Stabilization of a Two-Coordinate, Acyclic Diaminosilylene (ADASi): Completion of the Series of Isolable Diaminotetrylenes, :E(NR_2)$_2$ (E = Group 14 Element)

Terrance J. Hadlington,[a] Joseph A. B. Abdalla,[b] Rémi Tirfoin,[b] Simon Aldridge,*[,b] Cameron Jones*[,a]

[a] School of Chemistry, Monash University, PO Box 23, Melbourne, VIC, 3800, Australia.

[b]Inorganic Chemistry Laboratory, Department of Chemistry, University of Oxford, South Parks Road, Oxford, OX1 3QR, UK.

Electronic Supplementary Information (21 pages)

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1. Experimental

General considerations.

All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity dinitrogen. Diethyl ether was distilled over Na/K alloy (25:75), while THF, hexane, toluene and benzene were distilled over molten potassium. ^{1}H, ^{13}C{^{1}H}, ^{29}Si{^{1}H} and ^{11}B{^{1}H} NMR spectra were recorded on either Bruker DPX300, Bruker AvanceIII 400 or Varian Inova 500 spectrometers and were referenced to the resonances of the solvent used, external $SiMe_4$, or external $BF_3.OEt_2$. Mass spectra were collected using an Agilent Technologies 5975D inert MSD with a solid state probe. FTIR spectra were collected for solid samples on an Agilent Cary 630 attenuated total reflectance (ATR) spectrometer. Microanalyses were carried out at the Science Centre, London Metropolitan University. Melting points were determined in sealed glass capillaries under dinitrogen, and are uncorrected. (DAB)BBr,[1] $SiCl_2$(IPr)[2] and benzyl potassium[3] were prepared by literature procedures. All other reagents were used as received.

(DAB)BNH$_2$. Route (a): THF (100 mL) was added to a mixture of (DAB)BBr (20.0 g, 43.0 mmol) and $LiNH_2$ (1.2 g, 51.6 mmol) at ambient temperature. The mixture was then heated at 55 ºC for 18 h, after which time all volatiles were removed *in vacuo*. The solid residue was extracted into hot hexane (100 mL), and the resulting suspension filtered through a Celite pad in the air. The filtrate was stored at -30 ºC for 16 h to yield a large crop of the title compound as a colourless crystalline solid (12.0 g, 70 %). Evaporation of the mother liquor to dryness, followed by washing of the residue with cold hexane (10 mL), yielded a further 2.5 g of solid product, that was essentially pure, as determined by a ^{1}H NMR spectroscopic analysis (combined yield 14.5 g, 84%).

Route (b): A solution of (DAB)BBr (10 g, 21.5 mmol) in hexane (75 mL) at ambient temperature was rapidly stirred under a flow of dry NH_3, which immediately led to the formation of a white precipitate of NH_4Br. After 20 min the reaction vessel was sealed, and the mixture stirred for a further 4 h. The suspension was subsequently warmed to ~ 60 ºC and filtered. Removal of all volatiles from the filtrate *in vacuo* led to the isolation of essentially pure (DAB)BNH_2 as a colorless solid (6.5 g, 75 %). M.p. 76-80 ºC; ^{1}H NMR (C_6D_6, 400 MHz, 298 K), δ = 1.19 (br s, 2H, BNH_2), 1.25 (d, $^{3}J_{HH}$ = 7.6 Hz, 12H, CH(CH_3)$_2$), 1.27 (d, $^{3}J_{HH}$ = 7.6 Hz, 12H, CH(CH_3)$_2$), 3.37 (sept, $^{3}J_{HH}$ = 7.6 Hz, 4H, CH(CH$_3$)$_2$), 5.94 (s, 2H, NCH), 7.17-7.21 (m, 6H, Ar-H); ^{13}C{^{1}H} NMR (C_6D_6, 75.5 MHz, 298 K), δ = 24.3 (CH(CH$_3$)$_2$), 24.4 (CH(CH$_3$)$_2$), 28.6 (CH(CH$_3$)$_2$), 116.9 (NCH), 123.9, 127.6, 138.7, 147.6 (Ar-C); ^{11}B{^{1}H} NMR (C_6D_6, 128 MHz, 298 K), δ = 22.9; IR, ν/cm^{-1} (ATR): 3410 (m, NH_2), 2959 (s), 1592 (m), 1360 (m), 1276 (m), 1177 (m), 1118 (s), 1056 (m), 934 (w),

804 (s), 732 (m); MS/EI *m/z* (%): 404.2 (MH^+, 100); acc. mass calcd. for $C_{26}H_{39}BN_3$ (MH^+): 404.3237; found: 404.3240.

TBoNH. To a solution of (DAB)BNH_2 (10.0 g, 24.9 mmol) in diethyl ether (100 mL) at -80 ºC was added $LiBu^n$ (16.3 mL, 1.6 M in hexane, 26.1 mmol) over the course of 5 min. The reaction mixture was subsequently warmed to room temperature and stirred for 1 h. The reaction mixture was then cooled to 0 ºC and quenched with $SiMe_3Cl$ (3.32 mL, 26.1 mmol). The resultant suspension was filtered, and all volatiles removed from the filtrate *in vacuo* to yield TBoNH as an oil. This was shown to have a purity of > 97% by ^1H NMR spectroscopy. The oil was used without further purification (10.9 g, 92%); ^1H NMR (C_6D_6, 400 MHz, 298 K), δ = -0.29 (s, 9H, Si(CH_3)$_3$), 1.23 (d, $^3J_{HH}$ = 7.6 Hz, 12H, CH(CH_3)$_2$), 1.34 (d, $^3J_{HH}$ = 7.6 Hz, 12H, CH(CH_3)$_2$), 3.42 (sept, $^3J_{HH}$ = 7.6 Hz, 4H, C*H*(CH$_3$)$_2$), 6.01 (s, 2H, NC*H*), 7.15-7.31 (m, 6H, Ar-*H*); $^{13}C\{^1H\}$ NMR (C_6D_6, 75.5 MHz, 298 K), δ = 1.8 (Si(CH_3)$_3$), 23.8 (CH(*C*H$_3$)$_2$), 25.2 (CH(*C*H$_3$)$_2$), 28.6 (*C*H(CH$_3$)$_2$), 117.8 (N*C*H), 124.0, 127.8, 139.4, 147.4 (Ar-*C*); $^{11}B\{^1H\}$ NMR (C_6D_6, 128 MHz, 298 K), δ = 23.1; ^{29}Si NMR (C_6D_6, 80 MHz, 298 K), δ = 2.8; IR, ν/cm^{-1} (ATR): 3354 (br w, NH), 3067 (w), 3028 (w), 1249 (m), 1112 (w), 1070 (m), 900 (m), 834 (s), 803 (s), 696 (m); MS/EI *m/z* (%): 475.5 (MH^+, 100).

Li[TBoN]. To a solution of TBoNH (5.0 g, 10.5 mmol) in hexane (50 mL) at room temperature was added $LiBu^n$ (6.9 ml, 1.6 M in hexane, 11.0 mmol) over 10 min. The reaction mixture was then stirred for 3 days, over which time a white precipitate deposited. The suspension was subsequently concentrated to ~ 25 mL, and stored at -30 ºC overnight to afford further white precipitate, which was isolated by filtration, and dried *in vacuo*, yielding the title compound as a white powder. This was used for further reactions without purification (3.0 g, 59 %). ^1H NMR (C_6D_6, 400 MHz, 298 K), δ = -0.36 (s, 9H, Si(CH_3)$_3$), 1.25 (d, $^3J_{HH}$ = 7.0 Hz, 12H, CH(CH_3)$_2$), 1.35 (d, $^3J_{HH}$ = 7.0 Hz, 12H, CH(CH_3)$_2$), 3.72 (sept, $^3J_{HH}$ = 7.0 Hz, 4H, C*H*(CH$_3$)$_2$), 6.04 (s, 2H, NC*H*), 7.16-7.19 (m, 6H, Ar-*H*).

