Intramolecular base-stabilised adducts of main group halides

Simon Aldridge,*[a] Richard J. Calder,[a] Deborah L. Coombs,[a] Cameron Jones,[a] Jonathan W. Steed,[b] Simon Coles[c] and Michael B. Hursthouse[c]

[a] *Department of Chemistry, Cardiff University, PO Box 912, Park Place, Cardiff, UK CF10 3TB. E-mail: AldridgeS@cardiff.ac.uk*
[b] *Department of Chemistry, King's College London, Strand, London, UK WC2R 2LS*
[c] *Department of Chemistry, University of Southampton, Highfield, Southampton, UK SO17 1BJ*

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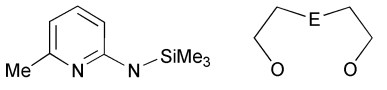
The coordination chemistry of alkoxo and amido ligands bearing pendant nitrogen or sulfur donors has been developed to include examples of main group complexes. The structural implications of amido ligand coordination augmented by a tethered pyridyl base have been investigated for group 13 and 14 derivatives {[6-(Me_3SiN)-2-Me-C_5H_3N]$SnCl_3$ and [6-(Me_3SiN)-2-Me-C_5H_3N]BBr_2}. Furthermore, the scope, kinetics and mechanism of the synthesis of alkoxo and amido derivatives from trimethylsilyl substituted precursors have been investigated in depth. The methodology is found to be applicable to a range of ligand frameworks of varying flexibility, stabilised by one or two "tether" arms.

Intramolecular coordination of a tethered base is an extensively used strategy for the stabilisation of complexes containing electronically unsaturated centres, unusual oxidation states or reactive bonds.[1,2] The coordination of such a base in effect provides a sizeable kinetic barrier to attack by external nucleophiles and also reduces the thermodynamic incentive for oligomerisation *via* bridging ligands.

Within the field of transition metal chemistry alkoxo and amido ligands have attracted widespread interest,[1,3,4] for example in the synthesis of non-metallocene olefin polymerisation catalysts.[5] The use of a tethered pyridyl base within the amido ligand framework as in **I** reduces the likelihood of oligomerisation, leading to tractable mononuclear catalyst precursors.[6] The electronic properties of the donor function and the conformational rigidity of the tether have been shown to be vital in controlling the reactivity of catalytic systems.[1a] Related ligands have also found use in the synthesis of early/late transition metal bimetallic systems,[7] in MOCVD precursors[8] and in electroluminescence.[9] The use of such ligands in main group chemistry is, however, much less widely exploited, despite several structural studies detailing the interesting effects of ligand architecture on the coordination geometry of post-transition metals.[8–18]

We have therefore sought to extend the coordination chemistry of ligands **I–III** (Chart 1) by the synthesis of derivatives in which the presence of a Lewis base function within the ligand framework brings about the isolation of stable mononuclear group 13 and 14 derivatives. Such a range of ligand frameworks allows the investigation of the roles of donor function and tether architecture on the geometry of complexes produced. Unlike their transition metal counterparts, structurally characterised species from groups 13–15 containing



I **II** (E = NMe) **III** (E = S)

Chart 1

ligand **I** are rare, with Group 13 derivatives in general being limited to a single 2 : 1 ligand : metal complex for aluminium and none as yet being reported for boron.[12,13] In addition, aside from the structural interest, the group 13 derivatives offer themselves as potential precursors to base-stabilised transition metal complexes of the types L_nMER and L_nMER_2 (*e.g.*, borylene and boryl derivatives for E = B) formed by metathetical reaction with organometallic anions. Despite intense interest in the structure and bonding of such complexes, the synthetic utility of a stabilising tethered base has only recently been touched upon.[19,20]

From a synthetic standpoint we have sought to exploit the utility of trimethylsilyl substituted amine/ether precursors as mild sources of the amido or alkoxo ligands.[14,21,22] The scope of this methodology, both in terms of the type of ligand framework available and the number of amido/alkoxo linkages that can be introduced, has been probed, as has the mechanism of intramolecular base-assisted elimination of the trimethylsilyl halide.

