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Reactions between tetraalkyldiboranes(6) and disilazanes – A convenient route to N-silylamino-dialkylboranes

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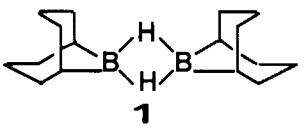
Abstract

Thermally stable tetraalkyldiboranes(6) such as bis(9-borabicyco[3.3.1]nonane (**1**) and the 1,2:1,2-bis(tetramethylene)diboranes(6) (**2,3**) react with disilazanes such as **4** [$(Me_3Si)_2NH$] or **5** [$Me_2SiCH_2SiMe_2$–NH] selectively by cleavage of the N–Si bond and formation of the Si–H bond. This affords N-silyl derivatives of 9-amino-9-borabicyclo[3.3.1]nonane (**7,8**) and of 1-amino-boracyclopentane (**11–13**) in high yield. INEPT-HEED experiments were used to determine coupling constants $^1J(^{29}Si^{15}N)$ in N-silylaminoboranes for the first time. Dimeric 9-amino-9-borabicyclo[3.3.1]nonane was isolated from crude reaction mixtures of **1** and **4**, and it was characterized by single crystal X-ray analysis (triclinic, space group $P\bar{1}$).

Keywords: Amide; Amine; Borane; Hydride; NMR; X-ray diffraction

1. Introduction

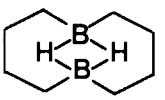
The reaction between boranes with one, two or three B–H bonds and various amines is well known to proceed via H_2 elimination to give aminoboranes [1]. The analogous reaction of such boranes with N-silylamines has received only scant attention [2,3], although the question whether the N–H or the N–Si bond is cleaved may be of considerable importance in the synthesis and chemistry of aminoboranes. It has been reported [2] that the reaction between diborane and hexamethyldisilazane, $(Me_3Si)_2NH$, gives an adduct which, on heating, produces H_2, Me_3SiH and the borazine $[HBNSiMe_3]_3$; with BH_3–THF in THF and $(Me_3Si)_2NH$, it was observed that various products were formed in the beginning and finally the same borazine was obtained [3], again by elimination of H_2 and Me_3SiH. This suggests that the cleavage of N–H and N–Si bond compete with each other. To the best of our knowledge, reactions between tetraalkyldiboranes(6) and N-silylamines have not been studied previously. In the present work we have examined the reactivity of the thermally stable tetraalkyldiboranes(6) (**1–3**) towards noncyclic (**4**) and cyclic disilazanes (**5,6**).



1

$(Me_3Si)_2N$–H

4



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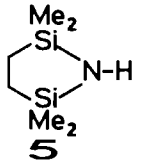

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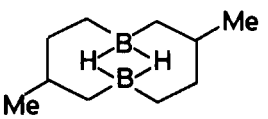

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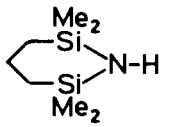

6

2. Results and discussion

All reactions between **1–3** and **4–6** require heating in boiling toluene for 24 to 48 h. In the case of **1**, a small amount of THF acts as a catalyst and the reactions become faster by a factor of two to three. It is