K[TBoN]. To a suspension of benzyl potassium (1.5 g, 11.6 mmol) in toluene (10 mL) at -40 ºC, was added a solution of TBoNH (5.0 g, 10.5 mmol) in toluene (40 mL) over 5 min. The reaction mixture was warmed to ambient temperature and stirred for 2 h, whereupon the majority of the suspended benzyl potassium had been consumed. The reaction mixture was allowed to settle, filtered, and all volatiles removed from the filtrate *in vacuo*. The resultant residue was washed with hexane (2 x 10 mL), and the residue dried *in vacuo*, giving the title compound as a free-flowing pale brown powder. This was used for further reactions without purification (4.7 g, 87 %). ^1H NMR (C_6D_6, 400 MHz, 298 K), δ = -0.23 (s, 9H, Si(CH_3)$_3$), 1.30 (d, $^3J_{HH}$ = 7.0 Hz, 12H, CH(CH_3)$_2$), 1.38

(d, $^3J_{HH}$ = 7.0 Hz, 12H, CH(CH_3)$_2$), 3.83 (sept, $^3J_{HH}$ = 7.0 Hz, 4H, CH(CH$_3$)$_2$), 6.12 (s, 2H, NCH), 7.08-7.13 (m, 6H, Ar-H).

:Si(TBoN)$_2$ 1. To a rapidly stirred solution of $SiCl_2$(IPr) (1.0 g, 2.06 mmol) in benzene (10 mL) at ambient temperature was added a solution of Li[TBoN] (1.0 g, 2.08 mmol) in benzene (10 mL) over 10 sec. After 5 min of stirring, all voltiles were removed from the pale yellow reaction solution *in vacuo*, and the residue extracted into warm hexane, and filtered. The filtrate was then either stirred under and atmosphere of CO_2, or a solution of $SiBr_4$ (1.04 mL, 2 M in hexane, 2.08 mmol) was added to it. In both cases, the resultant suspension rapidly stirred for 2 h, whereupon further copious white precipitate formed. The reaction mixture was again filtered, and all volatiles removed from the filtrate *in vacuo*. The residue was redissolved in diethyl ether (5 mL), then the solution concentrated to ~2 mL, and stored at -30 ºC for 18 h. After this time large pale yellow crystals of **1** had formed (520 mg, 51 %). M.p.: 152-160 ºC (melt); ^{1}H NMR (C_6D_6, 400 MHz, 298 K), δ = -0.12 (s, 18H, Si(CH_3)$_3$), 1.14 (br., 24H, CH(CH_3)$_2$), 1.28 (br, 24H, CH(CH_3)$_2$), 3.47 (br. sept, $^3J_{HH}$ = 7.0 Hz, 8H, CH(CH$_3$)$_2$), 6.02 (s, 4H, NCH), 7.05-7.25 (br. m, 12H, Ar-H); ^{13}C{^{1}H} NMR (C_6D_6, 75.5 MHz, 298 K), δ = 6.7 (Si(CH$_3$)$_3$), 23.5 (br., CH(CH$_3$)$_2$), 26.9 (br., CH(CH$_3$)$_2$), 28.5 (br., CH(CH$_3$)$_2$), 29.6 (br., CH(CH$_3$)$_2$), 120.8 (NCH), 124.2, 124.6, 141.1, 146.4 (Ar-C); ^{11}B{^{1}H} NMR (C_6D_6, 128 MHz, 298 K), δ = 23.7; ^{29}Si{^{1}H} NMR (C_6D_6, 80 MHz, 298 K), δ = 3.1 (Si(CH$_3$)$_3$), 204.6 (NSiN); UV/vis (hexane, λ_{max}, nm [ε, Lcm^{-1}mol^{-1}]: 385 [1750], 300 [2500]); IR, ν/cm^{-1} (ATR): 3064 (w), 1584 (w), 1377 (s), 1323 (m), 1297 (m), 1266 (s), 1118 (m), 1067 (m), 955 (m), 803 (s), 696 (s); MS/EI *m/z* (%): 977.1 (M$^+$, 2), 475.5 (TBoNH$^+$, 100); anal. calcd. for $C_{58}H_{90}B_2N_6Si_3$: C, 71.28 %; H, 9.28 %; N, 8.60 %; found: C, 71.15 %; H, 9.17 %; N, 8.50 %.

:Sn(TBoN)$_2$ 2. A solution of K[TBoN] (1.50 g, 2.9 mmol) in THF (25 mL) was added to a solution of $SnBr_2$ (0.40 g, 1.45 mmol) in THF (10 mL) at -80 ºC over 5 min. The reaction mixture was warmed to ambient temperature over 2 h, yielding a deep red/orange solution. All volatiles were subsequently removed *in vacuo*. Extraction of the residue into warm hexane (25 mL), filtration of the extract, and removal of volatiles from the filtrate *in vacuo* led to the isolation of essentially pure **2** as a free-flowing orange powder (1.22 g, 79 %). X-ray quality crystals of **2** were grown from a concentrated hexane solution stored at 4 ºC for 2 days. M.p.: 104-110 ºC (melt); ^{1}H NMR (C_6D_6, 400 MHz, 298 K), δ = 0.11 (s, 18H, Si(CH_3)$_3$), 1.16 (d, $^3J_{HH}$ = 7.0 Hz, 24H, CH(CH_3)$_2$), 1.29 (br. d, $^3J_{HH}$ = 7.0 Hz, 24H, CH(CH_3)$_2$), 3.43 (br. sept, $^3J_{HH}$ = 7.0 Hz, 8H, CH(CH$_3$)$_2$), 5.94 (s, 4H, NCH), 7.06-7.18 (m, 12H, Ar-H), ^{13}C{^{1}H} NMR (C_6D_6, 75.5 MHz, 298 K), δ = 5.6 (Si(CH$_3$)$_3$), 23.4 (br., CH(CH$_3$)$_2$), 26.4 (br., CH(CH$_3$)$_2$), 28.6 (br., CH(CH$_3$)$_2$), 119.8 (br., NCH), 124.0, 124.4, 141.7, 146.8 (Ar-C); ^{11}B{^{1}H} NMR (C_6D_6, 128 MHz, 298 K), δ = 23.2; ^{29}Si NMR (C_6D_6, 80 MHz, 298

K), δ = 4.2; IR, ν/cm^{-1} (ATR): 3063 (w), 1583 (w), 1305 (s), 1241 (s), 1178 (m), 1116 (s), 1065 (s), 971 (m), 934 (w), 890 (s), 661 (s); MS/EI *m/z* (%): 593.4 (M^+-TBoN, 0.5), 475.5 ($TBoNH^+$, 100); N.B. Elemental analyses repeatedly returned low carbon percentages, possibly due to the formation of involatile SiC compounds, as has been previously reported for compounds containing silyl amide ligands.[4] In addition, no signal was observed in the ^{119}Sn NMR spectrum of the compound.