Experimental

All manipulations were carried out under a nitrogen or argon atmosphere using standard Schlenk line or dry box techniques. Solvents were pre-dried over sodium wire and purged with nitrogen prior to distillation. Tetrahydrofuran (thf) and hexanes were distilled from potassium; benzene and toluene were distilled from sodium before use. Triethylamine was dried over sodium wire prior to use. Starting materials Me_3SiCl, $SnCl_4$, $BF_3{\cdot}OEt_2$, BCl_3, BBr_3, *N*-methyldiethanolamine, 2,2′-thiodiethanol and 2-amino-6-picoline were used as received (Aldrich) without further purification. 6-[Bis(trimethylsilyl)-amino]-2-picoline and 2-[bis(trimethylsilyl)aminomethyl]pyridine were prepared by minor modification of literature methods.[14,23]

NMR spectra were measured on a Bruker AM-400 or Jeol 300 Eclipse Plus FT-NMR spectrometer. Residual protons of solvent were used for reference for ^1H and ^{13}C NMR, while a sealed tube containing [($^nBu_4N$)(B_3H_8)] was used as an external

reference for ^{11}B NMR. Infrared spectra were measured for each compound pressed into a disk with an excess of dried KBr on a Nicolet 500 FT-IR spectrometer. Mass spectra were measured by the EPSRC National Mass Spectrometry Service Centre, University of Wales, Swansea. Perfluorotributylamine and polyethylenimine were used as the standards for high-resolution EI and CI mass spectra, respectively. Elemental analyses were carried out both by the departmental analysis service and by Warwick Analytical Service, University of Warwick.

Abbreviations: st = strong, m = medium, w = weak, sh = shoulder, s = singlet, d = doublet, t = triplet, q = quartet, pcq = partially collapsed quartet, mp = multiplet, b = broad.

Syntheses and kinetic studies

Synthesis of 6-[(trimethylsilyl)amido]-2-picolylboron dibromide (1c). Boron tribromide (2.65 g, 1.0 cm^3, 10.6 mmol) was added slowly to a solution of 6-[bis(trimethylsilyl)]amino-2-picoline (2.68 g, 10.6 mmol) in hexanes (40 cm^3) at −78 °C and stirred at this temperature for 30 min. Volatiles were then removed *in vacuo*, yielding a white precipitate that was recrystallised from hot hexanes to yield **1c** as a white crystalline material (1.32 g, 35.5%). Single crystals suitable for X-ray crystallography were grown by cooling a hexanes solution to −30 °C for 1 week. **1c** has been characterised by ^1H, ^{13}C and ^{11}B NMR, IR, mass spectroscopy, elemental analysis and single crystal X-ray diffraction. ^1H NMR (300 MHz, C_6D_6) δ 0.22 [9H, s, Si(CH_3)$_3$], 1.94 (3H, s, CH_3), 5.43 (1H, d, J = 7.5 Hz, aromatic), 5.50 (1H, d, J = 8.5 Hz, aromatic), 6.54 (1H, t, J = 8.1 Hz, aromatic). ^{13}C NMR (76 MHz, C_6D_6) δ 0.0 [Si(CH_3)$_3$], 17.1 (CCH_3), 104.2, 111.6, 144.9 (aromatic CH), 150.8, 163.1 (aromatic quaternary). ^{11}B NMR (96 MHz, C_6D_6) δ −9.9. IR (KBr, cm^{-1}): 2958 m, 1614 st, 1492 st, 1128 m, 1083 m, 1038 m, 976 w, 848 m, 669 m. MS (EI): $[M + Br]^+$ = 430 (100%). Anal. calcd. for $C_9H_{15}N_2SiBBr_2$: C 30.89%, H 4.33%, N 8.00%; found: C 31.14%, H 4.26%, N 8.38%. **1a** and **1b** were prepared in similar fashion from $BF_3{\cdot}OEt_2$ and BCl_3, respectively; spectroscopic data are in line with those reported previously.[14]

