

Electrophile-Induced Nucleophilic Substitution Reactions of 7-Trimethylamine-7-Carba-nido-Undecaborane, 7-Me₃N-nido-7-CB₁₀H₁₂

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Summary: The AlCl₃-catalysed chlorination and deuteration reactions of 7-Me₃N-nido-7-CB₁₀H₁₂ are presented. When 7-Me₃N-nido-7-CB₁₀H₁₂ is treated with anhydrous HCl in the presence of AlCl₃ electrophile induced nucleophilic chlorination occurs to yield 7-Me₃N-9-Cl-nido-7-CB₁₀H₁₁ as the major product, with a minor component of the disubstituted species, 7-Me₃N-6,9-Cl₂-nido-7-CB₁₀H₁₀. When DCl in the presence of AlCl₃ is used, deuterium substitution occurs in addition to chlorination and with the formation of 7-Me₃N-9-Cl-1,4,5,6,10-D₅-nido-7-CB₁₀H₁₀. A similar dichlorinated by-product, 7-Me₃N-6,9-Cl₂-1,4,5,10-D₄-nido-7-CB₁₀H₆ is also obtained. The structures of all isolated compounds were unambiguously determined via elemental analyses, IR, mass spectroscopy, ¹H, ¹¹B and 2-D ¹¹B-¹¹B NMR spectra.

Introduction

The monocarbon carborane, 7-Me₃N-nido-7-CB₁₀H₁₂ (I), (Fig. 1) has been reported earlier [1]. Boron substituted derivatives of I have been described previously [2,3]. Direct chlorination with Cl₂, or N-chlorosuccinimide yielded 7-Me₃N-4(6)-Cl-nido-7-CB₁₀H₁₁ and nido-[4(6)-Cl-7-CB₁₀H₁₂]⁻ [2]. Similarly, bromination with the aid of AlCl₃ catalyst gave nido-[4,6-Br₂-7-CB₁₀H₁₁]⁻ and 7-Me₃N-4,6-Cl₂-nido-7-CB₁₀H₁₀ [3]. Furthermore, compound 7-Me₃N-8,11-D₂-nido-7-CB₁₀H₁₀ [3], was prepared from the deuterated decaborane, 6,9-D₂-B₁₀H₁₂ [4]. Although the positions of substitution were not unambiguously determined by ¹¹B NMR spectroscopy.

This paper reports the chlorination and deuteration reactions of I with hydrogen chloride and deuterium chloride respectively, in the presence of AlCl₃ as a catalyst. Their structures were established unambiguously through two-dimensional ¹¹B-¹¹B NMR spectroscopy.

Results and Discussion

Preparation

The AlCl₃-catalysed substitution reactions of I with gaseous HCl in CS₂ at ambient temperature

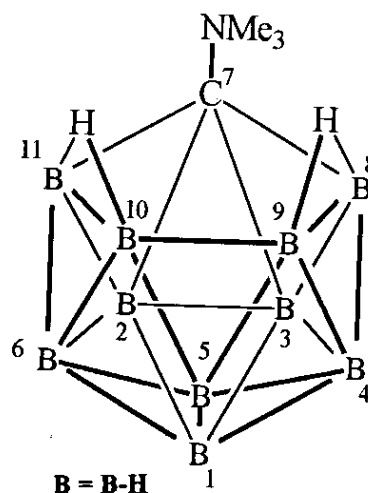


Fig. 1: Structure and numbering system of 7-Me₃N-nido-7-CB₁₀H₁₂(I)

gave rise to 7-Me₃N-9-Cl-nido-7-CB₁₀H₁₁ (Fig. 2a) as the major product, with a minor component of the disubstituted species, 7-Me₃N-6,9-Cl₂-nido-7-CB₁₀H₁₀ (Fig. 2b). When DCl in the presence of AlCl₃ was used, deuterium substitution occurred in addition to chlorination and with the formation of 7-Me₃N-9-Cl-1,4,5,6,10-D₅-nido-7-CB₁₀H₆ (IIIa)

Table-1: Signal assignments in the $^1\text{H-NMR}$ spectra* of chlorinated and deuterated derivatives of 7- $\text{Me}_3\text{N-nido-7-CB}_{10}\text{H}_{12}(\text{I})$