:Pb(TBoN)$_2$ 3. This compound was prepared in an analogous fashion to **2**, but using K[TBoN] (0.3 g, 0.59 mmol) and $PbBr_2$ (108 mg, 0.30 mmol). The crude reaction mixture, following removal of volatiles *in vacuo*, was extracted into warm hexane (20 mL), and the extract filtered. Storage of the filtrate at 4 ºC for 16 h led to the formation of large red/orange crystalline blocks of **3** (130 mg, 38 %). M.p.: 104-110 ºC (melt); ^{1}H NMR (C_6D_6, 400 MHz, 298 K), δ = 0.05 (s, 18H, Si(CH_3)$_3$), 1.17 (d, $^3J_{HH}$ = 7.0 Hz, 24H, CH(CH_3)$_2$), 1.31 (br. d, $^3J_{HH}$ = 7.0 Hz, 24H, CH(CH_3)$_2$), 3.39 (br., 4H, CH(CH$_3$)$_2$), 3.68 (br, 4H, CH(CH$_3$)$_2$), 5.94 (s, 4H, NCH), 7.06-7.18 (m, 12H, Ar-H), ^{13}C{^{1}H} NMR (C_6D_6, 75.5 MHz, 298 K), δ = 4.8 (Si(CH$_3$)$_3$), 22.7 (br., CH(CH$_3$)$_2$), 24.4 (br., CH(CH$_3$)$_2$), 25.6 (br., CH(CH$_3$)$_2$), 27.6 (br., CH(CH$_3$)$_2$), 28.0 (br., CH(CH$_3$)$_2$), 28.9 (br., CH(CH$_3$)$_2$), 119.5 (br., NCH), 124.1, 124.6, 141.8, 147.1, (Ar-C); ^{11}B{^{1}H} NMR (C_6D_6, 128 MHz, 298 K), δ = 23.3; ^{29}Si NMR (C_6D_6, 80 MHz, 298 K), δ = -6.9; IR, ν/cm^{-1} (ATR): 3063 (w), 1583 (w), 1305 (s), 1241 (s), 1178 (m), 1116 (s), 1065 (s), 971 (m), 934 (w), 696 (m), 661 (s); MS/EI *m/z* (%): 681.6 (M^+-TBoN, 5), 475.5 (TBoNH, 100); anal. calcd. for $C_{58}H_{90}B_2N_6Si_2Pb$: C, 60.24 %; H, 7.85 %; N, 7.27 %; found: C, 60.18 %; H, 7.73 %; N, 7.38 %. N.B. No signal was observed in the ^{207}Pb NMR spectrum of the compound.

:Ge(TBoN)Cl 4. A solution Li[TBoN] (2.0g, 3.6 mmol) in THF (30 mL) was added to a solution of $GeCl_2$(dioxane) (0.92 g, 3.97 mmol) in THF (5 mL) at -80 ºC over 5 mins. The reaction mixture was warmed to ambient temperature over the course of 4 h, and all volatiles subsequently removed *in vacuo*. The oily residue was extracted into hexane (20 mL), filtered, and the filtrate concentrated *in vacuo* to ~ 7 mL. Storage at -30 ºC for 18 h resulted in the formation of large colourless blocks of **4** (1.2 g, 57 %). M.p.: 104-110 ºC (melt); ^{1}H NMR (C_6D_6, 400 MHz, 298 K), δ = 0.16 (s, 9H, Si(CH_3)$_3$), 1.11 (d, $^3J_{HH}$ = 7.0 Hz, 12H, CH(CH_3)$_2$), 1.28 (d, $^3J_{HH}$ = 7.0 Hz, 12H, CH(CH_3)$_2$), 3.29 (sept, $^3J_{HH}$ = 7.0 Hz, 4H, CH(CH$_3$)$_2$), 6.18 (s, 2H, NCH), 7.07-7.18 (m, 6H, Ar-H), ^{13}C{^{1}H} NMR (C_6D_6, 75.5 MHz, 298 K), δ = 4.0 (Si(CH$_3$)$_3$), 22.9 (CH(CH$_3$)$_2$), 26.5 (CH(CH$_3$)$_2$), 29.3 (CH(CH$_3$)$_2$), 119.6 (NCH), 124.0, 124.4, 137.9, 145.5 (Ar-C); ^{11}B{^{1}H} NMR (C_6D_6, 128 MHz, 298 K), δ = 24.4; ^{29}Si NMR (C_6D_6, 80 MHz, 298 K), δ = 0.2; IR, ν/cm^{-1} (ATR): 3066 (w), 1570 (w), 1301 (m), 1245 (s), 1116 (m), 799 (s), 781 (m), 679 (s); MS/EI *m/z* (%): 580.5 (M^+-2H, 1), 403.4 ((DAB)BNH_2^+, 100); N.B. Elemental analyses repeatedly returned low carbon percentages, possibly due to the

formation of involatile SiC compounds, as has been previously reported for compounds containing silyl amide ligands.[4]

Si(OH)(TBoN)(κ²-*N,O*-TBoN^{-H}O) 5. A solution of **1** (150 mg, 0.15 mmol) in toluene (5 mL) was stirred under an atmosphere of dry O_2 for 20 min, and all volatiles subsequently removed *in vacuo*. The residue was extracted into hexane (5 mL), the extract filtered, and all volatiles removed from the filtrate *in vacuo*. The residue was redissolved in diethyl ether (5 mL), the solution concentrated to ~1 mL, then stored at ambient temperature for 3 days. During this time, colourless crystals of **5** deposited (60 mg, 39 %). M.p.: 166-175 ºC (melt); ^{1}H NMR (C_6D_6, 400 MHz, 298 K), δ = -0.15 (br. s, 9H, Si(C*H*$_3$)$_3$), 0.04 (s, 9H, Si(C*H*$_3$)$_3$), 1.21-1.65 (m, 48H, CH(C*H*$_3$)$_2$), 2.22 (s, 1H, SiO*H*), 3.31-3.82 (m, 7H, C*H*(CH$_3$)$_2$), 6.13 (m, 2H, NC*H*), 6.30 (m, 2H, NC*H*), 7.12-7.52 (m, 12H, Ar-*H*); ^{11}B{^{1}H} NMR (C_6D_6, 128 MHz, 298 K), δ = 23.2 (v. br.); ^{29}Si NMR (C_6D_6, 80 MHz, 298 K), δ = -72.4 (*Si*OH), 0.9, 2.3 (*Si*(CH$_3$)$_3$); IR, ν/cm^{-1} (ATR): 3200 (v. br., SiO–H), 3061 (w), 1624 (m), 1588 (w), 1382 (m), 1326 (m), 1258 (s), 1072 (s), 1043 (s), 967 (m), 922 (m), 695 (m); MS/EI *m/z* (%): 1009.1 (M$^+$, 0.5), 475.6 (TBoNH$^+$, 10). N.B. Elemental analyses repeatedly returned low carbon percentages, possibly due to the formation of involatile SiC compounds, as has been previously reported for compounds containing silyl amide ligands.[4] In addition, it proved difficult to assign the numerous, often broad and/or overlapping signals, in the ^{13}C{^{1}H} NMR spectrum of the compound.

Si(H)(TBoN)(NH$_2$)$_2$ 7. Route (a): A solution of **1** (150 mg, 0.15 mmol) in toluene (5 mL) was stirred under an atmosphere of dry NH_3 for 20 min, before all volatiles were removed *in vacuo*. The residue was extracted into hexane (5 mL), the extract filtered, and all volatiles removed from the filtrate *in vacuo*, giving an oily residue. The ^{1}H NMR spectrum of this residue (see Figure S1) showed it to contain **7** and TBoNH, in an approximately 1:1 ratio.