Synthesis of 6-[(trimethylsilyl)amido]-2-picolyltin trichloride (3). Tin tetrachloride (0.89 g, 0.4 cm^3, 3.42 mmol) was added slowly to a solution of 6-[bis(trimethylsilyl)]amino-2-picoline (0.78 g, 3.09 mmol) in hexanes (25 cm^3) at −78 °C and the reaction mixture allowed to warm slowly to room temperature. After stirring for 10 h, the pale yellow solution was filtered, concentrated to approximately 10 cm^3 and cooled slowly to −30 °C to yield pale yellow crystals of **3** in *ca.* 75% yield. Single crystals suitable for X-ray crystallography were grown by cooling a hexanes solution to −30 °C for 1 week. **3** has been characterised by ^1H, ^{13}C and ^{119}Sn NMR, IR, mass spectroscopy, elemental analysis and single crystal X-ray diffraction. ^1H NMR (300 MHz, C_6D_6) δ 0.22 [9H, s, Si(CH_3)$_3$], 2.02 (3H, s, CH_3), 5.80 (1H, d, J = 7.2 Hz, aromatic), 5.98 (1H, d, J = 8.5 Hz, aromatic), 6.69 (1H, t, J = 7.9 Hz, aromatic). ^{13}C NMR (76 MHz, C_6D_6) δ 1.4 [Si(CH_3)$_3$], 19.6 (CCH_3), 106.3, 114.5, 143.0 (aromatic CH), 153.8, 169.3 (aromatic quaternary). ^{119}Sn NMR (112 MHz, C_6D_6) δ −338.2. IR (KBr, cm^{-1}): 2966 w, 1639 m b, 1506 w, 1460 w, 1393 w, 1327 vw, 1265 m, 1173 w, 840 st, 789 st, 712 w, 549 w. MS (EI): $[M]^+$ = 404 (15%), $[M - CH_3]^+$ = 389 (100%). Anal. calcd. for $C_9H_{15}C_{l3}N_2SnSi$: C 26.73%, H 3.74%, N 6.92%; found: C 26.60%, H 3.76%, N 6.73%.

Reaction of 2-[bis(trimethylsilyl)aminomethyl]pyridine with boron trihalides. In a typical reaction BX_3 (X = Cl, Br) or $BF_3{\cdot}OEt_2$ (1.1 mmol) was added dropwise to a solution containing 1 equiv of 2-[bis(trimethylsilyl)aminomethyl]pyridine in *ca.* 40 cm^3 of hexanes at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 12 h. Filtration, removal of volatiles *in vacuo* and recrystallisation from warm hexanes led to the formation of **4a–c** in isolated yields of 28.0% (X = F), 29.4% (X = Cl) and 26.1% (X = Br). The adducts have been characterised by multinuclear NMR, mass spectrometry and elemental analysis.

4a ^1H NMR (300 MHz, C_6D_6) δ 0.00 [18H, s, Si(CH_3)$_3$], 4.91 (2H, s, CH_2), 6.19 (1H, t, J = 6.6 Hz, aromatic), 6.86 (1H, t, J = 7.6 Hz, aromatic), 7.67 (1H, d, J = 8.0 Hz, aromatic), 8.44 (1H, d, J = 5.5 Hz, aromatic). ^{13}C NMR (76 MHz, C_6D_6) δ 1.2 [Si(CH_3)$_3$], 46.4 (CH_2), 122.3, 124.2, 141.5, 143.7 (aromatic CH). ^{11}B NMR (96 MHz, C_6D_6) 0.35 (q, J_{BF} = 9.4 Hz). ^{19}F NMR (283 MHz, C_6D_6) −145.5 (pcq, J_{BF} = 9.4 Hz). MS (EI): $[M - BF_3]^+$ = 253 (100%), $[M - BF_3 - Me]^+$ = 237 (20%). Anal. calcd. for $C_9H_{15}BF_3N_2Si_2$: C 44.99%, H 7.57%, N 8.74%; found: C 44.61%, H 7.34%, N 8.99%.

