55	1.64	2.04	1.96	2.26	2.31	2.23	2.89	2.64	2.88	3.55
4-Me-3-Cl-3,3-$(NMe_2)_2$-3,1,2-$TaC_2B_9H_{10}$ (**2e**)	0.50	1.67	1.89	2.32	2.32	2.58	2.48	2.40	3.04	3.39	3.36	3.77, 3.75
Difference	*0.19*	*0.12*	*0.25*	*0.28*	*0.36*	*0.32*	*0.17*	*0.17*	*0.15*	*0.75*	*0.48*	*0.22, 0.20*
	B3Me	B6,11H		B4,8H		B5,12H	B10H		B9H	C1,7H		NMe_2
3-Me-2,2,2-$(NMe_2)_3$-2,1,7-$TaC_2B_9H_{10}$ (**1f**)	0.45	1.58		2.19		2.38	1.85		2.74	2.19		3.55
3-Me-2-Cl-2,2-$(NMe_2)_2$-2,1,7-$TaC_2B_9H_{10}$ (**2f**)	0.68	1.93		2.51		2.61	2.30		2.99	2.75		3.89
Difference	*0.23*	*0.35*		*0.32*		*0.23*	0.45		*0.25*	*0.56*		*0.34*
	B3,6H	B7,11H		B4,5H			B8,10H		B9H	C1H	C12H	NMe_2
2-Br-2,2-$(NMe_2)_2$-2,1,12-$TaC_2B_9H_{11}$ (**5c**)	2.28	1.96		3.08			2.96		3.71	2.96	3.30	3.29

[a] $^{11}B\{^1H$-selective$\}$ not recorded.

mide ligand on the ^{11}B NMR chemical shifts is, as expected, similar to that of chloride, except for a smaller effect on the butterfly (BE) boron atoms.

X-Ray Crystallography

As described above, the partial hydrolysis of **1a** leads to 3,3′-[3,3-$(NMe_2)_2$-3,1,2-$TaC_2B_9H_{11}]_2$(μ-O) (**4**), and crystals suitable for a diffraction study were obtained. Selected bond lengths and angles appear in Table III, and Fig. 1 shows a view of the molecular structure. The molecule has an almost linear Ta–O–Ta bridge (Ta–O–Ta = 176.73(15)°) and overall is close to C_2 symmetry. Each half of the molecule of **4** can be considered as an example of a $(C_2B_9H_{11})Ta(XL)_3$ fragment where XL denotes a ligand which is σ-bound and a potential π-donor to tantalum. In **4** each NMe_2 ligand is close to planar, with the sum of angles close to 360°, so that the amido ligands are acting as π-donors.

The orientation of the NMe_2 ligands with respect to the remainder of the metal coordination sphere can be described by the dihedral angle τ between the NC_2 and CbTaN planes, where Cb is the centroid of the co-ordinated dicarbollide face. In **4** the NMe_2 ligands containing N2A (τ = 77.2°) and

TABLE III
Selected bond lengths (in Å) and angles (in °) for compound **4**, where Cb means centroid of the C_2B_3 ring

Ta3A–O1	1.934(2)	Ta3B–O1	1.931(2)
Ta3A–N2A	1.941(3)	Ta3B–N2B	1.949(3)
Ta3A–N1A	1.953(3)	Ta3B–N1B	1.959(3)
C1A–C2A	1.572(5)	C1B–C2B	1.579(5)
C1A–B4A	1.685(6)	C1B–B4B	1.672(5)
C2A–B7A	1.685(6)	C2B–B7B	1.689(5)
B7A–B8A	1.767(6)	B7B–B8B	1.769(6)
B8A–B4A	1.775(6)	B8B–B4B	1.776(6)
Ta3A–CbA	2.006	Ta3B–CbB	2.000
O1–Ta3A–N1A	105.98(12)	O1–Ta3B–N1B	106.28(12)
O1–Ta3A–N2A	100.43(12)	O1–Ta3B–N2B	101.49(12)
N1A–Ta3A–N2A	97.68(14)	N1B–Ta3B–N2B	96.08(13)
Ta3A–O1–Ta3B	176.73(15)		

N2B (81.0°) are close to the "horizontal" orientation (90°) and the ligands containing N1A (10.9°) and N1B (11.5°) are close to "vertical" (0°). The horizontal ligands are approximately *trans* to the C–C bond of the $C_2B_9H_{11}$ unit, with (C1/C2 centroid)–Cb–Ta–N torsion angles of 176.3° (N2A) and 173.7° (N2B). Such ligand orientations are similar to those seen in other examples of [3,3,3-$(XL)_3$-*closo*-3,1,2-$TaC_2B_9H_{11}$] complexes where XL = NMe_2 [1], N=C(R)NMe_2 (R = Me, C_6H_4F)[2], S_2CNMe_2 [1], O_2CNMe_2 [1], and $OC_6H_3Me_2$ [2], and in each case the ligands are arranged in a manner that allows maximum possible π-electron donation to the metal from the ligands, often described as a strong *trans* influence of the dicarbollide ligand, and also observed in indenyl[17,18], pyrrolyl[19] and carbonyl[20] complexes.