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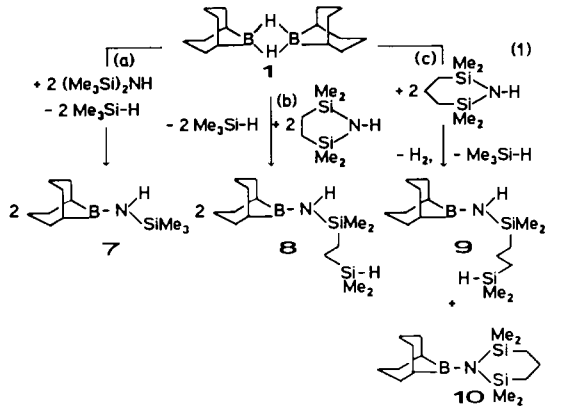
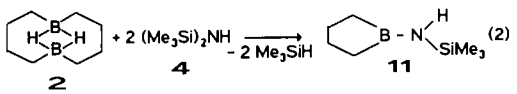
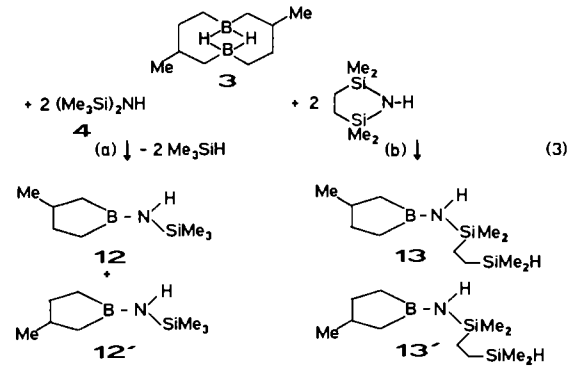
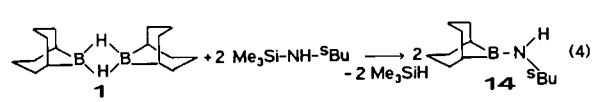
known [4] that **1** can be cleaved by THF to give the adduct THF-9-BBN which is much more reactive than **1**. The reactions proceed in the most clean way when the starting materials are mixed without any solvent and heated to 120–130°C for 5 to 6 h. There is clear evidence for cleavage of the N–Si and formation of the Si–H bond [Eqs. (1), (2) and (3)] rather than for cleavage of the N–H bond and formation of H_2. Only in the case of **1** and **6**, a 2:1 mixture of the aminoboranes **9** and **10** is observed, the latter being the result of H_2 elimination. Owing to restricted rotation about the B–N bond, the aminoboranes **12** and **12′** as well as **13** and **13′** are present in a 1:1 ratio. Except for the mixture of the compounds **9** and **10**, the products can be readily purified by distillation under reduced pressure to give in general > 80% of **7**, **8**, **11**, **12/12′**, and **13/13′** as moisture-sensitive, colorless liquids.



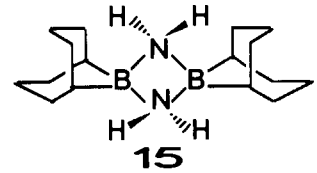




In order to check further on the competition between cleavage of the N–H and N–Si bond in reactions with tetraalkyldiboranes(6), we have carried out the reaction between **1** and Me_3SiNH-^{s}Bu (Eq. (4)). The sole product was **14** which results from elimination of Me_3SiH.



If crude reaction mixtures containing **7** and small amounts of the starting materials **1** and **4** were left without distillation, it was always observed that colorless crystals separated from these mixtures. Based on ^{1}H-, ^{11}B- and ^{13}C-NMR spectra this material was identified as bis(9-amino-9-borabicyclo[3.3.1]nonane) **15** [1g]. This was confirmed by determination of the molecular structure of **15** [5] by single crystal X-ray analysis (vide infra). Compound **15** can be obtained in high yield from the reaction between **1** and ammonia [1g]. In our case, **15** must have been formed in the course of exchange processes which do not take place in pure samples of **7**.



The straightforward synthesis of the N-trimethylsilylaminoboranes **7**, **8**, **11**, **12** and **13** [Eqs. (1)–(3)] has certain advantages over other potential routes: (i) alkali metal (M) derivatives of the type $MNHSiMe_3$ are not easily accessible; therefore salt elimination reactions are not helpful; (ii) cleavage of the Si–N bond by boron halides is thoroughly documented [2,6,8], however, side reactions may occur if N–H bonds are present [7,8] as in the silazanes **4**–**6** (the aminoborane **12** was prepared previously in moderate yield from 1-chloro-3-methyl-1-boracyclopentane and $(Me_3Si)_2NH$ [8]); (iii) the ring-opening of the cyclic silazane **5** to give **8** or **13/13′** is remarkable, since the synthesis of such aminoboranes would require a multi-step synthesis by other routes.

Aminoboranes of type **8** or **13** may have further synthetic potential considering the rich chemistry of silanes with Si–H bonds. Another interesting point concerns the lithiation of these aminoboranes, in particular the lithiation of **7** by using ^{t}Bu-Li. Reactions of this amide with metal halides should afford new metal amides.