4b ^1H NMR (300 MHz, C_6D_6) δ 0.02 [18H, s, Si(CH_3)$_3$], 5.44 (2H, s, CH_2), 6.06 (1H, t, J = 6.8 Hz, aromatic), 6.77 (1H, t, J = 7.3 Hz, aromatic), 7.87 (1H, d, J = 8.0 Hz, aromatic), 9.35 (1H, mp, aromatic). ^{11}B NMR (96 MHz, C_6D_6) 7.78. MS (EI): $[M - BCl_3 - Me]^+$ = 237 (100%). Anal. calcd. for $C_9H_{15}BCl_3N_2Si_2$: C 38.98%, H 6.56%, N 7.57%; found: C 38.55%, H 6.35%, N 7.59%.

4c ^1H NMR (300 MHz, C_6D_6) δ 0.03 [18H, s, Si(CH_3)$_3$], 5.59 (2H, s, CH_2), 5.97 (1H, t, J = 6.6 Hz, aromatic), 6.67 (1H, t, J = 7.6 Hz, aromatic), 7.87 (1H, d, J = 8.0 Hz, aromatic), 9.67 (1H, mp, aromatic). ^{13}C NMR (76 MHz, C_6D_6) δ 1.1 [Si(CH_3)$_3$], 49.2 (CH_2), 122.0, 125.3, 141.5, 148.1 (aromatic CH). ^{11}B NMR (96 MHz, C_6D_6) −9.45. MS (EI): $[M]^+$ = 503 (weak), $[M - BBr_3 - Me]^+$ = 237 (100%). Anal. calcd. for $C_9H_{15}BBr_3N_2Si_2$: C 28.65%, H 4.82%, N 5.57%; found: C 28.32%, H 4.83%, N 5.38%.

For each of the compounds **4a–c** observation of the parent ion using EI-MS (of solid samples) proved difficult, with ready fragmentation of the adducts occurring. The use of softer ionisation techniques was frustrated by the high sensitivity of the complexes to air and moisture.

Kinetic studies: formation of 5a from 4a. A solution containing 0.15 mmol of **4a** dissolved in 0.8 cm^3 of C_6D_6 was transferred to a Young's NMR tube, the ^1H NMR spectrum measured at room temperature and the sample then warmed to the desired thermolysis temperature (either 55 or 75 °C). The ^1H NMR spectrum of the reaction mixture was then measured periodically with the concentrations of **4a** and **5a** being evaluated on the basis of the integration of the methylene signals.† Cyclisation was judged to be complete after 23 days at 55 °C or 3 days at 75 °C. NMR data for **5a**: ^1H NMR (300 MHz, C_6D_6) δ 0.11 [9H, s, Si(CH_3)$_3$], 4.34 (2H, s, CH_2), 6.61 (1H, t, J = 5.3 Hz, aromatic), 7.14 (1H, t of d, J = 7.2, 1.8 Hz, aromatic), 7.28 (1H, d, J = 7.8 Hz, aromatic), 8.47 (1H, d, J = 4.3 Hz, aromatic). ^{13}C NMR (76 MHz, C_6D_6) δ 1.7 [Si(CH_3)$_3$], 51.1 (CH_2), 120.2, 120.9, 135.5, 149.1 (aromatic CH), 164.4 (aromatic quaternary). ^{11}B NMR (96 MHz, C_6D_6) δ 7.3

† Estimates of the relative concentrations of **4a** and **5a** in solution were made by integration of the ^1H NMR signal due to the methylene protons in each compound. A plot of ln(mole fraction of **4a**) *vs.* time (s) (Figs. 4 and 5) could be fitted to the linear relationship:

$$\ln(\text{mole fraction}) = (-4 \times 10^{-6})t + 4.411 \ (R^2 = 0.9954) \text{ at } 75\,^\circ\text{C}$$

or

$$\ln(\text{mole fraction}) = (-7 \times 10^{-7})t + 4.509 \ (R^2 = 0.9765) \text{ at } 55\,^\circ\text{C}$$

from which it is possible to obtain a value for the first order rate constant, k_1, of 4×10^{-6} s^{-1} at 75 °C and 7×10^{-7} s^{-1} at 55 °C. A similar treatment of the product **5a** gives values of k_1 of 7×10^{-6} and 9×10^{-7} s^{-1} at 75 and 55 °C, respectively. Graph fitting was carried out using Microsoft Excel and SigmaPlot.