The metallacarborane units in **4** are arranged in a *cisoid* fashion across the Ta–O–Ta unit, with the two Ta–O distances equal within experimental error and similar to those in $[TaCl_2(NHMe_2)(NMe_2)_2]_2$(μ-O) (1.928 and 1.917 Å)[15]. The Ta–O bonds are longer than those in $[TaX_3(\eta\text{-}C_5Me_5)]_2$(μ-O) (X = Me 1.909 Å, Br 1.909 Å)[14] and $[(TaX_5)_2(\mu\text{-}O)]^{2-}$ (X = F, Cl; 1.875 to 1.887 Å)[13], or

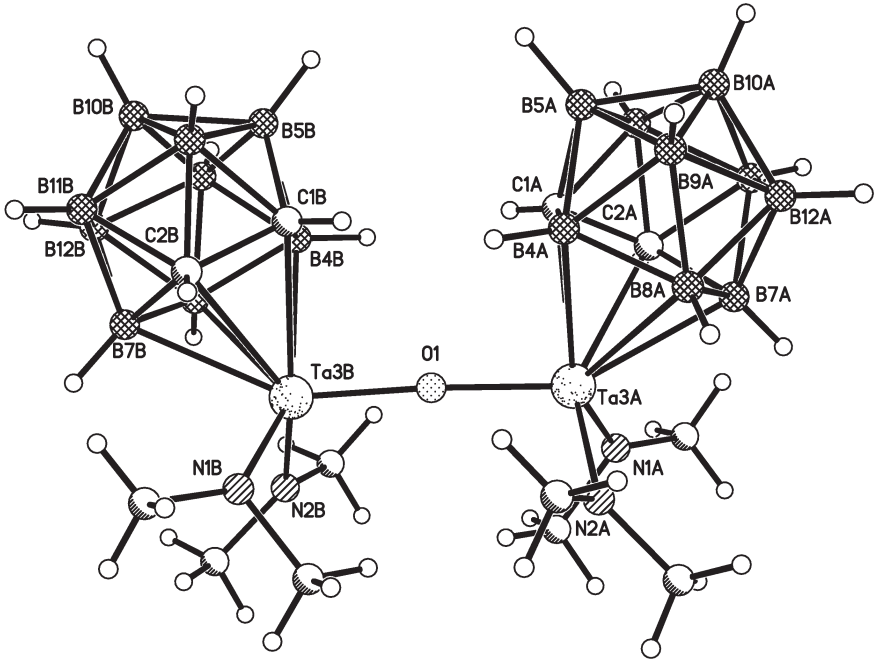


FIG. 1

The molecular structure of 3,3′-[3,3-$(NMe_2)_2$-3,1,2-$TaC_2B_9H_{11}]_2$(μ-O) (**4**) showing 50% probability ellipsoids, with hydrogen atoms as arbitrary sized spheres

$[TaCl_3\{CH(SiMe_3)_2\}]_2(\mu\text{-}O)$ (1.881 Å)[15], complexes without strong π-donor ligands. Compound **4** makes an interesting contrast with the amidinate analogue 3,3′-[3,3-$(MeC(=N)NMe_2)_2$-3,1,2-$TaC_2B_9H_{11}]_2(\mu\text{-}O)$[12], which shows a *transoid* arrangement of the boron ligands across the Ta–O–Ta unit and remarkably has two non-equal Ta–O distances (1.887(5) and 1.936(4) Å). The reasons for the asymmetry of this unit is not clear, although Ta–O bond lengths in these species are clearly defined by electronic factors.