Compound	C(7)NMe ₃	B(5)H	B(2,3)H	B(8,11)H	B(9,10)H	B(1)H	B(4,6)H	B(8,9) and B(10,11) μH
7- $\text{Me}_3\text{N-nido-7-CB}_{10}\text{H}_{12}(\text{I})$	3.12(9)	2.50(1)	2.35(2)	2.25(2)	1.28(2)	1.18(1)	0.4(2)	-3.54(2)
7- $\text{Me}_3\text{N-9-Cl-nido-7-CB}_{10}\text{H}_{11}(\text{IIa})$	3.14(9)	2.93(1)	2.37(1)	2.62(1)	1.61(1)	1.14(1)	0.72(1)	-1.54(1)
			2.21(1)	2.19(1)			0.48(1)	-3.08(1)
7- $\text{Me}_3\text{N-6,9-Cl}_2\text{-nido-7-CB}_{10}\text{H}_{10}(\text{IIb})$	3.14(9)	2.48(1)	2.27(1)	2.42(2)	1.44(1)	1.10(1)	0.50(1)	-1.96(1)
			1.94(1)					-3.52(1)
7- $\text{Me}_3\text{N-9-Cl-1,4,5,6,10-D}_3\text{-nido-7-CB}_{10}\text{H}_6(\text{IIIa})$	3.14(9)	-	2.37(1)	2.62(1)	-	-	-	-1.54(1)
			2.21(1)	2.19(1)	-	-	-	-3.08(1)
7- $\text{Me}_3\text{N-6,9-Cl}_2\text{-1,4,5,10-D}_4\text{-nido-7-CB}_{10}\text{H}_6(\text{IIIb})$	3.14(9)	-	2.27(1)	2.42(2)	-	-	-	-1.96(1)
			1.94(1)		-	-	-	-3.52(1)

* δ_{H} assignments based on 2-D and boron decoupled $^1\text{H-}(^{11}\text{B})$ spectra, all signals are singlets, relative intensities in parentheses.

Table-2: Signal assignments in the $^{11}\text{B NMR}$ spectra* of chlorinated and deuterated of 7- $\text{Me}_3\text{N-nido-7-CB}_{10}\text{H}_{12}(\text{I})$

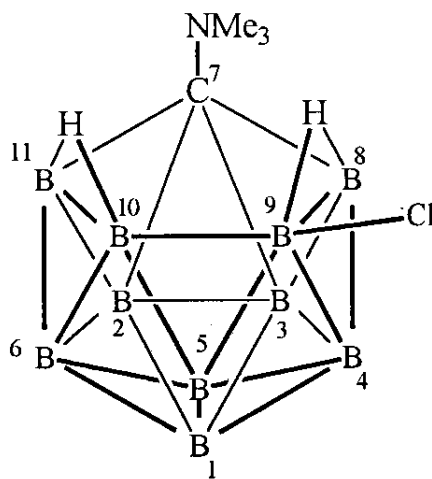
Compound	B(5)	B(2)	B(3)	B(8)	B(11)	B(9)	B(10)	B(1)	B(4)	B(6)
7- $\text{Me}_3\text{N-nido-7-CB}_{10}\text{H}_{12}(\text{I})$	2.6	-8.1	-8.1	-12.3	-12.3	-20.8	-20.8	-24.6	-31.4	-31.4
7- $\text{Me}_3\text{N-9-Cl-nido-7-CB}_{10}\text{H}_{11}(\text{IIa})$	3.9	-12.5	-9.4	-11.0	-13.5	-9.4 ^b	-18.8	-26.4	-28.5	-31.6
7- $\text{Me}_3\text{N-6-9-Cl}_2\text{-nido-7-CB}_{10}\text{H}_{10}(\text{IIb})$	3.3	-9.8	-11.5	-14.3	-14.3	-11.5 ^b	-21.0	-26.8	-30.6	-17.0 ^c
7- $\text{Me}_3\text{N-9-Cl-1,4,5,6,10-D}_3\text{-nido-7-CB}_{10}\text{H}_6(\text{IIIa})$	3.9 ^a	-12.5	-9.4	-11.0	-13.5	-9.4 ^b	-18.8 ^d	-26.4 ^d	-28.8 ^d	-31.6 ^d
7- $\text{Me}_3\text{N-6,9-Cl}_2\text{-1,4,5,10-D}_4\text{-nido-7-CB}_{10}\text{H}_6(\text{IIIb})$	3.3 ^d	-9.8	-11.5	-14.3	-14.3	-11.5 ^b	-21.0 ^d	-26.8 ^d	-30.6 ^d	-17.0 ^c

* δ_{B} assignments based on 2-D spectra, all signals in proton coupled spectra are doublets.