2.1. NMR spectroscopic results

^{11}B, ^{13}C, ^{14}N, ^{15}N and ^{29}Si NMR data of the aminoboranes **7**–**13** are listed in Table 1, ^{1}H NMR data are given in the experimental part. The ^{1}H and ^{13}C NMR data show for **7**, **8**, **9**, **11**, **12/12′**, **13/13′** and **14** that there is restricted rotation about the B–N bond. This was not mentioned in the literature for compound **12** [8]. In the case of **7** (at 100°C) and **12** (70°C), the ^{13}C NMR spectra allowed to evaluate [9] the energy of activation for this process (**7**: $\Delta G^{\#}_{(373K)} = 75 \pm 1$ kJ mol^{-1}; **12**: $\Delta G^{\#}_{(343\ K)} = 74 \pm 1$ kJ mol^{-1}). The chemical shifts δ^{11}B lie in the expected range [10] for

N-silylaminodialkylboranes. This is also true for the δN values [11] with ^{15}N resonances shifted to higher frequencies as compared to the disilazanes [δ^{15}N = −354.2 (**4**), −354.0 (**5**), −356.9 (**6**)]. It seems that the δ^{29}Si data do not reflect any BN(pp)π interactions if one compares with δ^{29}Si of the disilazanes [δ^{29}Si: +2.4 (**4**), +12.8 (**5**), +2.9 (**6**)].

^{15}N NMR spectra can be readily measured indirectly via ^{1}H detection by using ^{1}H/^{15}N HMQC techniques [12] since the presence of the boron atom has little influence on the ^{1}H(^{15}N) magnetization [13]. The direct measurement of ^{15}N NMR spectra is time-consuming, even for concentrated samples, since the ^{15}N NMR signals are significantly broadened (linewidths of 10–20 Hz) owing to partially relaxed scalar ^{15}N–^{11}B coupling. Therefore, ^{29}Si satellites are difficult to observe and this appears to be the reason for the absence of any data $^{1}J(^{29}Si^{15}N)$ for N-silylaminoboranes in the literature. However, N-silylaminoboranes are ideal candidates for applying Hahn-echo extended (HEED) pulse sequences [14] in order to facilitate the measurement of $^{1}J(^{29}Si^{15}N)$ from ^{29}Si NMR spectra (see Fig. 1). The delay in the Hahn-echo part of the sequence is selected in order to suppress magnetization of the ^{29}Si–^{14}N isotopomer, leaving the magnetization of the

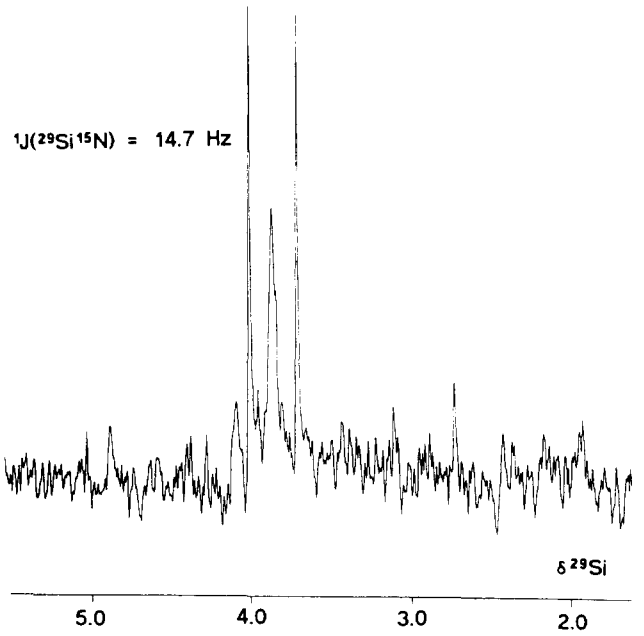


Fig. 1. 49.7 MHz ^{29}Si NMR spectrum of **7**, recorded by using the INEPT-HEED pulse sequence (refocused with ^{1}H decoupling; Hahn-echo delay 0.5 s). The residual signal of the ^{29}Si–^{14}N isotopomer is accompanied by the doublet due to the ^{29}Si–^{15}N isotopomer.