Route (b): A solution of Si(H)(TBoN)Cl$_2$ **8** (300 mg, 0.54 mmol) in hexane (15 mL) was stirred under an atmosphere of NH_3 for 3 days, after which time a white precipitate had deposited. The suspension was filtered, the residue washed with hexane (10 mL), and the extracts combined. Concentration of the combined extracts to ~5 mL *in vacuo*, and subsequent storage at 4 ºC for 4 days led to the formation of large colourless plates of **7** (180 mg, 63 %). M.p.: 64-70 ºC (melt); ^{1}H NMR (C_6D_6, 400 MHz, 298 K), δ = -0.05 (br. s, 4H, N*H*$_2$), -0.05 (s, 9H, Si(C*H*$_3$)$_3$), 1.16 (d, $^{3}J_{HH}$ = 7.0 Hz, 6H, CH(C*H*$_3$)$_2$), 1.19 (d, $^{3}J_{HH}$ = 7.0 Hz, 6H, CH(C*H*$_3$)$_2$), 1.36 (d, $^{3}J_{HH}$ = 7.0 Hz, 12H, CH(C*H*$_3$)$_2$), 3.39 (sept, $^{3}J_{HH}$ = 7.0 Hz, 2H, C*H*(CH$_3$)$_2$), 3.58 (sept, $^{3}J_{HH}$ = 7.0 Hz, 2H, C*H*(CH$_3$)$_2$), 4.72 (s, 1H, Si*H*, $^{1}J_{SiH}$ = 232 Hz), 6.18 (s, 2H, NC*H*), 7.14-7.20 (m, 6H, Ar-*H*), ^{13}C{^{1}H} NMR (C_6D_6, 75.5 MHz, 298 K), δ = 3.3 (Si(*C*H$_3$)$_3$), 22.8 (CH(*C*H$_3$)$_2$), 23.2 (CH(*C*H$_3$)$_2$), 26.3 (CH(*C*H$_3$)$_2$), 26.5 (CH(*C*H$_3$)$_2$), 28.4 (*C*H(CH$_3$)$_2$), 28.9 (*C*H(CH$_3$)$_2$), 118.8 (NC*H*), 123.8, 124.0, 127.5, 139.6,

146.3, 147.4 (Ar-*C*); $^{11}B\{^1H\}$ NMR (C_6D_6, 128 MHz, 298 K), δ = 23.9; ^{29}Si NMR (C_6D_6, 80 MHz, 298 K), δ = -35.7 (d, $^1J_{SiH}$ = 232 Hz. *Si*H), 2.4 (*Si*$(CH_3)_3$); IR, ν/cm^{-1} (ATR): 3473 and 3396 (m, NH_2), 3064 (w), 2167 (m, SiH), 1540 (m), 1380 (s), 1295 (m), 1247 (s), 1180 (w), 1119 (m), 835 (s), 803 (s), 691 (s); MS/EI *m/z* (%): 535.6 (M^+, 46); anal. calcd. for $C_{29}H_{50}BN_5Si_2$: C, 65.02 %; H, 9.41 %; N, 13.07 %; found: C, 64.84 %; H, 9.27 %; N, 12.89 %.

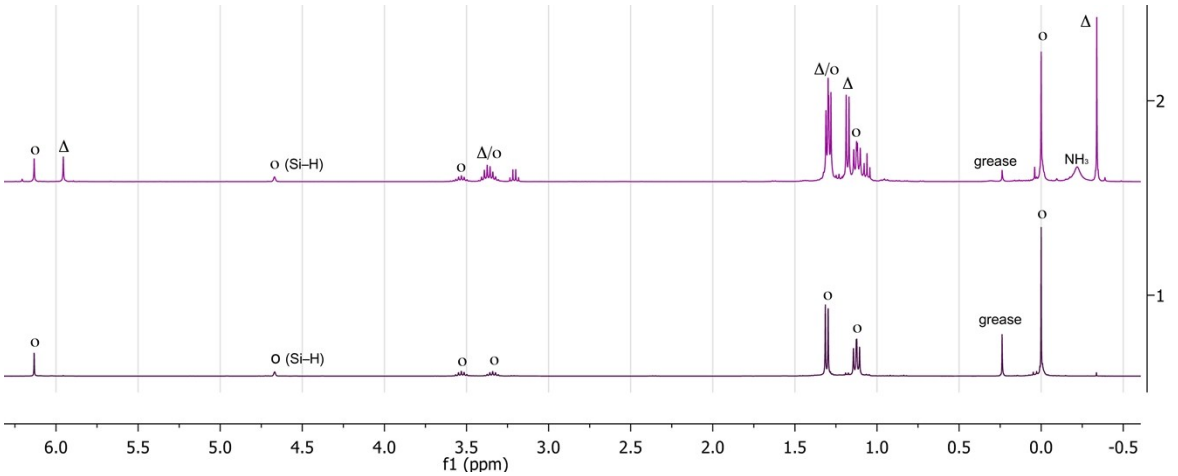

Figure S1. ^1H NMR spectra of the crude mixture arising from the reaction of **1** with excess NH_3, yielding an approximately 1:1 mixture of **7** and TBoNH *(above)*, and pure **7** synthesised by the addition of NH_3 to Si(H)(TBoN)Cl_2 *(below)*; Δ = ^{TMS}BoNH, o = Si(H)(TBoN)$(NH_2)_2$.

Si(H)(TBoN)Cl_2 8. To a solution of $SiHCl_3$ (0.21 mL, 2.18 mmol) in diethyl ether (10 mL) at 0 ºC was added a solution of Li[TBoN] (1.0 g, 1.81 mmol) in diethyl ether (5 mL) over 5 min. The reaction mixture was warmed to ambient temperature and stirred for 1 h, whereupon volatiles were removed *in vacuo*. The residue was extracted into hexane (10 mL), the extract filtered, and volatiles removed from the filtrate *in vacuo* to afford a colorless micro crystalline powder, which was essentially pure **8** (820 mg, 79 %). X-ray quality crystals of the compound were grown from a concentrated hexane solution, held at -30 ºC for 18 h. M.p.: 71-79 ºC (melt); ^1H NMR (C_6D_6, 400 MHz, 298 K), δ = -0.09 (s, 9H, Si(CH_3)$_3$), 1.11 (d, $^3J_{HH}$ = 7.0 Hz, 12H, CH(CH_3)$_2$), 1.33 (br., $^3J_{HH}$ = 7.0 Hz, 12H, CH(CH_3)$_2$), 3.15 (br. sept, $^3J_{HH}$ = 7.0 Hz, 2H, C*H*$(CH_3)_2$), 3.43 (br. sept, $^3J_{HH}$ = 7.0 Hz, 2H, C*H*$(CH_3)_2$), 5.65 (s, 1H, Si*H*), 6.10 (s, 2H, NC*H*), 7.12-7.23 (m, 6H, Ar-*H*), $^{13}C\{^1H\}$ NMR (C_6D_6, 75.5 MHz, 298 K), δ = 2.5 (Si(*C*H_3)$_3$), 23.0, 23.6 (CH(*C*H_3)$_2$), 26.4, 26.5 (CH(*C*H_3)$_2$), 28.4, 29.3 (*C*H$(CH_3)_2$), 119.5 (N*C*H), 124.1, 124.4, 138.4, 146.0, 146.7 (Ar-*C*); $^{11}B\{^1H\}$ NMR (C_6D_6, 128 MHz, 298 K), δ = 23.0; ^{29}Si NMR (C_6D_6, 80 MHz, 298 K), δ = -21.5 (d, $^1J_{SiH}$ = 232 Hz, *Si*H), 9.2 (*Si*$(CH_3)_3$); IR, ν/cm^{-1} (ATR): 3065 (w), 2260 (m, SiH), 1512 (w), 1326 (s), 1290 (m), 1252 (s), 1168 (m), 1119 (s), 891 (s), 830 (s), 758 (s), 698 (s), 657 (s); MS/EI *m/z* (%): 573.5 (M^+, 50 %); anal. calcd. for $C_{29}H_{46}BCl_2N_3Si_2$: C, 60.62 %; H, 8.07 %; N, 7.31 %; found: C, 60.63 %; H, 8.16 %; N, 7.16 %.