^b singlets of the chlorine substituted BH group, underneath the doublets of the unsubstituted B(3)

^c singlets of the second chlorine substituted BH group.

^d singlets of the deuterium substituted BH group.



B = B-H except for B(9)

Fig. 2: Structure of 7- $\text{Me}_3\text{N-9-Cl-nido-7-CB}_{10}\text{H}_{11}(\text{IIa})$

and a similar dichlorinated product, 7- $\text{Me}_3\text{N-6,9-Cl}_2\text{-1,4,5,10-D}_4\text{-nido-7-CB}_{10}\text{H}_6(\text{IIIb})$. It was observed that these reactions did not proceed without catalysis at any measurable rate, rather the proposed electrophile-induced nucleophilic substitution (EINS) mechanism [5] resulted in such chlorination of deuteration.

Structural characterization by N.M.R. Spectroscopy

The ^{11}B , ^1H , $^1\text{H-}[^{11}\text{B}]$ and 2-D $^{11}\text{B-}^{11}\text{B}$ NMR data for I and its substituted derivatives are presented in Tables 1-3. The assignments, which are unambiguous for most of the compounds examined, are based on considerations of the COSY coupling correlations together with bridge hydrogen locations. These were deduced from fine structure (on line narrowing) or broadening of ^{11}B resonances, or by decoupling specific boron environments in the $^1\text{H-}(^{11}\text{B})$ spectra [6].

The ^{11}B NMR signals of IIa (Table-2), show nine doublets, although the resonance of relative area two at δ 9.4 ppm can be attributed to superposition of the chlorine-coordinated B(9) and the unsubstituted B(3). If these signals are compared with the ^{11}B NMR data of the parent carborane I [3,7], the highfield (low frequency) resonance at δ 20.8 ppm in I is shifted downfield (high frequency) on substitution, giving a singlet underneath the doublet at δ 9.4 ppm.

The ^{11}B NMR signal assignment of IIIa shows five additional singlets at positions, B(1);

Table-3: Cross-peaks observed in the 2-D ^{11}B - ^{11}B NMR spectra of chlorinated and deuterated derivatives of 7-Me₃N-nido-7-CB₁₀H₁₂ (I)