(t, $J_{BF} = 35.4$ Hz). ^{19}F NMR (283 MHz, C_6D_6) −157.1 (pcq, $J_{BF} = 35.4$ Hz).

Synthesis of $(Me_3SiOCH_2CH_2)_2NMe$ (6). *N*-Methyldiethanolamine (20 cm^3, 0.18 mol) was dissolved in toluene (150 cm^3) and 4 equiv of triethylamine (100 cm^3, 0.72 mol) and 4 equiv of chlorotrimethylsilane (91 cm^3, 0.72 mol) were then added *via* syringe at room temperature. After 24 h the supernatent toluene solution was filtered and the $(Et_3NH)Cl$ precipitate washed with toluene (2×15 cm^3). After removal *in vacuo* of volatiles from the combined washings, **6** was isolated as a very pale brown liquid in yields of *ca.* 50%. At this point ^1H and ^{13}C NMR indicated that the compound was >99% pure and no further purification was therefore attempted. Characterisation of compound **6** was achieved by ^1H and ^{13}C NMR and mass spectrometry (including exact mass determination). ^1H NMR (300 MHz, C_6D_6) δ 0.02 (18 H, s, $SiMe_3$), 2.15 (3H, s, CH_3), 2.43 (4H, m, CH_2), 3.51 (4H, m, CH_2). ^{13}C NMR (76 MHz, C_6D_6) δ 0.1 ($SiMe_3$), 44.0 (CH_3), 61.2 (CH_2), 61.6 (CH_2). MS (CI): $[M+H]^+ = 264$ (55%). Exact mass calcd. for $C_{11}H_{30}NO_2Si_2$ $[M+H]^+$: 264.1815; found: 264.1813.

Synthesis of $(Me_3SiOCH_2CH_2)_2S$ (7). Compound **7** was prepared from 2,2′-thiodiethanol by an analogous method to that described above for **6** and was isolated as a colourless oil and characterised by ^1H and ^{13}C NMR and mass spectrometry (including exact mass determination). ^1H NMR (300 MHz, C_6D_6) δ 0.02 (18 H, s, $SiMe_3$), 2.53 (4H, t, $J = 7.2$ Hz, CH_2), 3.57 (4H, t, $J = 7.2$ Hz, CH_2). ^{13}C NMR (76 MHz, C_6D_6) δ 0.0 ($SiMe_3$), 35.6 (CH_2), 63.5 (CH_2). MS (CI): $[M+H]^+ = 267$ (45%). Exact mass calcd. for $C_{10}H_{27}O_2SSi_2$ $[M+H]^+$: 267.1270; found: 267.1269.

Synthesis of $MeN(CH_2CH_2O)_2BF$ (10a). To a solution of 9.2 g (35 mmol) of $(Me_3SiOCH_2CH_2)_2NMe$ (**6**) in benzene (200 cm^3) at room temperature was added slowly *via* syringe 1 equiv of $BF_3{\cdot}OEt_2$. The reaction mixture was heated to 55 °C and monitored by ^{11}B NMR over a period of 96 h until the signals due to intermediate species **8a** and **9a** had disappeared. At this point the colourless solution was separated from a small amount of brown oily precipitate by filtration. Cooling of the resultant colourless solution to room temperature led to the precipitation of **10a** as a white crystalline solid of >95% purity. Extremely slow cooling from 55 °C led to the formation of X-ray quality crystals. **10a** can be further purified by recrystallisation from benzene or toluene, or by sublimation at *ca.* 150 °C (10^{-4} Torr) onto a cold finger held at −78 °C. Yields are typically in excess of 90%. **10a** was characterised by ^1H, ^{13}C, ^{11}B and ^{19}F NMR, IR, mass spectrometry (including exact mass determination), elemental analysis and single crystal X-ray diffraction. ^1H NMR (300 MHz, C_6D_6) δ 1.8 (3H, d, $J_{H-F} = 1.9$ Hz, CH_3), 1.9 (4H, m, CH_2), 3.5 (4H, b m, CH_2). ^{13}C NMR (76 MHz, C_6D_6) δ 42.2 (d, $J_{C-F} = 4.9$ Hz, CH_3), 58.4 (d, $J_{C-F} = 2.0$ Hz, CH_2), 58.6 (s, CH_2). ^{11}B NMR (96 MHz, C_6D_6) δ 8.8 (d, $J_{B-F} = 25.3$ Hz). ^{19}F NMR (283 MHz, C_6D_6) δ −157.2 (q, $J_{F-B} = 25.3$ Hz). IR (cm^{-1}): 1102 st [ν(B–F)]. MS (EI): $M^+ = 147$ (100%). Exact mass calcd. for $C_5H_{11}BFNO_2$: 147.0867; found: 147.0868. Anal. calcd. for $C_5H_{11}BFNO_2$: C 40.87, H, 7.55, N 9.53; found: C 40.44, H 7.37, N 9.51%.

