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Group 4 metallacarboranes of constrained geometries derived from $B_{(cage)}$- and $C_{(cage)}$-silylamido-substituted carborane ligands: a synthetic and structural investigation

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Dedicated to Professor M. Frederick Hawthorne on the occasion of his 75th birthday, in recognition of his outstanding contribution to polyhedral boron chemistry

Abstract

The reactions of $RNHSi(Me)_2Cl$ (**1**, R = *t*-Bu; **2**, $R = 2,6\text{-}(Me_2CH)_2C_6H_3$) with the carborane ligands, *nido*-1-$Na(C_4H_8O)$-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_5$ (**3**) and Li[*closo*-1-R′-1,2-$C_2B_{10}H_{10}$] (**4**), produced two kinds of neutral ligand precursors, *nido*-5-$[Si(Me)_2N(H)R]$-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_5$, (**5**, R = *t*-Bu) and *closo*-1-R′-2-$[Si(Me)_2N(H)R]$-1,2-$C_2B_{10}H_{10}$ (**6**, R = *t*-Bu, R′ = Ph; **7**, $R = 2,6\text{-}(Me_2CH)_2C_6H_3$, R′ = H), in 85, 92, and 95% yields, respectively. Treatment of *closo*-2-$[Si(Me)_2NH(2,6\text{-}(Me_2CH)_2C_6H_3)]$-1,2-$C_2B_{10}H_{11}$ (**7**) with three equivalents of freshly cut sodium metal in the presence of naphthalene produced the corresponding cage-opened sodium salt of the “carbons apart” carborane trianion, [*nido*-3-$\{Si(Me)_2N(2,6\text{-}(Me_2CH)_2C_6H_3)\}$-1,3-$C_2B_{10}H_{11}]^{3-}$ (**8**) in almost quantitative yield. The reaction of the trianion, **8**, with anhydrous MCl_4 (M = Ti and Zr) in 1:1 molar ratio in dry tetrahydrofuran (THF) at −78 °C, resulted in the formation of the corresponding half-sandwich neutral d^0-metallacarborane, *closo*-1-$M[(Cl)(THF)_n]$-2-[1′-$\eta^1\sigma$-$N(2,6\text{-}(Me_2CH)_2C_6H_3)(Me)_2Si$]-2,4-$\eta^6$-$C_2B_{10}H_{11}$ (M = Ti (**9**), *n* = 0; M = Zr (**10**), *n* = 1) in 47 and 36% yields, respectively. All compounds were characterized by elemental analysis, ^1H-, ^{11}B-, and ^{13}C-NMR spectra and IR spectra. The carborane ligand, **7**, was also characterized by single crystal X-ray diffraction. Compound **7** crystallizes in the monoclinic space group $P2_1/c$ with $a = 8.2357(19)$ Å, $b = 28.686(7)$ Å, $c = 9.921(2)$ Å; $\beta = 93.482(4)°$; $V = 2339.5(9)$ Å^3, and $Z = 4$. The final refinements of **7** converged at $R = 0.0736$; $wR = 0.1494$; GOF = 1.372 for observed reflections.

Keywords: $B_{(cage)}$- and $C_{(cage)}$-silylamido-substituted carboranes; Ligand precursors; Metallacarboranes; Constrained geometry; Crystal structures; Group 4 carborane; Sigma-bonded ansa ligand

1. Introduction

Constrained geometry complexes, in which a metal is associated with an η^1-bonding group that is tethered to an η^5-π-bonding ligand, usually a derivative of cyclopentadienide, have received a great deal of attention in recent years [1–3]. The major emphasis for these studies stems from the potential of the early transition metal (Groups 3 and 4) constrained geometry complexes to act as olefin polymerization catalysts [1,4,5]. The first such complex described was $[\{\eta^5\text{-}(C_5Me_4)Me_2Si(\eta^1\text{-}NCMe_3)\}Sc(PMe_3)]_2(\mu\text{-}H)_2$ [4] and, while other η^1-base sites and linking groups have been described [6], the $Si(Me)_2(NCMe_3)$ moiety remains one of the most explored η^1-bonding group and has been incorporated into both single site and binuclear catalytic systems [7]. Another class of π-donor ligands are the dianionic *nido*-carboranes, especially those in the $[(CR)_2B_{10}H_{10}]^{2-}$, $[(CR)_2B_9H_9]^{2-}$ and $[(CR)_2B_4H_4]^{2-}$ cage systems [8]. It was found that the small cage half-sandwich com-

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pounds, $[Me_2P(CH_2)_3PMe_2]_2M'(Et_2C_2B_4H_4)$ ($M' = TiMe_2$ and $ZrCl_2$), when mixed with methylaluminoxane (MOA) exhibited efficient polymerization catalytic activity [9], but studies on the use of the mixed $Cp^*M[(CR)_2B_9H_9]$ ($Cp^* = C_5Me_5$; M = Group 3 or 4 metal) as olefin polymerization catalysts have produced mixed results [10,11]. On the other hand, the study of carborane-based constrained geometry ligands has been much more limited. While complexes with both neutral [12] and anionic [13] η^1-tethered groups have been reported, the number of such examples is small. Herein, we report the syntheses of several constrained geometry silylamido ligands in both the C_2B_4 and C_2B_{10} cage systems, along with the results of their metalation reactions.

2. Experimental

2.1. Materials

Benzene, tetrahydrofuran (THF), toluene, and pentane were dried over Na metal and doubly distilled before use. Naphthalene was sublimed before use. All other solvents were dried over 4–8 Å mesh molecular sieves (Aldrich) and were either saturated with dry argon or degassed before use. The synthesis of 2,3-bis(trimethylsilyl)-2,3-dicarba-*nido*-hexaborane (**8**), and its subsequent conversion to *nido*-1-$Na(C_4H_8O)$-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_5$ (**3**) followed published procedures [14,15]. *Closo*-1-R-1,2-$C_2B_{10}H_{11}$ (R = H, Ph) was obtained from KATCHEM and used without further purification. Prior to use, $ZrCl_4$ (Aldrich) was degassed under vacuum at 120 °C for 24 h. *Tert*-butyllithium, *t*-BuLi (1.7 M solution in pentane, obtained from Aldrich) was used as received.