Table 1
^{11}B-, ^{13}C- and ^{14}N, ^{15}N NMR data [a] of the N-silylaminoboranes **7–13** and of the aminoborane **14**

Compound	δ^{11}B	δ^{13}C (BR_2)	δ^{13}C ($NSiMe_3$) and others	δN	δ^{29}Si
7	+54.6	25.2, 29.2 (BCH) 33.4, 34.0 (CH_2) 23.6 ($-CH_2-$)	1.7	−287.0 (^{15}N)	+3.7 [14.7]
8	+55.0	25.6, 29.2 (BCH) 33.9, 33.2 (CH_2) 23.6 ($-CH_2-$)	−0.4 ($SiMe_2$), −4.6 ($SiMe_2H$) 10.8 ($NSiCH_2$) 6.4 ($HSiCH_2$)	−291.0 (^{14}N)	+5.8 [41.1] −9.7
9	+55.7	29.1, 25.4 (BCH) 33.9, 33.4 (CH_2) 23.6 ($-CH_2-$)	−0.1 ($SiMe_2$), −4.3 ($SiMe_2H$) 22.3 ($NSiCH_2$), 18.9 ($-CH_2-$) 18.8 ($HSiCH_2$)	−283.5 (^{14}N)	+2.9 −14.0
10	+58.0	27.3 (BCH) 33.4 (CH_2) 23.0 ($-CH_2-$)	3.2 ($SiMe_2$) 20.5 ($NSiCH_2$), 17.2 ($-CH_2-$)	−291.5 (^{14}N)	+4.0
11	+57.6	21.0, 19.1 (BCH_2) 28.1, 26.7 (CH_2)	1.2	−287.8 (^{14}N)	+4.8 [14.5]
12,12′	+57.6	21.0, 18.7 (BCH_2) 31.0, 29.0 (BCH_2) 22.8, 22.9 (CH_3) 35.0, 34.9 (CH_2) 36.5, 36.2 (CH)	1.2	−287.1 (^{15}N)	+4.8 [14.4]
13,13′	+58.3	20.1, 18.3 (BCH_2) 30.6, 18.8 (BCH_2) 22.2, 22.1 (CH_3) 34.3, 34.2 (CH_2) 35.7, 35.5 (CH)	−1.7 ($SiMe_2$), −5.5 ($HSiMe_2$) 9.5 ($NSiCH_2$), 5.4 ($HSiCH_2$)	−290.0 (^{14}N)	+6.8
14	+48.1	27.1, 22.4 (BCH) 33.8, 33.8, 33.1, 33.0 (CH_2) 23.9, 23.8 ($-CH_2-$)	49.4 (NCH), 33.4 (CH_2) 24.9 ($NCCH_3$), 11.1 (CH_3)	−265.5 (^{14}N)	–

[a] In C_6D_6 (≈ 10–30%, V/V) at 25 ± 1°C; coupling constants $^{1}J(^{29}Si^{15}N)$ in Hz are given in square brackets.

Table 2
Data for the X-ray analysis of bis(9-amino-9-borabicyclo [3.3.1]nonane) (**13**) [a]

Formula	$C_{16}H_{32}B_2N_2$
Molecular mass	274.1
Crystal size (mm^3)	$0.35 \times 0.35 \times 0.30$
Lattice parameters	$a = 660.7(2)$, $b = 719.7(2)$, $c = 950.9(2)$ pm; $\alpha = 76.86(2)$, $\beta = 89.82(2)$, $\gamma = 66.01(2)°$
Space group; Z	$P\bar{1}$; 1
Volume ($Å^3$); ρ (calc) ($g\ cm^{-3}$)	400.3(2); 1.137
Diffractometer	Siemens P4; graphite Monochromator
Radiation	Mo Kα, $\lambda = 0.71073$ Å
Temperature [K]	296
2Θ Range	4 to 55
Reflections collected	2294
Unique reflections	1820 (no reflections omitted)
System used	SHELXTL-PLUS
Solution	Direct methods
Weighting scheme	$w = 1/\sigma^2(F)$
R; wR	0.050; 0.045
Number of param. refined	108
Max./min. resid. elec. dens.	$0.33/-0.19$ ($e/Å^3$)

[a] All non-hydrogen atoms were refined with anisotropic thermal parameters. The position of hydrogen atoms was calculated assuming ideal geometry. In subsequent Fourier syntheses the hydrogen atoms were taken into account.

$^{29}Si-^{15}N$ isotopomer almost unaffected. In the case of **7**, **8**, **11–13**, we found by this technique that $^1J(^{29}Si^{14}N)$ ranges between 14.1 to 14.7 Hz, the values being only slightly increased as compared with $^1J(^{29}Si^{15}N)$ in the disilazanes [13.5 (**4**), 13.7 (**5**) [15], 11.6 Hz (**6**)].