Kinetic studies: formation of 10a from 6 and $BF_3{\cdot}OEt_2$. A sample of *ca.* 100 mg of $(Me_3SiOCH_2CH_2)_2NMe$ (**6**) was dissolved in C_6D_6 and transferred to a Young's NMR tube. One equivalent of $BF_3{\cdot}OEt_2$ was added by syringe at room temperature and the ^{11}B NMR spectrum measured at this point revealed that the sole boron containing species present was the adduct $Me(Me_3SiOCH_2CH_2)_2N{\cdot}BF_3$ (**8a**). The solution was then heated to 55 °C in the NMR spectrometer and maintained at that temperature for a period of 96 h, during which the ^{11}B and ^{19}F spectra were measured hourly. During the course of the thermolysis reaction resonances characteristic of **8a** and the intermediate **9a** were observed, both sets of signals ultimately disappearing to leave only those characteristic of the final product **10a**. NMR data for **8a**: ^1H NMR (300 MHz, C_6D_6) δ 0.04 [18 H, s, $Si(CH_3)_3$], 2.58 (3H, s, CH_3), 3.24 (4H, m, CH_2), 3.74 (4H, m, CH_2). ^{13}C NMR (76 MHz, C_6D_6) δ 0.1 [$Si(CH_3)_3$], 44.2 (CH_3), 56.4 (CH_2), 61.3 (s, CH_2). ^{11}B NMR (96 MHz, C_6D_6) δ −0.3 (q, $J_{B-F} = 16.2$ Hz). ^{19}F NMR (283 MHz, C_6D_6) δ −156.0 (q, $J_{F-B} = 16.1$ Hz). The intermediate **9a** is only ever formed in very small quantities in the presence of much larger amounts of **8a** and **10a**; no attempts to isolate the intermediate have been made and we merely report the positions of NMR resonances determined during kinetic runs: ^{11}B NMR (96 MHz, C_6D_6) δ 3.9 (t, $J_{B-F} = 21.1$ Hz). ^{19}F NMR (283 MHz, C_6D_6) δ 157.1 (q, $J_{F-B} = 21.0$ Hz).

Reaction of 6 with BCl_3. To a sample of 2.26 g (8.6 mmol) of **6** in toluene at room temperature was added by syringe 1 equiv of BCl_3 (8.6 cm^3 of a 1 M solution in heptane); the ^{11}B NMR spectrum measured at this point revealed that the sole boron containing species present was the adduct $Me(Me_3SiOCH_2CH_2)_2N{\cdot}BCl_3$ (**8b**). Removal of all volatile species *in vacuo*, followed by extraction with hexanes (2×40 cm^3), filtration and removal of volatiles in high vacuum (10^{-4} Torr) led to the isolation of **8b** as a colourless oil in 80–90% yield and >99% purity. Thermolysis of an approximately 1 M solution of **8b** in toluene or benzene led to the evolution of Me_3SiCl and the formation of a mixture of the mono- and di-cyclised species **9b** and **10b**. Despite extensive variation in temperature, concentration and reaction time it proved impossible to drive the reaction to completion, such that the reaction mixture at this point, although predominantly consisting of **10b**, was always contaminated with the intermediate **9b**. Removal of volatiles *in vacuo*, extraction of the residual solid with hexanes (5×20 cm^3) and recrystallisation from concentrated hexanes solution at −30 °C led to the isolation of the intermediate **9b** as a white solid in 10–15% isolated yield. The remaining solid, insoluble in hexanes, was found to consist predominantly of the di-cyclised species **10b**; despite many attempts it proved impossible to obtain samples of **10b** prepared this way free from traces of **9b**. **8b** and **9b** have been characterised by ^1H, ^{13}C and ^{11}B NMR and mass spectrometry, and the ^1H, ^{13}C and ^{11}B signals due to **10b** deduced from impure product contaminated with traces of **9b**.