2.2. Spectroscopic procedures

Proton, boron-11, carbon-13 NMR spectra were recorded on a Bruker Fourier-transform multinuclear spectrometer at 200, 64.2, 50.3 MHz, respectively. Infrared spectra were recorded on a Perkin–Elmer Model 1600 FT-IR spectrophotometer and Nicolet Magna 550 FT-IR spectrophotometer. Elemental analyses were determined by in-house facility at Northern Illinois University using a Perkin–Elmer 2400 CHN elemental analyzer.

2.3. Synthetic procedures

All experiments were carried out in Pyrex glass round-bottom flasks of 100 ml capacity, equipped with magnetic stirring bars and high vacuum Teflon valves, or in a dry-box under an argon atmosphere. After their initial purifications, non-volatile substances were manipulated in either a dry-box, or an evacuable glove bag, under an atmosphere of dry nitrogen. All known compounds among the products were identified by comparing their IR and ^{1}H-NMR spectra with those of authentic samples.

2.4. Synthesis of $RNHSi(Me)_2Cl$ (**1**, R = *t*-Bu; **2**, R = 2,6-$(Me_2CH)_2C_6H_3$)

A 15.6 ml sample of 1.7 M *t*-BuLi in pentane (26.51 mmol) was slowly added in vacuo to a flask containing RNH_2 (R = *t*-Bu, 1.93 g, 26.39 mmol; R = 2,6-$(Me_2CH)_2C_6H_3$, 4.70 g, 26.51 mmol) in 20 ml pentane at −78 °C. The resulting mixture was slowly warmed to room temperature, during which time a white precipitate was produced; stirring was continued over night. The solvents and volatile *t*-BuH (2-methylpropane) in the flask were removed under vacuum to give an off-white solid of lithium amide. To the flask containing 50 ml Me_2SiCl_2 at −78 °C, the solid lithium amide product was slowly added under nitrogen using a funnel designed specifically for adding solids. After complete addition of the solid, the reaction mixture was slowly warmed to room temperature and stirred further for 6 h. The reaction mixture was then filtered to collect a clear filtrate. The unreacted dichlorodimethylsilane from the filtrate was removed in vacuo to collect an oily liquid that was distilled under reduced pressure to give colorless liquid products [**1**, R = *t*-Bu, 3.12 g, 18.83 mmol, 71% yield; **2**, R = 2,6-$(Me_2CH)_2C_6H_3$, 4.88 g, 18.08 mmol, 68% yield]. Anal. data: Calc. (Found) for $C_6H_{16}ClNSi$ (**1**): C, 43.48 (43.51); H, 9.73 (9.56); N, 8.45 (8.49)%. $C_{14}H_{24}ClNSi$ (**2**): C, 62.30 (62.58); H, 8.96 (9.01); N, 5.19 (5.48)%. The IR spectrum of **1** is identical to that in the literature [16]. NMR data for **1**: ^{1}H-NMR ($CDCl_3$, external Me_4Si) δ 1.12 [9H, s, $C(CH_3)_3$], 0.13 [6H, s, $Si(CH_3)_2$], 1.13 [1H, s, NH]; ^{13}C-NMR ($CDCl_3$, external Me_4Si) δ 40.31 [$C(CH_3)_3$], 33.80 [$C(CH_3)_2$], 3.51 [$Si(CH_3)$]; **2**: ^{1}H-NMR ($CDCl_3$, external Me_4Si) δ 7.23 [3H, s, $-C_6H_3$], 3.62 [2H, m, $CH(CH_3)_2$ $J = 6.91$ Hz], 2.51 [1H, s, NH], 1.43 [12H, d, $CH(CH_3)_2$ $J = 6.91$ Hz], 0.84[6H, s, $Si(CH_3)_2$]; ^{13}C-NMR ($CDCl_3$, external Me_4Si) δ146: [*p*-$C_{(Ph)}$H], 136.7 [N–$C_{(Ph)}$], 125.8 [*i*-Pr–$C_{(Ph)}$], 123.5 [*o*-$C_{(Ph)}$], 28.6 [$CH(CH_3)_2$], 24.1 [$CH(CH_3)_2$], 2.7 [$Si(CH_3)$]; IR (cm^{-1}, KBr) **2**: 3371(m, s), 3063(s, w), 2960(s, s), 2928(s, w), 2867(s, s), 2573(s, s), 1618(m, m), 1596(s, m), 1518(s, m), 1459(s, s), 1439(s, s), 1385(s, m), 1359(s, m), 1326(m, s) 1256(s, m), 1193(s, s), 1078(s, s), 1053(s, s), 1042(s, s), 924(s, s), 882(s, w), 795(s, s) 736(m, m) 672(s, m), 645(s, w), 470(s, s).