2.2. X-ray analysis of 15 [16]

Experimental data of the X-ray analysis of **15** are given in Table 2. The molecular structure of **15** is depicted in Fig. 2 and the caption of Fig. 2 contains selected bond distances and angles. The four-membered NBNB ring is planar and almost square. Both six-membered rings of the bicyclic systems adopt the chair conformation as usual [17,18]. In spite of the small bond angle NBN = 91.2(1)° in the four-membered ring, the other endocyclic bond angle C(1)BC(5) = 108.1(1)° remains close to the ideal angle for tetrahedral surrounding. This is presumably enforced by the bicyclic system. All bond distances and other bond angles are found in the expected range.

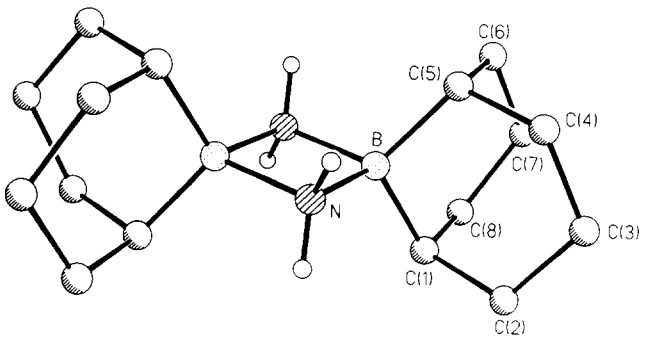


Fig. 2. Molecular structure of the dimeric 9-amino-9-borabicyclo [3.3.1]nonane (**15**). Selected bond lengths [pm] and bond angles [°]: N–B 161.3(1), B–C(1) 159.5(2), B–C(5) 160.1(2), C–C 152.8(2)–154.5(2); NBN 91.2(1), BNB 88.8(1), NBC(1) 113.8, NBC(5) 114.6(1), C(1)BC(5) 108.1 (1).

3. Experimental details

All preparative work and the handling of the samples was carried out under N_2 atmosphere, using dry glassware and dry solvents. Hexamethyldisilazane (**4**) was used as a commercial product; the boranes **1** [19], **2** [20] and **3** [21] and the silazanes **5** [22] and **6** [22,23] were prepared following literature procedures. Elemental analyses: Fa. Pascher, Remagen; El-MS spectra (70 eV): Varian MAT CH 7 with direct inlet. – NMR spectra: Jeol FX 90 Q (^{11}B, ^{29}Si), Jeol EX 270 (^{13}C, ^1H), Bruker ARX 250 and Bruker AC 300 (^1H, ^{11}B, ^{13}C, ^{15}N, ^{29}Si); chemical shifts are given with respect to Me_4Si ($\delta^1H(C_6D_5H) = 7.15$; $\delta^{13}C(C_6D_6) = 128.0$; $\delta^{29}Si$: $\Xi(^{29}Si) = 19.867184$ MHz), Et_2O-BF_3 ($\delta^{11}B$: $\Xi(^{11}B) = 32.083971$ MHz), neat $MeNO_2$ ($\delta^{14}N$: $\Xi(^{14}N) = 7.226455$ MHz; $\delta^{15}N$: $\Xi(^{15}N) = 10.136767$ MHz).

3.1. 9-Trimethylsilylamino-9-borabicyclo[3.3.1]nonane (7)

A mixture of 6 g (24.6 mmol) of bis(9-borabicyclo[3.3.1]nonane) (**1**) and 12 g (200 mmol) of $(Me_3Si)_2NH$ (**4**) was prepared at room temperature and heated to 120–130°C for 5 h. Then the excess of **4** was distilled off and fractional distillation gave 9.0 g (89.7%) of **7** as a colorless liquid (b.p. 75°C/0.1 Torr). El-MS: m/z (%) = 209 (38) [M^+]; 194 (30) [M^+–Me]; 100 (55) [$C_3H_{11}BNSi^+$]; 98 (50) [$C_3H_9BNSi^+$]; 74 (100) [$C_3H_9Si^+$]. ^1H NMR (in C_6D_6, 270 MHz): $\delta^1H = 3.41$ broad s, 1H, NH, $^1J(^{15}N^1H) = 69.1$ Hz; 0.08 s, 9H, $SiMe_3$; 1.45 and 0.95 m, 2H, BCH; 1.40 m and 1.90 m, 12H, CH_2. $C_{11}H_{24}BNSi$ (209.2): Calc. C 63.16, H 11.48, N 6.48%; Found C 62.71, H 11.67, N 6.69%. The other aminoboranes were prepared in the same way as **7**.