Compound	Cross peaks
7-Me ₃ N-nido-7-CB ₁₀ H ₁₂ (I)	B(5) [(9,10) ^s , B(1) ^m , B(4,6) ^m] B(2,3) [B(8,11) ^w , B(1) ^s , B(4,6) ^s] B(8,11) [B(2,3) ^w , B(9,10) ^o , B(4,6) ^s] B(9,10) [B(5) ^s , B(8,11) ^o , B(4,6) ^s] B(1) [B(5) ^m , B(2,3) ^s , B(4,6) ^s] B(4,6) [B(5) ^m , B(2,3) ^s , B(8,11) ^s , B(9,10) ^o , B(1) ^s]
7-Me ₃ N-9-Cl-nido-7-CB ₁₀ H ₁₁ (IIa)	B(5) [B(9) ^s , B(10) ^s , B(1) ^s , B(4) ^m , B(6) ^m] B(9,3) [B(5) ^s , B(8) ^o , B(2) ^w , B(10) ^s , B(1) ^s , B(4) ^s] B(8) [B(3,9) ^o , B(4) ^m] B(2) [B(3) ^w , B(11) ^o , B(1) ^m , B(6) ^m] B(11) [B(2) ^o , B(10) ^o , B(6) ^m] B(10) [B(5) ^s , B(9) ^s , B(11) ^o , B(6) ^s] B(1) [B(5) ^s , B(3) ^s , B(2) ^s , B(4) ^w , B(6) ^m] B(4) [B(5) ^m , B(9,3) ^s , B(8) ^m , B(1) ^m] B(6) [B(5) ^m , B(2) ^m , B(11) ^m , B(10) ^s , B(1) ^m]
7-Me ₃ N-6-9-Cl ₂ -nido-7-CB ₁₀ H ₁₀ (IIb)	B(5) [B(9) ^s , B(6) ^m , B(10) ^s , B(1) ^s , B(1) ^s , B(4) ^m] B(2) [B(3) ^w , B(11) ^w , B(6) ^m , B(1) ^m] B(3,9) [B(5) ^s , B(2) ^w , B(8) ^o , B(10) ^s , B(4) ^s] B(8,11) [B(2) ^w , B(3,9) ^o , B(6) ^m , B(10) ^o , B(10) ^s , B(4) ^m] B(6) [B(5) ^m , B(2) ^m , B(11) ^m , B(10) ^s , B(1) ^m] B(10) [B(5) ^s , B(9) ^s , B(11) ^o , B(6) ^s] B(1) [B(5) ^s , B(2) ^s , B(3) ^s , B(6) ^m , B(4) ^w] B(4) [B(5) ^m , B(9,3) ^s , B(8) ^m , B(1) ^w]
7-Me ₃ N-9-Cl-1,4,5,6,10-D ₅ -nido-7-CB ₁₀ H ₆ (IIIa)	B(5) [B(9) ^s , B(10) ^s , B(1) ^s , B(4) ^m , B(6) ^m] B(9,3) [B(5) ^s , B(8) ^o , B(2) ^w , B(10) ^s , B(1) ^s , B(4) ^s] B(8) [B(3,9) ^o , B(4) ^m] B(2) [B(3) ^w , B(11) ^o , B(1) ^m , B(6) ^m] B(11) [B(2) ^o , B(10) ^o , B(6) ^m] B(10) [B(5) ^s , B(9) ^s , B(11) ^o , B(6) ^s] B(1) [B(5) ^s , B(3) ^s , B(2) ^s , B(4) ^w , B(6) ^m] B(4) [B(5) ^m , B(9,3) ^s , B(8) ^m , B(1) ^w] B(6) [B(5) ^m , B(2) ^m , B(11) ^m , B(10) ^s , B(1) ^m]
7-Me ₃ N-6,9-Cl ₂ -1,4,5,10-D ₄ -nido-7-CB ₁₀ H ₆ (IIIb)	B(5) [B(9) ^s , B(6) ^m , B(10) ^s , B(1) ^s , B(4) ^m] B(2) [B(3) ^w , B(11) ^w , B(6) ^m , B(1) ^m] B(3,9) [B(5) ^s , B(2) ^w , B(8) ^o , B(10) ^s , B(4) ^s] B(8,11) [B(2) ^w , B(3,9) ^o , B(6) ^m , B(10) ^o , B(4) ^m] B(6) [B(5) ^m , B(2) ^m , B(11) ^m , B(10) ^s , B(1) ^m] B(10) [B(5) ^s , B(9) ^s , B(11) ^o , B(6) ^s] B(1) [B(5) ^s , B(2) ^s , B(3) ^s , B(6) ^m , B(4) ^w] B(4) [B(5) ^m , B(9,3) ^s , B(8) ^m , B(1) ^w]

*atoms giving cross peaks with the observed atom (on diagonal) are listed in brackets with right superscripts indicate intensities of the off-diagonal interactions (s-strong, m=medium, w-weak, 0-zero interaction). Observed atoms (off brackets) are listed upfield.

B(4); B(5); B(6) and B(10) after deuterium substitution. The most interesting feature is that only the terminal positions were deuterated, the other four terminal and bridge sites remained protonated.

Similarly, ^{11}B NMR spectra of IIb and IIIb were also recorded whose signal assignments are given in Table-2.

Additional insight was given by 2-D- ^{11}B - ^{11}B NMR measurements of I, IIa,b and IIIa,b. In the scheme, presented in Table-3, all adjacent borons give rise to observed cross peaks expected in 2-D spectra for the geometry depicted in Fig. 1 except

for those between the B(8)-B(9) and B(10)-B(11) nuclei (four borons coupled to hydrogen bridges) which are not observable. It is in close agreement with the reported study [8] that in boron clusters no correlation is observed between hydrogen bridged boron nuclei since the electron density in the B-H-B bond is negligible along the B-B vector [9].

Table-4 reflects the influence of the B(6) and B(9) chlorine substitution on the ^{11}B NMR chemical shifts in terms of $\Delta\delta$, $\Delta\delta$ and K_2 values. Taking unsubstituted boron atoms of IIa, b and IIIa,b into account, $\Delta\delta$ and K_2 values of the dichlorinated species are greater than the monochlorinated species.