2.5. Synthesis of *nido*-5-*t*-$BuNHSi(Me)_2$-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_5$ (**5**)

A 20 ml tetrahydrofuran (THF) solution of *nido*-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_6$ (1.10 g, 5.03 mmol) was poured in vacuo onto a heterogeneous mixture of NaH (0.25 g, 10.00 mmol) and THF at -78 °C, and the reaction mixture was slowly warmed to room temperature. The flask was occasionally cooled to -196 °C, to control the evolution and buildup of H_2 gas. The evolved H_2 gas was pumped out of the flask, and the reaction was continued until H_2 evolution ceased. The mixture was then filtered in vacuo through a glass frit to collect the filtrate which was a THF solution *nido*-1-Na(C_4H_8O)-2,3-($SiMe_3$)$_2$-2,3-$C_2B_4H_5$ (**3**) according to the literature [14]. Then, the clear filtrate was added slowly to a solution of *t*-BuNHSi(Me)$_2$Cl (**1**) (0.83 g, 5.00 mmol) in dry THF at -78 °C over a period of 2 h with constant stirring. After warming to room temperature the mixture was stirred for 24 h and then filtered in vacuo to give a light yellow filtrate. The solvent from the filtrate was removed under reduced pressure to produce a pale yellow residue that was purified by chromatography using silica gel column under inert atmosphere with pentane as eluting solvent to collect a yellow oily product, identified as *nido*-5-*t*-BuNHSi(Me)$_2$-2,3-($SiMe_3$)$_2$-2,3-$C_2B_4H_5$ (**5**) (1.49 g, 4.27 mmol, 85% yield). Anal. data: Calc. (Found) for $C_{14}H_{39}B_4NSi_3$ (**5**): C, 48.19 (48.43); H, 11.27 (11.16); N, 4.01 (4.23)%. NMR data for **5**: ^{1}H-NMR (C_6D_6, external Me_4Si) δ 1.21 to -0.44 [2H, br, B–*H*–B], 0.22 [6H, s, B–Si–(C*H*$_3$)$_2$], 0.43 [18 H, s, 2C–Si–(C*H*$_3$)$_3$], 0.94 [1H, s, N*H*], 1.28 [C(C*H*$_3$)$_3$]; ^{13}C-NMR (C_6D_6, external Me_4Si) δ 0.02 [B–Si–(*C*H$_3$)$_2$], 2.05 [C–Si(*C*H$_3$)$_3$], 33.87 [C(*C*H$_3$)$_3$], 49.31 [N–*C*(CH$_3$)$_3$], 141 [C$_{\text{(cage)}}$]; ^{11}B-NMR (C_6D_6, relative to external $BF_3\cdot OEt_2$) δ -50.22 [d, 1 apical *B*H], 0.90 [d, 2 basal *B*H], 14.74 [br, 1 basal *B*–Si]; IR (cm^{-1}, KBr) 3391(m, s), 2960(s, s), 2925(s, s), 1404(s, s), 1378(s, s), 1358(s, s), 1312(s, s), 1255(s, vs), 1224(s, vs), 1096(s, s), 958(s, m), 938(s, s), 784(s, s), 758(s, s) 688(s, m), 636(s, m), 625(s, m), 482(s, m).

2.6. Synthesis of 1-R′-2-N(R)HSi(Me)$_2$-1,2-$C_2B_{10}H_{10}$ (6, R = t-Bu, R′ = Ph; 7, R = 2,6-(Me_2CH)$_2$$C_6H_3$, R′ = H)

A 5.67 ml solution of 1.7 M *t*-BuLi in hexane (9.64 mmol) was slowly added to a THF solution of 9.63 mmol of 1-R-1,2-$C_2B_{10}H_{12}$ (R = Ph, 2.13 g; R = H, 1.39 g) under nitrogen at -78° C. After complete addition, the reaction mixture was slowly warmed to room temperature and then stirred for 4 h at this temperature. The solvent from the reaction mixture was removed under reduced pressure to give Li[1-R′-1,2-$C_2B_{10}H_{10}$] (**4**, R′ = Ph or H) as an off-white solid. The flask containing the lithium salt was then attached to a high vacuum line and pumped at pressures below 5 mTorr to remove any additional solvating THF. After complete removal of the solvated THF, if any, 25 ml of anhydrous toluene was transferred into the flask in vacuo and the resulting mixture was stirred for 2 h until all of the solid monolithium salt was well dispersed in the flask. This heterogeneous mixture was cooled to -78° C and to this 9.63 mmol of RNHSi(Me)$_2$Cl (**1**, R = *t*-Bu, 1.60 g; **2**, R = 2,6-(Me_2CH)$_2$$C_6H_3$, 2.60 g) in 10 ml toluene was slowly added. After complete addition, the mixture was slowly warmed to room temperature, and stirred for 24 h at this temperature. The resulting heterogeneous mixture was then filtered in vacuo to remove the solid LiCl giving a clear yellow filtrate. Solvent from the clear filtrate was then removed in vacuo to collect a yellow residue that was identified as 1-R′-2-RNHSi(Me)$_2$-1,2-$C_2B_{10}H_{10}$ (R = *t*-Bu, R′ = Ph (**6**), 3.11 g, 8.90 mmol, 92% yield; R = 2,6-(Me_2CH)$_2$$C_6H_3$, R′ = H (**7**), 3.48 g, 9.26 mmol, 96% yield). Anal. data: Calc. (Found) for $C_{14}H_{31}B_{10}NSi$ (**6**): C, 48.10 (47.86); H, 8.94 (8.72); N, 4.01 (4.22)%. $C_{16}H_{35}B_{10}NSi$ (**7**): C, 50.89 (51.20); H, 9.34 (8.92); N, 3.71 (3.83)%. NMR data for **6**: ^{1}H-NMR (C_6D_6, external Me_4Si) δ 0.07 [6H, s, Si(C*H*$_3$)$_2$], 0.35 [1H, s, N*H*], 0.94 [9H, s, C(C*H*$_3$)$_3$], 6.95–7.55 [5H, m, C_6H_5], ^{13}C-NMR (C_6D_6, external Me_4Si) δ [Si–(*C*H$_3$)$_2$], 33.51 [C(*C*H$_3$)$_3$], 49.95 [N–*C*(CH$_3$)$_3$], 78.59 [Si–*C*$_{\text{(cage)}}$], 83.52 [Ph–C$_{\text{(cage)}}$], 127.16–133.27 [*C*$_6$H$_5$]. ^{11}B-NMR (C_6D_6, relative to external $BF_3\cdot OEt_2$) δ -8.9 [d, basal *B*H, $^1J(^{11}B\text{–}^1H) = 144$ Hz], -3.05 [s, basal *B*H, $^1J(^{11}B\text{–}^1H) = 144$ Hz], -2.29 [d, apical *B*H, $^1J(^{11}B\text{–}^1H) = 154$ Hz], 0.65 [s, apical *B*H $^1J(^{11}B\text{–}^1H) = 123$ Hz]; IR data for **6** (cm^{-1}, KBr) 3401(s, w), 2966(s, s), 2930(s, s), 2904(s, m), 2868(s, m), 2582(vs, br), 2274(s, s), 1470(s, s), 1445(s, m), 1404(s, m), 1383(s, s), 1363(s, s), 1260(s, s), 1219(s, s), 1081(s, s), 1035(s, s), 1020(s, s), 856(s, s), 518(s, s), 492(vs, s), 472(s, w), 415(s, m). NMR data for **7**: ^{1}H-NMR (C_6D_6, external Me_4Si) δ 0.04 [6H, s, –Si(C*H*$_3$)$_2$], 1.17 [12H, d, –CH(C*H*$_3$)$_2$, $J(^1H\text{–}^1H) = 6.88$ Hz], 2.21 [1H, N*H*] 3.38 [2H, m, –C*H*(CH$_3$)$_2$, $J(^1H\text{–}^1H) = 6.88$ Hz], 7.10–7.14 [3H, m, –C$_6$*H*$_3$], ^{13}C-NMR ($CDCl_3$, external Me_4Si) δ -1.43 [Si–(*C*H$_3$)$_2$], 23.48 [CH(*C*H$_3$)$_2$], 27.85 [*C*H(CH$_3$)$_2$], 59.88 [Si–*C*$_{\text{(cage)}}$], 66.82 [C$_{\text{(cage)}}$], 123.50–145.78 [–*C*$_6$H$_3$]. ^{11}B-NMR (C_6D_6, relative to external $BF_3\cdot OEt_2$) δ -12.15 [overlapped, basal *B*H], -7.06 [d, basal *B*H, $^1J(^{11}B\text{–}^1H) = 152$ Hz], -1.14 [b, apical *B*H, $^1J(^{11}B\text{–}^1H) = 141$ Hz]; IR data for **7** (cm^{-1}, KBr) 3382(s, w), 3360(s, w), 3070(s, s), 2964(s, s), 2969(s, m), 2574(s, s), 1617(s, m), 1459(vs, br), 1438(s, s), 1410(s, w), 1382(s, m), 1322(s, s), 1258(s, s), 1188(s, s), 1098(s, s), 1072(s, s), 1031(s, s), 914(s, s), 875(s, m), 864(s, w), 834(s, w), 812(s, s), 763(s, w), 724(s, m), 677(s, w), 634(s, w).