8: yield: 91%; b.p. 105–107°C/0.1 Torr; El-MS: m/z (%) = 281 (12) [M^+]; 59 (100) [Me_2SiH^+]. ^1H NMR (in C_6D_6, 270 MHz): $\delta^1H = 3.63$ broad s, 1H, NH; 3.97 m, 1H, SiH, $^1J(^{29}Si^1H) = 182.4$ Hz; 0.20 s, 6H, $NSiMe_2$; 0.12 d, 6H, $HSiMe_2$, $^3J(^1H^1H) = 3.7$ Hz; 0.60 m, 4H, $SiCH_2CH_2Si$; 1.40 m and 0.91 m, 2H, BCH; 1.80 m and 1.34 m, 12H, CH_2. $C_{14}H_{32}BNSi$ (281.4): Calc. C 60.39, H 11.63, N 5.16%; Found C 59.79, H 11.39, N 4.98%.

9/10: 87%; b.p. 118–125°C/0.1 Torr; ^1H NMR (in C_6D_6, 270 MHz); δ^1H (**9**) = 3.46 broad s, 1H, NH; 4.08

m, 1H, SiH; 0.25 s, 6H, $NSiMe_2$; 0.08 d, $^3J(^1H^1H) = 3.7$ Hz, 6H, $HSiMe_2$; δ^1H (**10**) = 0.15 s, $SiMe_2$; all other ^1H resonances of this mixture consist of overlapping multiplets.

11: 90% yield; b.p. 27–30°C/0.1 Torr; EI-MS: *m/z* (%) = 155 (10) [M^+]; 140 (100) [M^+–Me]; 73 (5) [Me_3Si^+]. - ^1H-NMR: 3.47 broad t, $^1J(^{14}N^1H) = 39$ Hz, 1H, NH; 0.04 s, 9H, $SiMe_3$; 1.7 m, 4H, BCH_2; 0.90 m and 0.83 m, 4H, CH_2.

12/12′: 86% yield; 33–35°C/0.1 Torr; EI-MS: *m/z* (%) = 169 (21) [M^+]; 154 (100) [M^+–Me]; 73 (8) [Me_3Si^+]. ^1H NMR (in C_6D_6, 270 MHz): $\delta^1H = 3.7$ broad s, 2H, NH; 0.09 s, 18H, $SiMe_3$; 0.99 two d, 6H, Me; 0.35–0.5 m, 0.7–0.9 m, 1.1–1.3 m, 1.88 m, 14 H, BCH_2, CH and CH_2. $C_8H_{20}BNSi$ (169.2): Calc. C 56.80, H, 11.83, N 8.28%; Found C 56.00, H 11.94, N 8.34%.

13/13′: 85% yield; b.p. 78°C/0.1 Torr; ^1H NMR (in C_6D_6, 270 MHz); $\delta^1H = 3.69$ broad s, 2H, NH; 3.94 m, 2H, SiH, $^1J(^{29}Si^1H) = 183.6$ Hz; 0.15 s, 12 H, $NSiMe_2$; 0.10 d, $^3J(^1H^1H) = 3.7$ Hz, 12H, $HSiMe_2$; 0.57 m, 8H, $NSiCH_2CH_2Si$; 1.03 two d, 6H, Me; 0.10–0.25 m, 0.45–0.60 m, 0.65–1.00 m, 1.61 m, 14H, BCH_2, CH and CH_2.

14: 95% yield; b.p. 68°C/0.1 Torr; ^1H NMR (in C_6D_6, 270 MHz): $\delta^1H = 3.68$ broad s, 1H, NH; 3.30 m, 1H, NCH; 1.14 d, 3H, NCHMe; 0.95 t, 3H, CH_2Me; 1.6–2.0 m and 1.2–1.5 m, 16H, BCH and CH_2.

Acknowledgements

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