8b ^1H NMR (300 MHz, C_6D_6) δ 0.01 [18H, s, $Si(CH_3)_3$], 2.67 (3H, m, CH_3), 3.36 (4H, m, CH_2), 3.62 (4H, m, CH_2). ^{13}C NMR (76 MHz, C_6D_6) δ 0.1 [$Si(CH_3)_3$], 45.7 (CH_3), 58.6 (CH_2), 60.7 (CH_2). ^{11}B NMR (96 MHz, C_6D_6) δ 11.1 (s). MS (EI): $M^+ = 379$ (weak), $[M - BCl_3]^+ = 263$ (100%).

9b ^1H NMR (300 MHz, C_6D_6) δ 0.27 [9H, s, $Si(CH_3)_3$], 2.02 (3H, s, CH_3), 2.38 (2H, t, $J = 5.9$ Hz, CH_2), 2.53 (2H, t, $J = 7.1$ Hz, CH_2), 3.24 (2H, t, $J = 7.1$ Hz, CH_2), 3.86 (2H, t, $J = 5.9$ Hz, CH_2). ^{13}C NMR (76 MHz, C_6D_6) δ 0.9 [$Si(CH_3)_3$], 41.5 (CH_3), 42.3 (CH_2), 58.5 (CH_2), 59.5 (CH_2), 61.6 (CH_2). ^{11}B NMR (96 MHz, C_6D_6) δ 17.2 (s). MS (EI): $M^+ = 271$ (100%).

10b ^1H NMR (300 MHz, C_6D_6) δ 2.01 (3H, s, CH_3), 2.30 (4H, m, CH_2), 3.08 (4H, m, CH_2). ^{13}C NMR (76 MHz, C_6D_6) δ 42.7 (CH_3), 57.4 (CH_2), 58.9 (CH_2). ^{11}B NMR (96 MHz, C_6D_6) δ 13.0 (b s).

Synthesis of $S(CH_2CH_2O)_2BF$ (12a). Compound **12a** was prepared from $(Me_3SiOCH_2CH_2)_2S$ (**7**) by a method analogous to that described for **10a**. Purification of the crude product by recrystallisation from hot toluene or benzene resulted in the isolation of **12a** as an off-white crystalline solid in *ca.*

73% yield. Compound **12a** has been characterised by ^{1}H, ^{13}C and ^{11}B NMR, IR, mass spectrometry (including exact mass determination) and elemental analysis. ^{1}H NMR (300 MHz, C_6D_6) δ 2.6 (4H, m, CH_2), 3.9 (4H, m, CH_2). ^{13}C NMR (76 MHz, C_6D_6) δ 33.7 (s, CH_2), 62.2 (s, CH_2). ^{11}B NMR (96 MHz, C_6D_6) δ 17.3 (b). ^{19}F NMR (283 MHz, C_6D_6) δ −150.0. IR (cm^{-1}): 1068 st [ν(B–F)]. MS (EI): $M^+ = 150$ (100%). Exact mass calcd. for $C_4H_8BFO_2S$: 150.0322; found: 150.0321. Anal. calcd. for $C_4H_{18}BFO_2S$: C 32.02, H, 5.37%; found: C 31.86, H 5.14%.