2.7. Synthesis of [Na^+(THF)$_n$]$_3$[nido-3-{Si(Me)$_2$N(2,6-(Me_2CH)$_2$$C_6H_3$)}-1,3-$C_2B_{10}H_{11}$]$^{3-}$ (8)

A 9.26 mmol (3.48 g) sample of [1-(2,6-diisopropany-lanilinyldimethylsilyl)-1,2-$C_2B_{10}H_{11}$] (**7**) was reacted with 28.90 mmol (0.70 g) of freshly cut sodium metal and 28.90 mmol (4.00 g) of anhydrous naphthalene in dry THF (100 ml) at −78 °C. The reaction mixture was then allowed to warm to room temperature slowly, during which time the heterogeneous mixture turned dark yellow. After stirring the mixture at room temperature over night, the dark yellow solution in the flask was filtered in vacuo and all of the volatiles, including naphthalene, were removed from the filtrate at 60 °C. The yellow residue was dissolved in 60 ml THF and filtered to remove the excess sodium metal. After removal of the solvent from the filtrate, a yellow solid, identified as $[Na^+(THF)_n]_3[\textit{nido}\text{-}3\text{-}\{Si(Me)_2N(2,6\text{-}(Me_2CH)_2C_6H_3)\}\text{-}1,3\text{-}C_2B_{10}H_{11}]^{3-}$ [**8**, 4.08 g, 1.67 mmol; m.p. > 265 °C, moderately air-stable, soluble in polar solvents only], was obtained in 90% yield. Anal. data: Calc. (Found) for $C_{80}H_{170}B_{50}N_5Na_{15}Si_5 \cdot 3(C_4H_8O)$ (**8**): C, 45.20 (45.23); H, 8.00 (8.05); N, 2.86 (3.02)%. NMR data for **8**: ^1H-NMR (C_4D_8O, external Me_4Si) δ −0.08 [6H, $-Si(CH_3)_2$], 1.07 [12H, d, $-CH(CH_3)_2$, $J(^1H-^1H) = 6.87$ Hz], 1.77 [m, −THF], 3.63 [m, −THF], 3.87 [1H, m, $-CH(CH_3)_2$, $J(^1H-^1H) = 6.87$ Hz], 7.10–7.14 [3H, m, $-C_6H_3$]; ^{13}C-NMR (C_4D_8O, external Me_4Si) δ 0.60 [$Si-(CH_3)_2$], 22.11 [$CH(CH_3)_3$], 27.52 [$CH(CH_3)_3$], 26.01, 68.02 [$C-_{THF}$], 66.04 [$C-_{Cage}$], 122.00, 128.12, 131.60, 141.2 [C_6H_3]; ^{11}B-NMR (C_4D_8O, relative to external $BF_3 \cdot OEt_2$) δ −8.32 [2*B*], −19.21 [2*B*], −23.86 [2*B*]; −29.10 [2*B*], −38.0[1*B*], −42.08 [1*B*]; IR (cm^{-1}, KBr) 2959(s, s), 2922(s, m), 2863(s, w), 2470(s, s), 1618(s, w), 1458(s, w), 1438(s, s), 1400(s, s), 1358(s, m), 1257(s, s), 1102(br, m), 1041(br, m), 803(s, s).

2.8. Synthesis of *closo*-1-Ti(Cl)-2-[1′-$\eta^1\sigma$-N(2,6-$(Me_2CH)_2C_6H_3)(Me)_2Si$]-2,4-$\eta^6$-$C_2B_{10}H_{11}$ (**9**)