2. X-Ray Crystallography

Crystals of **1**-**5**, **7** and **8** suitable for X-ray structural determination were mounted in silicone oil. Crystallographic measurements were made using either an Oxford Supernova or Gemini Ultra diffractometer employing a graphite monochromator with Mo Kα radiation (λ = 0.71073 Å) or Cu Kα radiation (1.54180 Å); or the MX1 beamline of the Australian Synchrotron (λ = 0.71080 Å). The software package Blu-Ice[5] was used for synchrotron data acquisition, while the program XDS[6] was employed for synchrotron data reduction. All structures were solved by direct methods and refined on F^2 by full matrix least squares (SHELX97[7]) using all unique data. Hydrogen atoms are included in calculated positions (riding model), except the hydroxyl hydrogen of **5**, and the hydride atoms of **7** and **8**, the positional and atomic displacement parameters of which were refined isotropically. The absolute structure parameter for **8** was refined to 0.13(0.12). Crystal data, details of data collections and refinements for all structures can be found in their CIF files and are summarized in Table S1.

Table S1. Crystal structure and refinement data for **1**-**5**, **7** and **8**

	1·$(Et_2O)_{0.5}$	**2**	**3**	**4**·$(hexane)_{0.5}$	**5**	**7**	**8**
empirical formula	$C_{60}H_{95}B_2N_6O_{0.5}Si_3$	$C_{58}H_{90}B_2N_6Si_2Sn$	$C_{58}H_{90}B_2N_6Si_2Pb$	$C_{32}H_{52}ClGeN_3Si$	$C_{58}H_{90}B_2N_6O_2Si_3$	$C_{29}H_{50}BN_5Si_2$	$C_{29}H_{46}BCl_2N_3Si_2$
formula weight	1014.31	1067.85	1156.35	625.71	1009.25	535.73	574.58
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic
space group	$P2_1/n$	$C2/c$	$C2/c$	$C2/c$	$P2_1/c$	$P2_1/c$	$P2_12_12_1$
a (Å)	13.1200(2)	26.444(5)	26.6148(7)	23.6484(2)	13.1700(2)	10.0089(5)	10.1620(6)
b (Å)	22.7890(2)	12.059(2)	12.0185(4)	10.2456(1)	20.1290(3)	16.8248(7)	16.8562(8)
c (Å)	21.2000(3)	18.181(4)	18.1788(5)	30.4820(2)	22.9510(4)	19.7026(10)	19.2329(13)
α (º)	90	90	90	90	90	90	90
β (º)	103.7060(10)	98.06(3)	97.896(1)	108.410(1)	104.647(2)	104.172(2)	90
γ (º)	90	90	90	90	90	90	90
V (Å^3)	6158.13(14)	5740(2)	5759.7(3)	7007.56(10)	5886.56(16)	3216.9(3)	3294.5(3)
Z	4	4	4	8	4	4	4
T (K)	150(2)	100(2)	123(2)	150(2)	150(2)	150(2)	123(2)
ρ_{calcd} (g·cm^3)	1.094	1.236	1.334	1.186	1.139	1.106	1.158
μ (mm^{-1})	1.016	0.528	3.012	2.383	1.081	0.135	0.292
F(000)	2212	2272	2400	2664	2192	1168	1232
reflns collected	12885	23997	49975	39385	35449	24857	55301
unique reflns	12885	6469	6035	7319	12249	5861	7508
R_{int}	0.0286	0.0321	0.0955	0.0231	0.0299	0.0585	0.0815
R1 [I > 2σ(I)]	0.0382	0.0336	0.0365	0.0266	0.0448	0.0691	0.0672
wR2 (all data)	0.1075	0.0876	0.0661	0.0688	0.1259	0.1903	0.2101
largest peak and hole (e·Å^{-3})	0.39, -0.30	0.51, -0.99	1.11, -1.18	0.40, –0.41	1.02, –0.67	1.29, –1.05	0.52, -0.97
CCDC no.	1429705	1429706	1429707	1429708	1429709	1429710	1429711

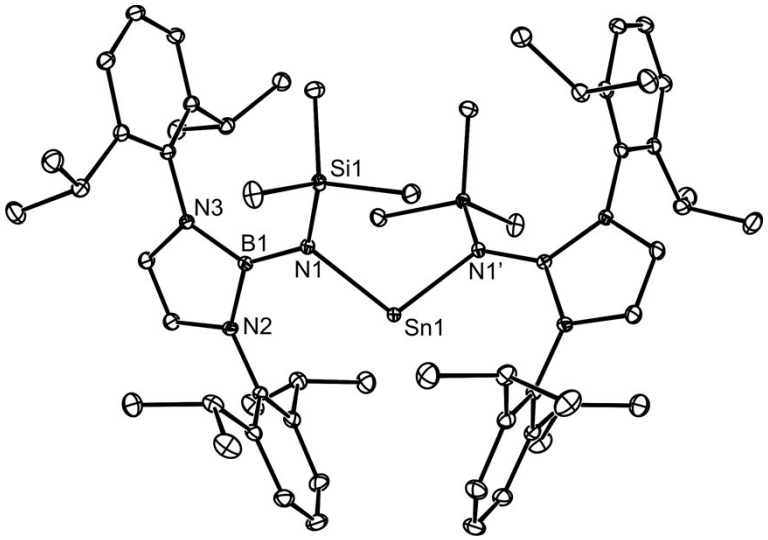

Figure S2. ORTEP diagram of **2** (20% thermal ellipsoids; hydrogen atoms omitted). Selected bond lengths (Å) and angles (º): Sn(1)-N(1) 2.1587(14), Si(1)-N(1) 1.7333(15), N(1)-B(1) 1.445(2), N(1)'-Sn(1)-N(1) 106.13(8), B(1)-N(1)-Si(1) 127.66(12).

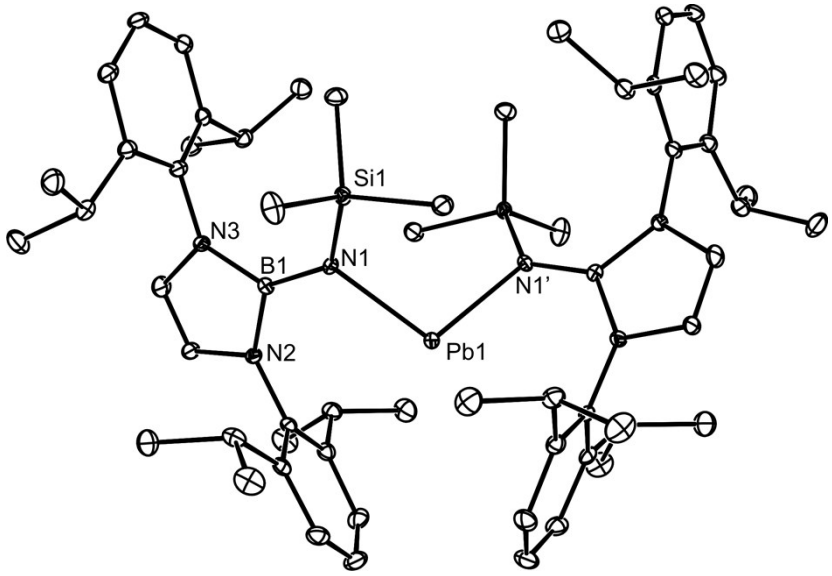

Figure S3. ORTEP diagram of **3** (20% thermal ellipsoids; hydrogen atoms omitted). Selected bond lengths (Å) and angles (º): Pb(1)-N(1) 2.281(3), Si(1)-N(1) 1.724(3), N(1)-B(1) 1.430(4), N(1)'-Pb(1)-N(1) 105.75(14), B(1)-N(1)-Si(1) 130.0(2).