Table-4: ^{11}B NMR chemical shift changes ($\Delta\delta_i$)^a for chlorinated and deuterated derivatives of 7-Me₃N-nido-7-CB₁₀H₁₄(I)

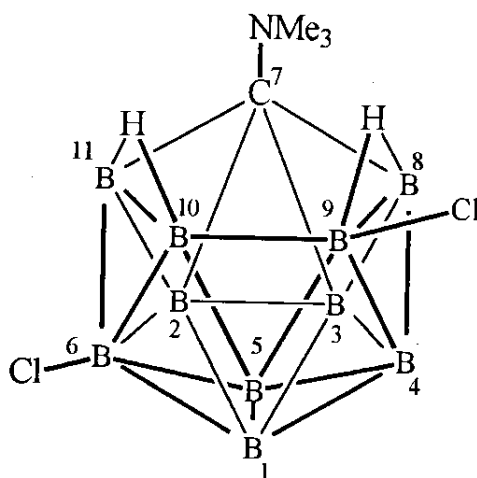
Compound	B(1)	B(2)	B(3)	B(4)	B(5)	B(6)	B(8)	B(9)	B(10)	B(11)	Δ^b_B	K_2^c
7-Me ₃ N-9-Cl-nido-7-CB ₁₀ H ₁₁ (IIa)	-1.8	-4.4	-1.3	2.8	1.3	-0.2	1.3	1.14	2.0	-1.2	-0.17	5.09
7-Me ₃ N-6-9-Cl ₂ -nido-7-CB ₁₀ H ₁₀ (IIb)	-2.2	-1.7	-3.4	0.8	0.7	14.4	-2.0	9.3	-0.2	-2.0	-12.5	146.92
7-Me ₃ N-9-Cl-1,4,5,6,10-D ₅ -nido-7-CB ₁₀ H ₆ (IIIa)	-1.8	-4.4	-1.3	2.8	1.3	-0.2	1.3	1.14	2.0	-1.2	-0.17	5.09
7-Me ₃ N-6,9-Cl ₂ -1,4,5,10-D ₄ -nido-7-CB ₁₀ H ₆ (IIIb)	-2.2	-1.7	-3.4	0.8	0.7	14.4	-2.0	9.3	-0.2	-2.0	-12.5	146.92

^a δ_i (substituted δ_i (parent compound))^b mean shift for unsubstituted atoms defined as

$$\Delta\delta = \frac{i = n}{i = 1} \sum (n = \text{number of unsubstituted atoms})$$

^c variance of the shift from the mean value defined as

$$K_2 = \frac{i = n}{i = n} \sum (\Delta\delta_i - \Delta\delta)^2$$

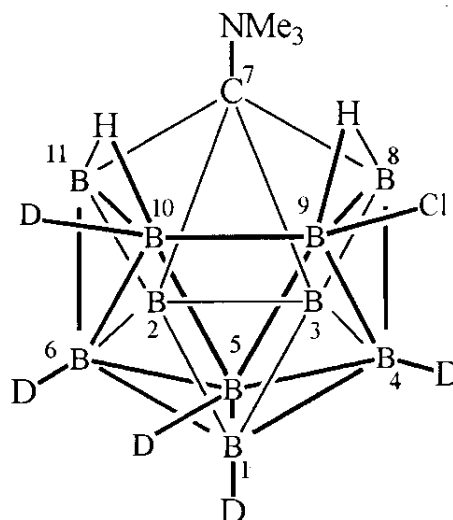
**B = B-H except for B(6) and B(9)**Fig. 3; Structure of 7-Me₃N-6,9-Cl₂-nido-7-CB₁₀H₁₀(IIb)

The relevant IR absorption frequencies of all the substituted derivatives had B-H stretching modes in the region 2530 cm⁻¹ and 2500 cm⁻¹. The IR spectra of the deuterated derivatives showed, in addition to the B-H stretching modes, strong bands at 1900 cm⁻¹ which were assigned to the terminal B-D stretching modes [10].

Experimental

Physical measurements

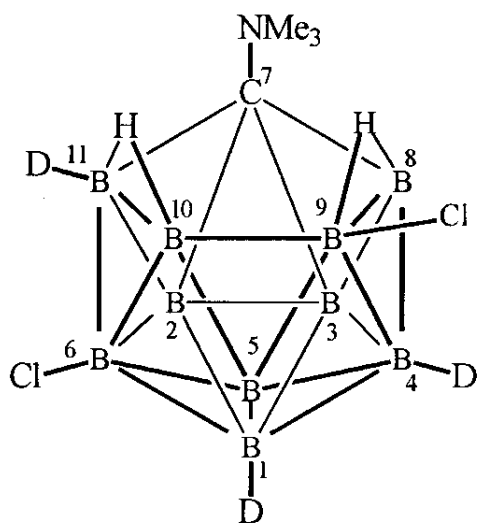
IR spectra were recorded as mulls in nujol between KBr plates on Perkin-Elmer 457 Grating infrared spectrometer (ν_{max} in cm⁻¹), the mass spectra on A.E.I. MS9 spectrometer and the NMR spectra were recorded on Bruker WH 360 spectrometer (¹H, 360; ¹¹B, 115.5 MHz) in CD₃CN. Chemical shifts are quoted as positive to high