A 0.95 g (0.39 mmol) sample of $[Na^+(THF)_n]_3[\textit{nido}\text{-}3\text{-}\{Si(Me)_2N(2,6\text{-}(Me_2CH)_2C_6H_3)\}\text{-}1,3\text{-}C_2B_{10}H_{11}]^{3-}$ (**8**) was dissolved in 20 ml THF in vacuo and the resulting solution was cooled to −78 °C. To which 0.39 ml (0.39 mmol, 1M in toluene) of $TiCl_4$ was added in vacuo and the resulting mixture was warmed slowly to room temperature and stirred for 24 h. The dark-brown colored reaction mixture was then filtered, and the solvents from the filtrate were removed under reduced pressure to collect a dark solid residue. This residue was extracted with 80 ml dry benzene and the benzene extract was concentrated to a total volume of 10 ml in vacuo and then mixed with 70 ml of dry pentane to precipitate a brown solid out of the solution that was later identified as *closo*-1-Ti(Cl)-2-[1′-$\eta^1\sigma$-N(2,6-$(Me_2CH)_2C_6H_3)(Me)_2Si$]-2,4-$\eta^6$-$C_2B_{10}H_{11}$ (**9**). After purification by repeating the above process, 0.42 g (0.80 mmol, 47% yield) of the product **9** was obtained. Anal. data: Calc. (Found) for $C_{16}H_{34}B_{10}NClSiTi$ (**9**): C, 41.78 (41.50); H, 7.45 (7.30); N, 3.05 (3.35)%. NMR data for **9**: ^1H-NMR (C_6D_6, external Me_4Si) δ 0.13 [6H, s, $-Si(CH_3)_2$], 1.23 [12H, m, $-CH(CH_3)_2$, $J(^1H-^1H) = 6.88$ Hz], 3.48 [1H, m, $-CH(CH_3)_2$, $J(^1H-^1H) = 6.88$ Hz], 7.10–7.14 [3H, m, $-C_6H_3$]; ^{13}C-NMR (external Me_4Si) δ 1.06 [$Si-(CH_3)_2$], 25.43 [$CH(CH_3)_3$], 29.70 [$CH(CH_3)_3$], 67.50 [$C-_{Cage}$], 122.50, 124.50, 129.01, 141.6 [C_6H_3]; ^{11}B-NMR (C_6D_6, relative to external $BF_3 \cdot OEt_2$) δ −3.52 [d, 2*B*H, $^1J(^{11}B-^1H) = 140$ Hz], −7.72 [d, 2*B*H,], −12.25 [1*B*H, ill-defined], −13.84 [2*B*H, ill-defined], −14.69 [2*B*H, d, $^1J(^{11}B-^1H) = 112$ Hz], −43.18 [1*B*H, ill-defined]; IR (cm^{-1}, KBr) 2957(s, s), 2913(s, m), 2862(s, w), 2843(s, w), 2508(br, s), 1398(s, s), 1259(s, s), 1096(br, s), 1043(s, s), 1015(s, s), 806(s, s).

2.9. Synthesis of *closo*-1-Zr[(Cl)(THF)]-2-[1′-$\eta^1\sigma$-N(2,6-$(Me_2CH)_2C_6H_3)(Me)_2Si$]-2,4-$\eta^6$-$C_2B_{10}H_{11}$ (**10**)

A 0.61 g (0.25 mmol) sample of $[Na^+(THF)_n]_3[\textit{nido}\text{-}3\text{-}\{Si(Me)_2N(2,6\text{-}(Me_2CH)_2C_6H_3)\}\text{-}1,3\text{-}C_2B_{10}H_{11}]^{3-}$ (**8**) in 20 ml THF was slowly poured onto 0.29 g of $ZrCl_4$ (1.25 mmol) in 10 ml THF at −78 °C. The reaction mixture was stirred for about an hour at this temperature and then slowly warmed to room temperature and stirred for an additional 24 h. The resulting heterogeneous brown colored reaction mixture was filtered in vacuo to collect a clear brown filtrate by removing the off-white solid, presumably NaCl. The solvent, THF, was then removed from the filtrate in vacuo, and the resulting brown solid residue was extracted with three 30 ml aliquots of dry benzene. The combined benzene extracts were concentrated in vacuo to a total volume of 15 ml, after which 70 ml of dry pentane was added to precipitate a brown solid, identified as *closo*-1-Zr[(Cl)(THF)]-2-[1′-$\eta^1\sigma$-N(2,6-$(Me_2CH)_2C_6H_3)(Me)_2Si$]-2,4-$\eta^6$-$C_2B_{10}H_{11}$ (**10**), in 36% (0.24 g, 0.43 mmol) yield. Anal. data: Calc. (Found) for $C_{20}H_{42}B_{10}NOSiZrCl$ (**10**): C, 41.75 (41.76); H, 7.36 (7.50); N, 2.43 (2.67). NMR data for **10**: ^1H-NMR (C_6D_6, external Me_4Si) δ 0.12 [6H, s, $-Si(CH_3)_2$], 1.29 [12H, m, $-CH(CH_3)_2$, $J(^1H-^1H) = 6.90$ Hz], 1.95 [4H, m, THF], 3.48 [1H, m, $CH(CH_3)_2$, $J(^1H-^1H) = 6.90$ Hz], 3.88 [4H, m, THF], 7.14–7.27 [3H, m, $-C_6H_3$]; ^{13}C-NMR (external Me_4Si) δ 1.02 [$Si-(CH_3)_2$], 23.90 [$CH(CH_3)_3$], 27.84, 67.33 [$C-_{THF}$], 28.61 [$CH(CH_3)_3$], 70.46 [$C-_{Cage}$], 123.13, 124.92, 129.05, 141.03 [C_6H_3]; ^{11}B-NMR (C_6D_6, relative to external $BF_3 \cdot OEt_2$) δ 8.8 [basal 2*B*H], 2.61 [b, 2*B*H, $^1J(^{11}B-^1H) = 154$ Hz], −2.61 [b, 2*B*H, $^1J(^{11}B-^1H) = 140$ Hz], −5.47 [ill-defined, 1*B*H], −12.05 [ill-defined, 2B*H*], −33,57 [ill-defined, 1*B*H], IR (cm^{-1}, KBr) 2958(s, s), 2921(s, m), 2860(s, w), 2539(s, s), 1400(s, s), 1260(s, w), 1094(s, s), 1018(s, s), 799(s, s).

2.10. X-ray structural analysis of *closo*-2-[$Si(Me)_2NH(2,6\text{-}(Me_2CH)_2C_6H_3)$]-1,2-$C_2B_{10}H_{11}$ (7)

Crystals of **7** were grown from a hexane/benzene (40/60, v/v) solution by slow evaporation. The selected crystal was then mounted on a Bruker SMART CCD PLATFORM diffractometer, under a low-temperature stream of nitrogen. The crystallographic data and other experimental details are summarized in Table 1. Unit cell parameters and orientation matrix were obtained from the least-squares refinement of 113 reflections measured in three different sets of 15 frames each, in range of $4.36° < 2\theta < 50°$. At the end of the data collection, the first 50 frames containing 231 reflections, were re-collected to monitor crystal decay, which was not observed, so that no time-decay corrections were applied. Of 9670 reflections collected ($4.36° < 2\theta < 50°$), 3626 reflections were considered as observed [$I > 2\sigma(I)$] and were corrected for Lorentz, polarization and absorption effects [17]. The structure was solved by direct methods, and refined by full-matrix least-squares techniques using SHELXTL [18]. All non-H atoms were refined anisotropically. The cage H atoms, the phenyl and alkyl groups were located, while the H on the nitrogen was calculated, and all were refined with fixed isotropic thermal parameters. The final refinements converged at $R_1 = 0.0736$, $wR_2 = 0.1494$, and GOF = 1.372. The atomic coordinates and selected interatomic distances and angles are listed in the supplementary materials.