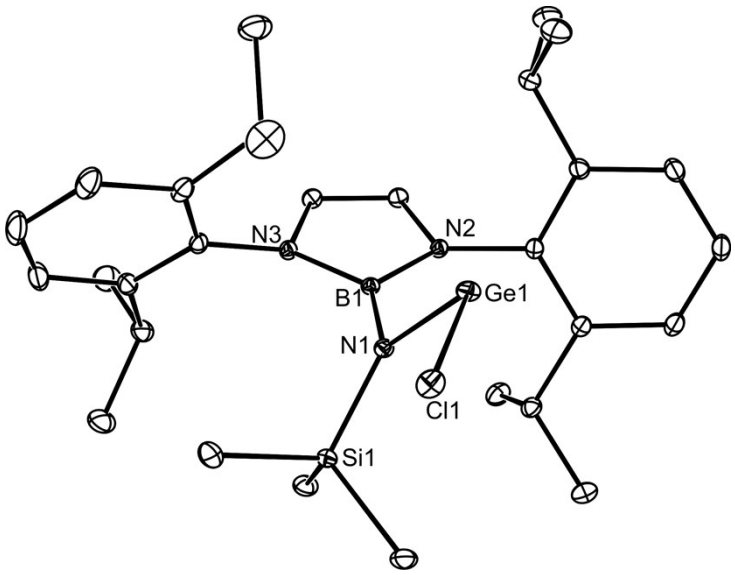

Figure S4. ORTEP diagram of **4** (20% thermal ellipsoids; hydrogen atoms omitted). Selected bond lengths (Å) and angles (º): Ge(1)-N(1) 1.8510(11), Ge(1)-Cl(1) 2.3577(3), Si(1)-N(1) 1.7602(11), N(1)-B(1) 1.4634(16), N(1)-Ge(1)-Cl(1) 99.52(3), B(1)-N(1)-Si(1) 120.36(8).

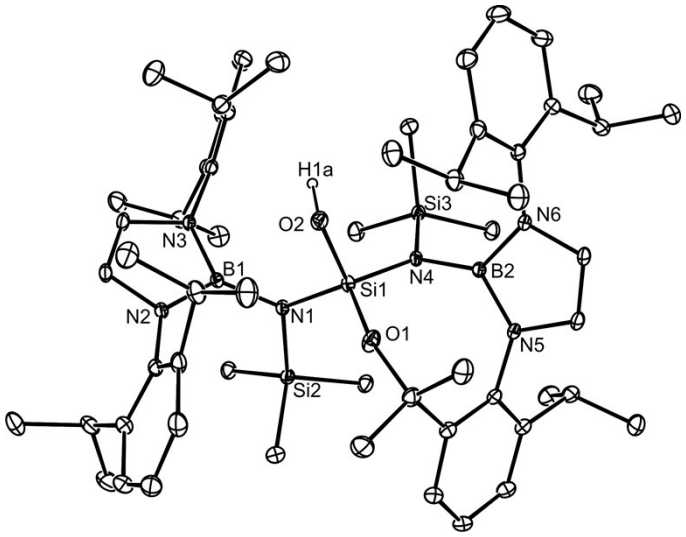

Figure S5. Molecular structures of **5** (20% ellipsoids; hydrogen atoms, except hydride and hydroxyl hydrogens, omitted). Relevant bond lengths (Å) and angles (°): Si(1)-O(1) 1.6203(12), Si(1)-O(2) 1.6384(12), Si(1)-N(1) 1.7282(12), Si(1)-N(4) 1.7292(12), O(1)-Si(1)-O(2) 106.59(7), N(1)-Si(1)-N(4) 117.93(6).

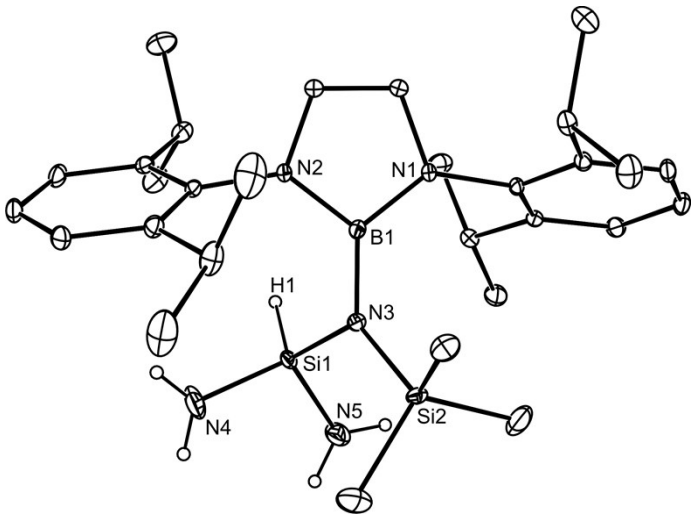

Figure S6. Molecular structures of **7** (20% ellipsoids; hydrogen atoms, except hydride and amino hydrogens, omitted). Relevant bond lengths (Å) and angles (°): Si(1)-N(5) 1.703(3), Si(1)-N(4) 1.711(3), Si(1)-N(3) 1.787(3), Si(1)-H(1) 1.28(4), N(5)-Si(1)-N(4) 105.07(17), N(3)-Si(1)-H(1) 109.1(16), B(1)-N(3)-Si(2) 126.9(2).

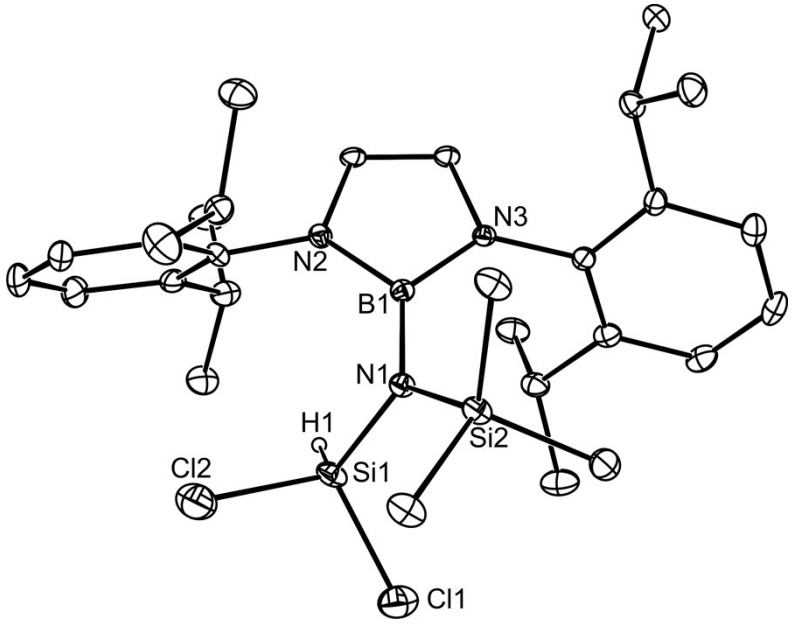

Figure S7. ORTEP diagram of **8** (20% thermal ellipsoids; hydrogen atoms, except the hydride H(1), omitted). Selected bond lengths (Å) and angles (º): Cl(1)-Si(1) 1.9639(19), Si(1)-N(1) 1.710(3), Si(1)-Cl(2) 2.054(2), Si(1)-H(1) 1.37(4), N(1)-B(1) 1.463(6), N(1)-Si(2) 1.776(3), Cl(1)-Si(1)-Cl(2) 105.50(8), Cl(1)-Si(1)-H(1) 107.3(17), B(1)-N(1)-Si(2) 123.0(3).