**B = B-H except for B(1,4,5,6,9 & 10)**Fig. 4; Structure of 7-Me₃N-9-Cl-1,4,5,6,10-D₅-nido-7-CB₁₀H₆(IIIa)

frequency of the reference standards SiMe₄ or Et₂O.BF₃. Two-dimensional ¹¹B-¹¹B NMR spectra were produced on samples via procedures described elsewhere [5]. The TLC was performed by using dichloromethane as mobile phase and the spots were detected by iodine vapours.

Chemicals and syntheses

Carborane I was prepared by the previously reported method [1e]. Deuterium chloride was prepared by adding dropwise D₂O over PCl₅, condensed at -78°C and then generated by slow evaporation. Carbon disulphide was distilled prior to use and other commercially available chemicals were reagent grade and used as purchased except where otherwise indicated. All syntheses and standard isolation procedure were conducted in an inert atmosphere or *in vacuo*.



B = B - H except for B (1,4,5,6,9 & 10)

Fig. 5: Structure of 7-Me₃N-6,9-Cl₂-1,4,5,10-D₄-nido-7-CB₁₀H₆ (IIIb)

Preparation of 7-Me₃N-9-Cl-nido-7-CB₁₀H₁₁ and 7-Me₃N-6,9-Cl₂-nido-7-CB₁₀H₁₀ (IIa,b)

Carborane I (0.5g, 2.6 mmole) and anhydrous AlCl₃ (0.347g, 2.6 mmole) were placed in a 250 cm³ vessel fitted with a greaseless stopcock and was evacuated. Dry CS₂ was condensed in, and the mixture warmed to room temperature to form a suspension. Gaseous HCl (ca. 1.23g, 33.8 mmole) was condensed in, the mixture warmed at 25°C and stirred for ca. 24 hours. The evolved gas and solvent were removed in vacuo. TLC analysis on SiO₂ showed two products; the major component (R_f 0.7) was separated from the minor component (R_f 0.58) by column chromatography on SiO₂ to yield 7-Me₃N-9-Cl-nido-7-CB₁₀H₁₁ (IIa) (ca. 0.32g, 55%). (Found: C, 22.0; H, 9.4; N, 6.2; Cl, 15.4%. C₄H₂₀B₁₀ClN requires: C, 21.3; H, 8.9; N, 6.2; Cl, 15.7%). The mass spectrum showed a group of ions with a mass cut-off at m/e 227 corresponding to the ion [¹¹B₁₀ ¹²C₄ ¹H₁₈ ¹⁴N₁ ³⁷Cl₁]⁺ (loss of 2H from the parent ion). The minor component was characterised as 7-Me₃N-6,9-Cl₂-nido-7-CB₁₀H₁₀ (IIb). The mass spectrum showed a cut-off at m/e 265, corresponding to the ion [¹¹B₁₀ ¹²C₄ ¹H₁₅ ²D₄ ¹⁴N₁ ³⁷Cl₂]⁺.

Preparation of 7-Me₃N-9-Cl-1,4,5,6,10-D₅-nido-7-CB₁₀H₆ and 7-Me₃N-6,9-Cl₂-1,4,5,10-D₄-nido-7-CB₁₀H₆ (IIIa,b)

A reaction was carried out under similar conditions to that for IIa, b except that DCI was used. TLC gave components with similar R_f values and yields. (Found: C, 21.4; H(D), 10.6; N, 6.0; Cl, 15.4%. C₄H₁₅D₅B₁₀ClN requires: C, 20.8; H(D), 10.9; N, 6.1; Cl, 15.4%). The mass spectrum showed a cut-off at m/e 230 corresponding to the ion [¹¹B₁₀ ¹²C₄ ¹H₁₅ ²D₃ ¹⁴N₁ ³⁷Cl₁]⁺ (loss of D₂ from the parent ion). The minor component (IIIb) was similar to that from the previous reaction, the mass spectrum of which showed a cut-off at m/e 269, corresponding to [¹¹B₁₀ ¹²C₄ ¹H₁₅ ²D₄ ¹⁴N₁ ³⁷Cl₂]⁺.

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