Table 1
Crystallographic data for **7**

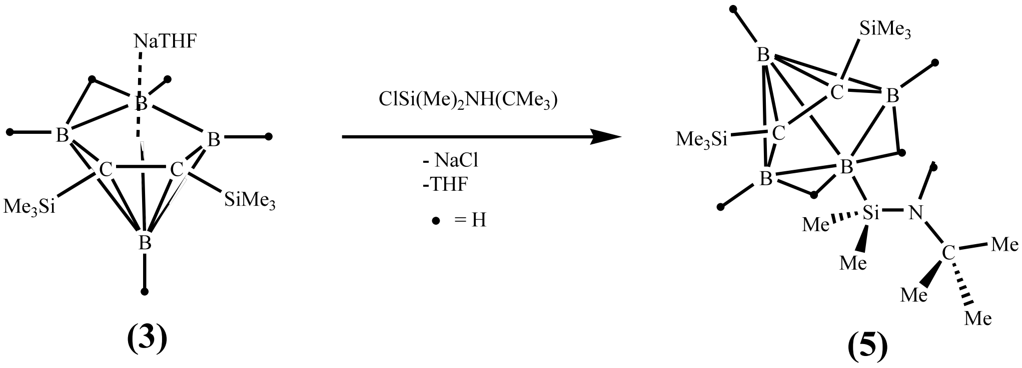
Empirical formula	$C_{16}H_{35}B_{10}NSi$
Formula weight	377.64
Temperature (K)	173(2)
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	8.2357(19)
b (Å)	28.686(7)
c (Å)	9.921(2)
β (°)	93.482(4)°
V (Å^3)	2339.5(9)
Z	4
Density, calculated (Mg m^{-3})	1.072
Absorption coefficient (mm^{-1})	0.103
$F(0\,0\,0)$	808
Crystal size (mm^3)	0.10 × 0.10 × 0.08
Theta range for data collection (°)	2.18–25.00
Index ranges	$-9 \le h \le 9$, $-18 \le k \le 34$, $-11 \le l \le 11$
Reflections collected	9670
Independent reflections	3626 [$R_{int} = 0.0303$]
Completeness to theta = 25.00° (%)	88.1
Absorption correction	Semi-empirical from equivalents
Max./min. transmission	1.000, 0.660111
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3626/0/289
Goodness-of-fit on F^2	1.372
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0736$, $wR_2 = 0.1494$
R indices (all data)	$R_1 = 0.0752$, $wR_2 = 0.1502$
Extinction coefficient	0.0010(6)
Largest difference peak and hole (e Å^3)	0.388 and −0.359

3. Results and discussion

3.1. Synthesis and spectroscopy

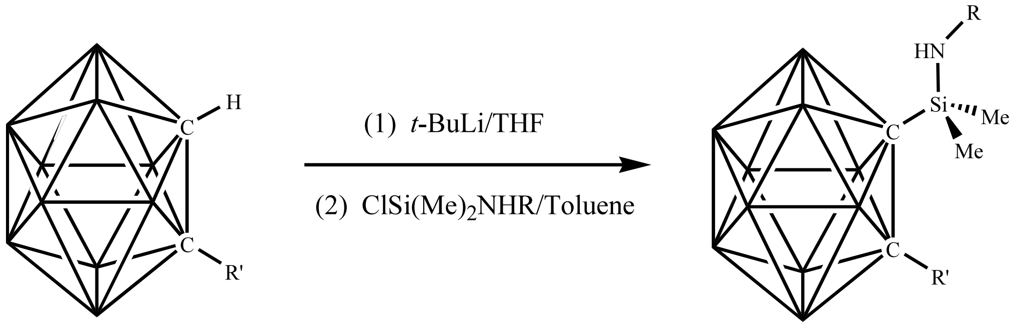
The chlorosilylamine precursors, $RNHSi(Me)_2Cl$ (**1**, R = *t*-Bu, **2**, R = 2,6-$(Me_2CH)_2C_6H_3$) were prepared in 71 and 68% yields, respectively, by the reaction of the corresponding lithium amide with neat Me_2SiCl_2. The excess dichlorodimethylsilane could easily be recycled by simple distillation after completion of the reaction. The reaction of *nido*-1-Na(C_4H_8O)-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_5$ (**3**) with (*t*-Bu)$NHSi(Me)_2Cl$ (**1**) in a 1:1 mol ratio in THF, followed by extraction and purification, produced a new five-substituted small cage carborane, *nido*-5-(*t*-Bu)$NHSi(Me)_2$-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_5$, (**5**) in 85% yield, as shown in Scheme 1. Elemental analysis clearly shows that a (*t*-Bu)$NHSi(Me)_2$ moiety has been substituted for a terminal H in the molecule. The assignment of amine substitution at the five-position is based on our previous work that showed that the presence of the bis(trimethylsilyl) groups on the cage carbons leads exclusively to substitution at the five-position of the *nido*-carborane cage for a variety of different alkyl groups [19]. The ^{11}B-NMR spectra showed peaks at $\delta = -50.22$, 0.90 and 14.74 ppm in a 1:2:1 peak area ratio; these are quite similar to the 1:2:1 peak area ratio pattern at $\delta = -49.53$, 1.09 and 14.51 ppm reported for *nido*-5-*i*-Bu-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_5$ whose dimeric monosodium compound has been structurally characterized [19]. In addition, the ^{1}H-NMR spectrum showed only a single, broad signal for the B–H–B bridge hydrogen, consistent with a C_s cage symmetry. Although **5** can be produced in good yield, it is of limited use as a constrained geometry ligand. Attempts to deprotonate the ligand with soluble bases, such as BuLi, and with NaH resulted in the cleavage of the B–Si bond. Reaction of the neutral ligand with the metalating agent, $Zr(NMe_2)_4$, lead to reaction, with all groups still attached to the ligand. However, the spectra were quite complex, indicating a formation of a mixture of products that could not be separated.