3. Computational Studies

DFT calculations were carried out using the Amsterdam Density Functional (ADF 2013) software package.[8,9] Calculations were performed using the Volko-Wilk-Nusair local density approximation with exchange from Becke[10] and correlation functions from Perdew (BP).[11] Slater-type orbitals[12] were used for the triple zeta basis set with an additional set of polarization functions (TZP). The large frozen core basis set approximation was applied with no molecular symmetry. General numerical integration was 6.

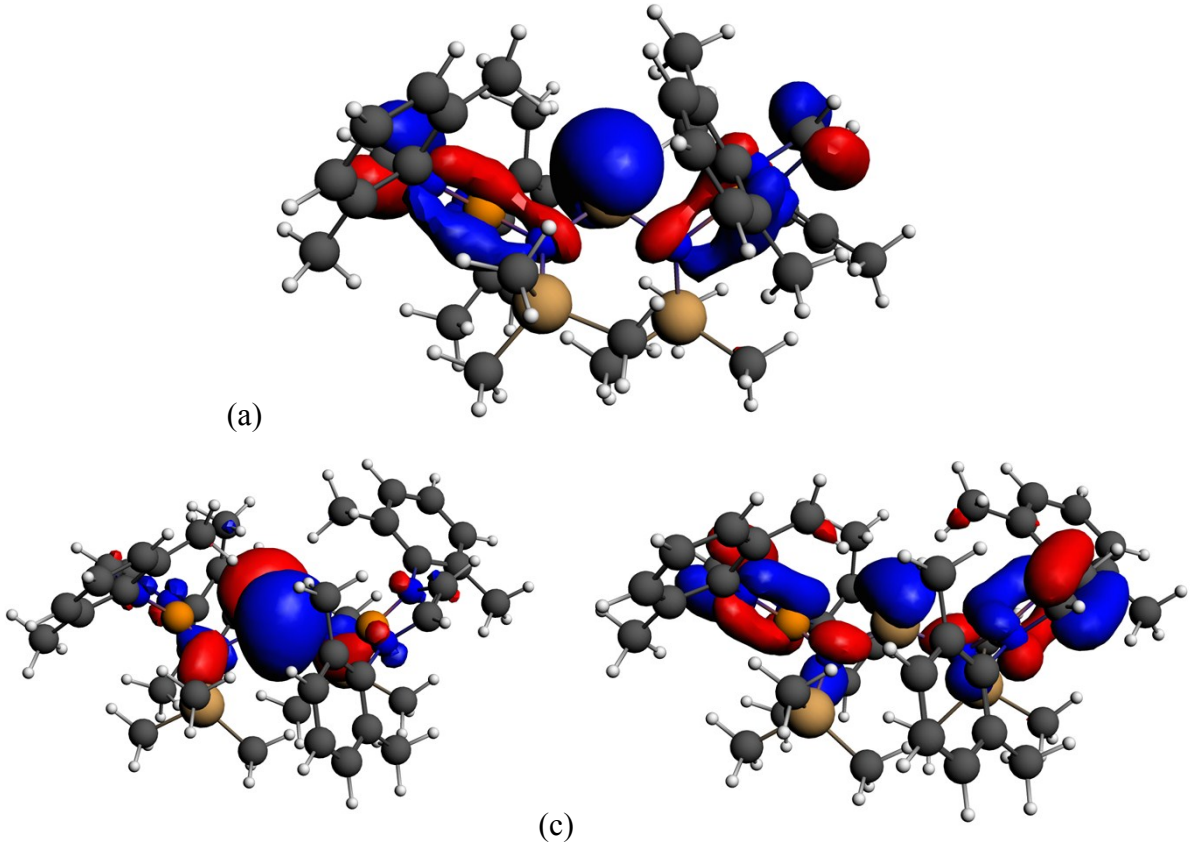

Figure S8. (a) Representations of the HOMO-2 of **1'** (singlet state), (b) HOMO of **1'** (triplet state), and HOMO-1 of **1'** (triplet state).

Table S2. Coordinates and computational details for the calculated molecule, **1'**.

Compound 1' (singlet state)

ATOMS

1 Si	-2.524517350000	8.582558538000	5.421461531000
2 N	-1.377882220000	8.377197177000	4.041560469000
3 Si	-1.730012769000	8.016889327000	2.308484059000
4 C	-0.342629647300	6.964936396000	1.547647713000
5 C	-3.363043296000	7.080589643000	2.088647275000
6 C	-1.982406352000	9.553422421000	1.236183404000
7 B	-0.058438597310	8.914336657000	4.463487885000
8 N	0.788467675600	9.987743636000	3.909763835000
9 C	0.609474100900	10.981925430000	2.884876765000
10 C	1.402397803000	10.934934850000	1.717870462000
11 C	2.439069942000	9.859611648000	1.491571878000
12 H	-3.024592813000	8.085563343000	8.387965236000
13 H	-6.202341354000	7.367109611000	3.509635636000
14 C	1.233740147000	11.941193590000	0.753596117200
15 C	0.329167853700	12.982888770000	0.949640447700
16 C	-0.411240596000	13.040623580000	2.130731874000
17 C	-0.279164554000	12.054730780000	3.117434085000
18 C	-1.043616799000	12.163421380000	4.410686304000
19 H	-7.725276039000	8.251711745000	3.555191381000
20 H	-5.172381247000	12.235924780000	1.285547162000
21 C	1.950502324000	10.098600960000	4.693652592000
22 C	1.910090767000	9.201151886000	5.705512498000
23 N	0.724522354300	8.455659653000	5.621038116000
24 C	0.516727022400	7.420617618000	6.600232440000
25 C	0.868970557700	6.093031280000	6.274872287000
26 C	1.425840368000	5.754235410000	4.915301585000
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30 C	0.287804947000	5.419471392000	8.540546691000
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37 Si	-3.696453557000	5.547450623000	5.388653041000
38 C	-5.192627141000	4.857959998000	4.441986610000
39 C	-3.559312608000	4.622287978000	7.033033423000
40 C	-2.094372831000	5.013877226000	4.536452941000
41 B	-5.033921147000	7.972429219000	6.131333299000
42 N	-5.740559675000	9.136097799000	5.576706076000
43 C	-6.837750812000	9.446640745000	6.394289062000
44 C	-6.891612288000	8.572844089000	7.426067213000
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62 C	-4.844743701000	12.044836840000	3.410522709000
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102 55 110 1.0
103 55 111 1.0
104 58 59 1.5
105 58 63 1.5
106 59 60 1.5
107 59 67 1.0
108 60 95 1.0
109 60 61 1.5
110 61 62 1.5
111 62 93 1.0
112 62 63 1.5
113 63 64 1.0
114 64 68 1.0
115 64 94 1.0
116 67 85 1.0
END

BASIS
type TZP
core Large
createoutput None
END

XC
GGA Becke Perdew
END

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GEOMETRY
   optim Delocalized
   iterations 60
END

SAVE  TAPE21 TAPE13

SCF
iterations 100
END

FULLSCF
INTEGRATION 6

NoBeckeGrid
NOPRINT LOGFILE

eor
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Compound 1' (triplet state)