Conclusion

Monochlorination of the six complexes of general formulae $[(NMe_2)_3TaC_2B_9H_{11}]$ **1a**–**1c** and $[(NMe_2)_3TaC_2B_9H_{10}Me]$ **1d**–**1f** with CD_2Cl_2 gave complexes $[Cl(NMe_2)_2TaC_2B_9H_{11}]$ **2a**–**2c** and $[Cl(NMe_2)_2TaC_2B_9H_{10}Me]$ **2d**–**2f** with an amido ligand replaced by a chloride in excellent yields. Monobromination of [2,2,2-$(NMe_2)_3$-*closo*-2,1,12-$TaC_2B_9H_{11}$] (**1c**) with CH_2Br_2 gave the analogous monobromide [2-Br-2,2-$(NMe_2)_2$-*closo*-2,1,12-$TaC_2B_9H_{11}$] (**5c**), indicating that monobromination of the tris(amido) complexes with CH_2Br_2 is straightforward. The molecular structure of the hydrolysed product 3,3′-[3,3-$(NMe_2)_2$-3,1,2-$TaC_2B_9H_{11}]_2(\mu\text{-}O)$ (**4**) from [3,3,3-$(NMe_2)_3$-3,1,2-$TaC_2B_9H_{11}$] (**1a**) was determined by X-ray crystallography and its insolubility in CD_2Cl_2 eliminates itself as a product in the reaction of $[(NMe_2)_3TaC_2B_9H_{11}]$ (**1a**) with CD_2Cl_2.

EXPERIMENTAL

General Comments

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. When required, solvents were dried by prolonged reflux over the appropriate drying agent prior to distillation and deoxygenation by freeze-pump-thaw processes where appropriate. NMR solvents were vacuum-distilled from suitable drying agents and stored under a dry nitrogen atmosphere. NMR spectra were recorded on a Varian Unity-300 (^1H, ^{11}B, ^{13}C) or Varian 500 (^{11}B, ^1H, ^{13}C, 2D ^{11}B-$^{11}B\{^1H\}$ COSY). $^1H\{^{11}B$-selective$\}$ spectra were recorded on the Unity-300. All chemical shifts are reported in δ (ppm) and coupling constants in Hz. ^1H NMR spectra were referenced to residual ^1H impurity in the solvent ($CDHCl_2$, 5.32 ppm; C_6D_5H, 7.15 ppm). ^{13}C NMR spectra were referenced to the solvent resonance (C_6D_6, 128 ppm; CD_2Cl_2 53.8 ppm). ^{11}B NMR spectra were referenced externally to $Et_2O{\cdot}BF_3$ in Et_2O, δ = 0 ppm. Except where otherwise indicated, all spectra were recorded at ambient temperature.

General Reaction with CD_2Cl_2

A crystalline sample of **1a** (0.025 g, 0.0625 mmol) was dissolved in CD_2Cl_2 (0.5 ml) in a NMR tube and flame-sealed. The ^1H NMR was recorded to confirm the initial purity of the sample. Spectroscopic properties (^1H, ^{11}B) were then inspected at two-day intervals and full data recorded following completion of the reaction as determined by the relative intensities of the M–NMe_2 and Me_2NCD_2Cl resonances in the ^1H NMR spectrum.

Identical procedures were followed for the reactions of **1b**–**1f** with CD_2Cl_2.

Reaction of **1c** with CH_2Br_2

A solution of dry CH_2Br_2 (20 μl) in benzene-d_6 (0.5 ml) was transferred into a NMR tube containing a crystalline sample of **1c** (0.025 g, 0.0625 mmol) and the tube flame-sealed. The ^1H NMR spectrum was then recorded to confirm the number of mole equivalents of CH_2Br_2 (by integration of CH_2Br_2 resonance relative to NMe_2). Spectroscopic properties (^1H, ^{11}B) were then inspected at two-day intervals and full data recorded following completion as determined by the relative intensities attributed to M–NMe_2 and Me_2NCH_2Br resonances in the ^1H NMR spectrum.

TABLE IV
Crystallographic data for compound **4**·$(CH_2Cl_2)_2$

Empirical formula	$C_{14}H_{50}B_{18}Cl_4N_4OTa_2$
Formula weight	988.86
Temperature, K	120(2)
Crystal system	Triclinic
Space group	P-1
a, Å	12.372(1)
b, Å	12.388(1)
c, Å	13.144(1)
α, °	81.400(4)
β, °	74.815(4)
γ, °	70.236(4)
U, Å^3	1 825.5(3)
Z	2
μ(MoKα), mm^{-1}	6.303
Reflections collected	20 859
Independent reflections	8 971
R(int)	0.0206
$R[I > 2\sigma(I)]$	0.0251
$wR(F^2)$ (all data)	0.0696

X-Ray Crystallography

Single-crystal diffraction experiments on **4** were carried out with a Smart 1K CCD area detector, using graphite-monochromatised MoKα radiation ($\bar{\lambda}$ = 0.71073 Å). The reflection intensities were corrected for absorption by numerical integration based on measurements of the crystal and face-indexing using SHELXTL software[21]. The structure was solved by direct methods and refined by full-matrix least squares against F^2 of all data, using SHELXTL programs[21]. Crystal data and experimental details are listed in Table IV.
CCDC 182523 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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