1-R′-2-[$Si(Me)_2N(H)R$]-1,2-$C_2B_{10}H_{10}$ (**6**, R = *t*-Bu, R′ = Ph; **7**, R = 2,6-$(Me_2CH)_2C_6H_3$, R′ = H) was prepared by the reaction of the salt, Li[1-R′-1,2-$C_2B_{10}H_{10}$] (R′ = Ph or H) with $N(R)HSi(Me)_2Cl$ (**1**, R = *t*-Bu; **2**, R = 2,6-$(Me_2CH)_2C_6H_3$), as outlined in Scheme 2. The yield of this reaction was quite dependent on both the



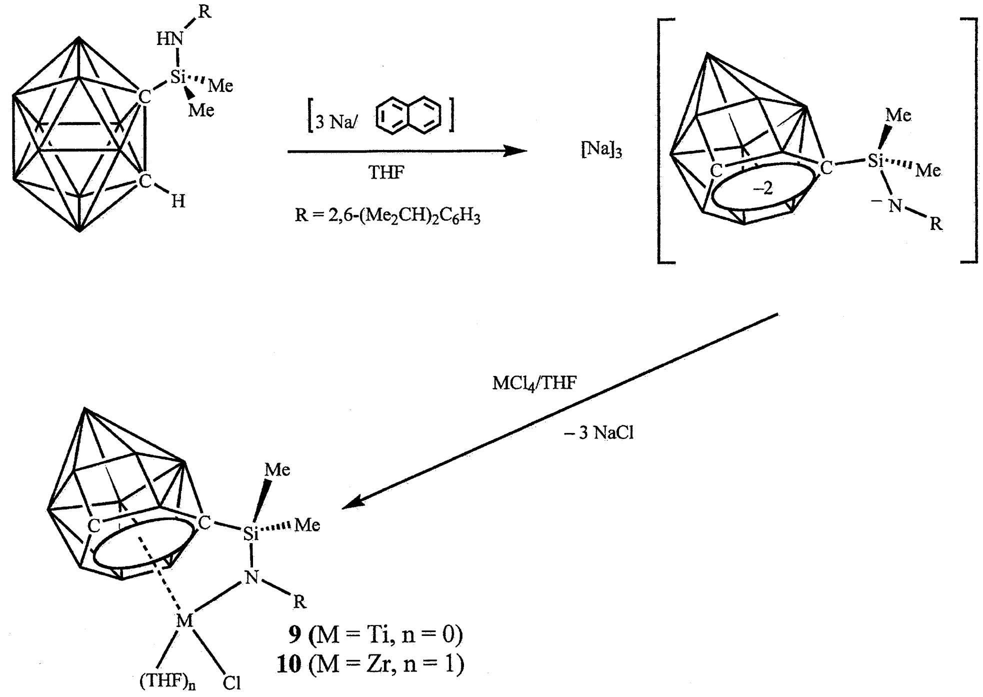
Scheme 1. Synthesis of **5**.

solvent and the temperature, in toluene at −78 °C the yields were 92 and 96% for **6** and **7**, respectively. On the other hand, when the reaction was carried out in THF, a number of side products were formed that were difficult to remove, resulting in both lower yields and products of lower purity. This somewhat complicates the synthetic procedure in that, although lithiation of the *closo*-1-R-1,2-$C_2B_{10}H_{11}$ precursor is carried out in THF, it must be replaced by toluene for the reaction with N(R)HSi$(Me)_2$Cl to give **6** and **7**. The *closo*-compound, [1-(2,6-diisopropanylanilinyldimethylsilyl)-1,2-$C_2B_{10}H_{11}$] (**7**) was reductively opened with sodium naphthalide in THF to give the corresponding carbons apart trianion, [*nido*-3-{Si$(Me)_2$N(2,6-$(Me_2CH)_2C_6H_3$)}-1,3-$C_2B_{10}H_{11}$]$^{3-}$ (**8**) (see Scheme 3), in 90% yield. The trianion, **8**, could be reacted further with MCl_4 (M = Ti and Zr) in THF to give the metallacarboranes, *closo*-1-M[(Cl)$(THF)_n$]-2-[1′-$\eta^1\sigma$-N(2,6-$(Me_2CH)_2C_6H_3$)$(Me)_2$Si]-2,4-η^6-$C_2B_{10}H_{11}$ (M = Ti, *n* = 0 (**9**); M = Zr, *n* = 1 (**10**)) in 47 and 36% yields, respectively. The lower coordination number of the Ti in **9**, compared with that of Zr in **10**, is most likely due to smaller size of the former metal atom. A large group such as the 2,6-diisopropanylanilinyldimethylsilyl should increase the lability of the other ligands around the titanium to the extent that its fourth coordination site is vacant in **9**. Advantage could be taken of the influence of the size of the pendant nitrogen group on the lability of the other ligands on the capping metal atom in complexes such as **9** and **10**. The carbons apart structures for **8**–**10**, shown in Scheme 3, were assigned on the basis of the structural analysis of the *nido*-carborane products of the reactions of *closo*-1,2-$(C_6H_5CH_2)_2$-1,2-$C_2B_{10}H_{10}$ with a number of Group 1 metals, by Xie and coworkers [20], and on the assumption that metalation would not lead to cage isomerization. The NMR spectra, as well as the chemical analyses, of compounds **8**–**10** are consistent with their formulations. For example, the ^{1}H-NMR spectra of these compounds show resonances for both the silicon-bound and carbon-bound methyl groups as well as for the *i*-propyl and phenyl hydrogens. However, it is significant that the resonances attributable to N-bound hydrogens are absent in the ^{1}H-NMR spectra of **8**–**10**. While the ^{11}B-NMR spectroscopy proved very useful in elucidating the structure of **5**, it is of limited help as a structural probe for **8**–**10**. Consequently, the ^{11}B-NMR spectra of these compounds consisted of a series of broad, overlapping peaks that were difficult to interpret in terms of specific boron resonances. This same ambiguity was noted in the ^{11}B-NMR spectra of a number of Group 1 salts of [$(C_6H_5CH_2)_2C_2B_{10}H_{10}$]$^{2-}$ dianion reported by Xie and coworkers [20]. Further characterization of **8**–



6 (R′ = Ph, R = *t*-Bu); **7** (R′ = H, R = 2,6-$(Me_2CH)_2C_6H_3$)

Scheme 2. Syntheses of **6** and **7**.