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ATOMS
1 Si     -2.546542435000      8.441827339000      5.297485460000
2 N      -1.229393683000      8.381450628000      4.081861656000
3 Si     -1.574961502000      8.524089477000      2.315231663000
4 C      -0.033705151740      8.029756682000      1.325416871000
5 C      -2.934020360000      7.291216056000      1.867987047000
6 C      -2.132555916000     10.239136240000      1.772103115000
7 B       0.093553734030      8.707742194000      4.653205095000
8 N       0.879533246900      9.942388627000      4.483311940000
9 C       0.582282639700     11.207604450000      3.870132316000
10 C      1.311810415000     11.632872490000      2.737779601000
11 C      2.433005826000     10.815371250000      2.137885624000
12 H     -2.942918174000      8.987977028000      7.795646994000
13 H     -5.926363797000      6.579721770000      3.229882140000
14 C      1.002800110000     12.878588520000      2.168349309000
15 C      0.018518709010     13.698652660000      2.714795609000
16 C     -0.656779185800     13.289403760000      3.864602134000
17 C     -0.380653110300     12.054810140000      4.467089765000
18 C     -1.076086691000     11.672727710000      5.745593846000
19 H     -7.569541403000      7.097357225000      3.601532638000
20 H     -6.103065291000     10.895250420000      0.090625369470
21 C      2.101081962000      9.798332090000      5.163728394000
22 C      2.144585109000      8.584167122000      5.761941112000
23 N      0.961764978800      7.876196264000      5.493256795000
24 C      0.808059118100      6.587592302000      6.115685377000
25 C      1.010969448000      5.415327014000      5.359865052000
26 C      1.289114086000      5.482584271000      3.880274788000
27 H     -5.302109297000      3.650019038000      5.726220733000
28 H     -2.306836683000      3.877296471000      4.728790015000
29 C      0.973616245300      4.177534456000      6.018634590000
30 C      0.761564409700      4.100094457000      7.394342844000
31 C      0.568993790900      5.268932414000      8.130364418000
32 C      0.583855240900      6.525970495000      7.509858801000
33 C      0.351449370400      7.776820730000      8.320332261000
34 H     -7.913806840000     10.019360230000      5.410706243000
35 H     -2.142616649000      5.652198199000      7.644894204000
36 N     -3.969148795000      7.364340855000      5.474933572000
37 Si    -3.773451716000      5.591089327000      5.753951830000
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38 C	-5.439305307000	4.720263813000	5.496844329000
39 C	-3.101075989000	5.145844666000	7.456011126000
40 C	-2.589199878000	4.905721938000	4.452155873000
41 B	-5.194533017000	8.091765885000	5.865422627000
42 N	-6.060921420000	8.940983727000	5.041279527000
43 C	-7.137380821000	9.385968380000	5.825977751000
44 C	-7.027790617000	8.891426934000	7.081930584000
45 N	-5.864973980000	8.107475653000	7.177397062000
46 C	-5.499345488000	7.578505741000	8.462578579000
47 C	-6.282684954000	6.565512653000	9.058821638000
48 C	-7.530690164000	6.013584099000	8.408486747000
49 H	-6.021418923000	11.842100110000	5.341927705000
50 H	1.508545597000	4.485066153000	3.479521536000
51 C	-5.903214349000	6.077066765000	10.319327340000
52 C	-4.795945930000	6.591032224000	10.990007060000
53 C	-4.063433545000	7.628421717000	10.413135340000
54 C	-4.406097339000	8.147109517000	9.157344329000
55 C	-3.639166284000	9.312333661000	8.593183020000
56 H	3.411853041000	11.221411840000	2.439171425000
57 H	-0.463951841100	8.371333549000	7.877835581000
58 C	-5.980296555000	9.433305900000	3.691223642000
59 C	-6.366720367000	8.604388479000	2.618754979000
60 C	-6.393900379000	9.148660231000	1.326267902000
61 C	-6.067481227000	10.485127710000	1.100646775000
62 C	-5.693000776000	11.295057990000	2.172427309000
63 C	-5.637867820000	10.788068840000	3.478348709000
64 C	-5.207797272000	11.674706180000	4.620506922000
65 H	-7.684416487000	9.040469244000	7.931520019000
66 H	2.393663104000	10.846677870000	1.040482089000
67 C	-6.770171198000	7.170960735000	2.850389403000
68 H	-4.871692324000	12.650084980000	4.246792587000
69 H	2.140504254000	6.143362780000	3.663316955000
70 H	-0.253576710600	8.181607783000	0.255169994700
71 H	0.847483917800	8.637616892000	1.570673651000
72 H	0.229349692900	6.970914873000	1.462746491000
73 H	-3.294227955000	7.506843335000	0.849338828300
74 H	-3.793648114000	7.364212025000	2.548299775000
75 H	-2.560929780000	6.258031535000	1.888614722000
76 H	-2.421592679000	10.200306830000	0.708566369300
77 H	-3.016107650000	10.564097400000	2.341736985000
78 H	-1.344814007000	10.998017960000	1.886119641000
79 H	2.403121849000	9.770821313000	2.464725154000
80 H	1.240639025000	8.424305684000	8.343886002000
81 H	0.081611937180	7.523197633000	9.353206837000
82 H	-6.494725774000	5.280101770000	10.775444860000
83 H	-4.514864369000	6.197680108000	11.967764820000
84 H	-3.217563741000	8.062939658000	10.949957460000
85 H	-7.121176882000	6.709784603000	1.918782538000
86 H	1.551194343000	13.202829830000	1.281097537000
87 H	-0.209974693100	14.662004030000	2.257069434000
88 H	-1.402874482000	13.943419900000	4.320746012000
89 H	-1.870605955000	10.923266430000	5.563547922000
90 H	-7.572517535000	6.238824708000	7.337809862000
91 H	-1.550257337000	12.548655330000	6.206828074000
92 H	-0.375809071800	11.227899000000	6.465039541000
93 H	-5.425587386000	12.339687990000	2.000251373000
94 H	-4.380516180000	11.205119700000	5.176534696000
95 H	-6.693276529000	8.511146871000	0.491701508400
96 H	2.843986354000	10.587769190000	5.171767610000
97 H	2.939062992000	8.148825699000	6.358412778000
98 H	0.427575937900	5.889987430000	3.334953459000
99 H	-6.229653184000	5.100509281000	6.157789257000

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100 H    -5.793644045000    4.793897339000    4.458438273000
101 H    -2.913396156000    4.059762441000    7.493054624000
102 H    -1.666571190000    5.498477547000    4.384895945000
103 H    -3.057770145000    4.877602478000    3.458832308000
104 H    -3.797294862000    5.401622984000    8.268010833000
105 H     1.131122296000    3.266094566000    5.438074604000
106 H     0.745390206000    3.130116895000    7.892854701000
107 H     0.392171311900    5.213763590000    9.206512870000
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109 H    -7.593171150000    4.925580649000    8.546718348000
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93 48 108 1.0
94 49 64 1.0
95 51 82 1.0
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113 63 64 1.0
114 64 68 1.0
115 64 94 1.0
116 67 85 1.0
END

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CHARGE 0.0 2.0

UNRESTRICTED

BASIS
type TZP
core Large
createoutput None
END

XC
GGA Becke Perdew
END

GEOMETRY
   optim Delocalized
   iterations 60
END

SAVE  TAPE21 TAPE13

SCF
iterations 100
END

FULLSCF
INTEGRATION 6

NoBeckeGrid
NOPRINT LOGFILE
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