Scheme 3. Cage opening and metalation of **7**.

10 must await their X-ray analyses. We are presently attempting to grow suitable crystals for this purpose.

3.2. X-ray analysis of 7

The *closo*-2-[Si(Me)$_2$NH(2,6-(Me$_2$CH)$_2$C$_6$H$_3$)]-1,2-C$_2$B$_{10}$H$_{11}$ (**7**) is a key synthon in the production of the constrained geometry metallacarboranes, **9** and **10**. Of special concern is the availability of the amine nitrogen to form additional bonds with the capping metals. Compounds **8**–**10** have not as yet been structurally characterized, however, the crystal structure of **7** could be obtained and is shown in Fig. 1. Table 1 gives the pertinent crystallographic information and some selected bond distances and angles are given in the caption for Fig. 1. A more complete listing of bond distances and angles, as well as the atomic coordinates are given in Section 5. The structure of **7** shows that it consists of a closed C$_2$B$_{10}$ polyhedron with a distorted icosahedral cage geometry. The intracage bond distances are quite similar to those reported for *closo*-1-(methyl)-2-(phthalimidomethyl)-1,2-C$_2$B$_{10}$H$_{10}$ [21]. The *exo*-polyhedral Si(Me)$_2$NH(2,6-(Me$_2$CH)$_2$C$_6$H$_3$) group in **7** is attached to a cage carbon by a standard 2*c*2*e* bond. The Si–C(02) bond distance of 1.911(3) Å in this compound is larger than Si–C bond distances of 1.869(6) Å in (C$_5$Me$_4$SiMe$_2$N-*t*-Bu)Ti(prone-2,4-hexadiene) [22], and 1.861(6) Å in η^5:σ-Me$_2$Si(C$_9$H$_6$)-η^6-(C$_2$B$_{10}$H$_{10}$CH$_2$-NMe)Zr(NC$_5$H$_5$) [23]. The four groups on the silicon atom are in a distorted tetrahedral arrangement, with the X–Si–Y angles ranging from 103.53° for N–Si–C(02) to 114° for N–Si–C(03/04). The most interesting aspect of this structure is the large C(1)–N–Si angle of 125.5(2)°. This is most likely due to the repulsion between the Si–Me groups and the large diisopropylphenyl moiety. Such an angle indicates that the lone pair on nitrogen atom would not be particularly available for bonding. However, from the formulations of **9** and **10**, it seems that η^1-coordination of the N is possible after removal of its H to form the amido group.

4. Conclusions

We have prepared and characterized two new constrained geometry carborane ligands, *nido*-5-*t*-BuNH-Si(Me)$_2$-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_5$ (**5**) and [Na$^+$-(THF)$_n$]$_3$[*nido*-3-{Si(Me)$_2$N(2,6-(Me$_2$CH)$_2$C$_6$H$_3$)}-1,3-C$_2$B$_{10}$H$_{11}$]$^{3-}$ (**8**). Compound **5** proved of limited use as a ligand since it could not withstand deprotonation with a strong base. Reaction of **5** with M(NMe$_2$)$_4$ (M = Zr and Ti) lead to reaction and possible metalation, but no characterizable products could be isolated. On the other hand, [Na$^+$(THF)$_n$]$_3$[*nido*-3-{Si(Me)$_2$N(2,6-(Me$_2$CH)$_2$-C$_6$H$_3$)}-1,3-C$_2$B$_{10}$H$_{11}$]$^{3-}$ (**8**) reacted with MCl$_4$ (M = Ti, Zr) to give the respective metallacarboranes, *closo*-1-M[(Cl)(THF)$_n$]-2-[1′-$\eta^1\sigma$-N(2,6-(Me$_2$CH)$_2$C$_6$H$_3$)-(Me)$_2$Si]-2,4-η^6-C$_2$B$_{10}$H$_{11}$ (M = Ti, $n = 0$ (**9**); M = Zr, $n = 1$ (**10**)), in moderate yields. The metallacarboranes were characterized by NMR spectra and elemental analyses.

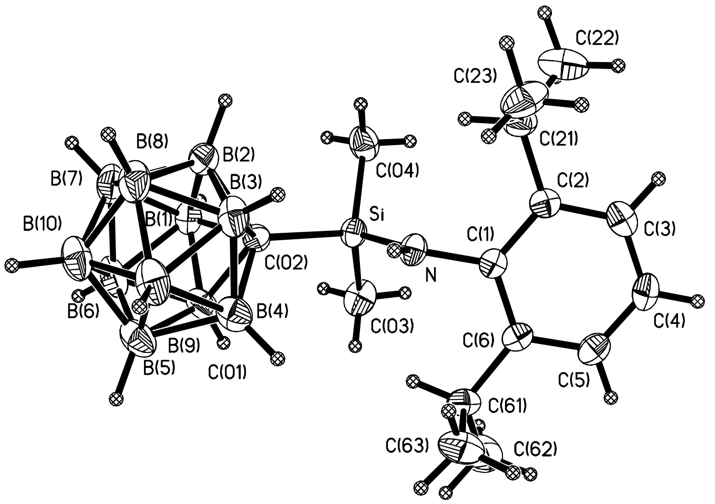


Fig. 1. Perspective view of **7** with thermal ellipsoids drawn at the 50% probability level and showing the atomic numbering scheme. Selected bond lengths (Å) and angles (°) are: Si–N 1.717(3), Si–C(02) 1.911(3), N–C(1) 1.439(4), Si–C(04) 1.848(4), Si–C(03) 1.853(3), C(01)–C(02) 1.653(4), B(1)–C(01) 1.699(5), B(1)–C(02) 1.722(5), B(4)–C(01) 1.706(5), B(4)–C(02) 1.726(5); C(02)–Si–N, 103.53(14), C(04)–Si–N 114.12(16), C(03)–Si–N 113.73(15), C(04)–Si–C(03) 107.99(18), C(1)–N–Si 125.5(2).

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 204610 for compound **7**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (Fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk or web: http://www.ccdc.cam.ac.uk).

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