General crystallographic method

Single crystals of compounds **1c**, **3** and **10a** were mounted on an Enraf Nonius Kappa CCD diffractometer equipped with an Mo-Kα radiation source ($\lambda = 0.71073$ Å). Data collection was carried out at 100(2) K (**1c**) or at 150(2) K (**3** and **10a**). Data collection and cell refinement were carried out using DENZO,[24a] and structure solution and refinement (by full-matrix least-squares) using SHELXS-97 and SHELXL-97,[24b] respectively. Fuller details of each data collection, structure solution and refinement can be found in Table 1, with relevant bond lengths and angles for compounds **1c** and **3** being listed in Tables 2 and 3, respectively. In the case of compound **10a**, the molecule was found to sit on a mirror plane containing the atoms N(1), C(2), C(1), O(1) and B(1). There appeared to be a positional disorder across the mirror plane whereby the site labelled F(1) was 50% occupied by the atom O(2) and *vice versa*. The positional and thermal parameters of F(1) and O(2) were successfully refined together using the EXYZ and EADP commands of SHELX 97. In addition, the atom C(4) was disordered over the mirror plane in a 50 : 50 ratio and therefore the atom C(4) was refined with 50% occupancy. Only one of the sites occupied by C(4) is shown in the ORTEP. Hydrogens were only added to C(1) and C(2) in calculated positions using the riding model. As a result of the disorder in the molecule and the fact that F(1) and O(2) were refined using the same positional and thermal parameters no comments can be made about the bond lengths and angles within the molecule. However, the gross molecular framework of the molecule is unequivocal and is fully supported by the spectroscopic data.

CCDC reference numbers 183227–183229. See http://www.rsc.org/suppdata/nj/b1/b110692a/ for crystallographic data in CIF or other electronic format

Table 1 Crystallographic data for **1c**, **3** and **10a**

	1c	**3**	**10a**
Empirical formula	$C_9H_{15}BBr_2N_2Si$	$C_9H_{15}Cl_3N_2SiSn$	$C_5H_{11}BFNO_2$
Formula weight	349.95	404.36	146.96
Crystal system	Monoclinic	Triclinic	Orthorhombic
Space group	$P2_1/n$	$P\bar{1}$	$Cmc2_1$
a/Å	6.8246(7)	9.2498(18)	9.800(2)
b/Å	13.9297(17)	9.708(19)	12.045(2)
c/Å	14.2729(17)	17.738(4)	5.9433(12)
α/°	90	93.62(3)	90
β/°	93.113(9)	90.61(3)	90
γ/°	90	104.26(3)	90
U/Å^3	1354.8(3)	1540.1(5)	701.6(2)
Z	4	4	4
T/k	100(2)	150(2)	150(2)
μ mm^{-1}	6.043	2.235	0.118
Reflections collected	6753	23521	1698
Independent reflections	2643	6924	628
R_{int}	0.1559	0.0809	0.0549
Final R_1 [$I > 2\sigma(I)$]	0.0622	0.0307	0.0790
Final wR_2 [$I > 2\sigma(I)$]	0.1337	0.0769	0.2346
R_1 (all data)	0.0826	0.0386	0.1072
wR_2 (all data)	0.1446	0.0812	0.2531

Table 2 Selected bond lengths (Å) and angles (°) for **1c**

Br1–B1	1.993(7)	N1–C1	1.367(8)
Si1–N2	1.747(5)	N1–B1	1.577(9)
Si1–C8	1.857(7)	C1–N2	1.368(8)
Si1–C7	1.857(8)	B1–N2	1.547(9)
Si1–C9	1.860(7)	B1–Br2	2.004(7)
N1–C5	1.345(8)		
N2–Si1–C8	107.8(3)	N2–B1–N1	84.1(5)
N2–Si1–C7	109.5(3)	N2–B1–Br1	116.3(4)
C8–Si1–C7	110.2(3)	N1–B1–Br1	113.3(4)
N2–Si1–C9	104.6(3)	N2–B1–Br2	115.6(4)
C8–Si1–C9	113.6(3)	N1–B1–Br2	113.4(4)
C7–Si1–C9	110.9(3)	Br1–B1–Br2	111.5(3)
C5–N1–B1	148.1(5)	C1–N2–B1	88.6(5)
C1–N1–B1	87.4(5)	C1–N2–Si1	132.8(5)
N1–C1–N2	99.9(5)	B1–N2–Si1	138.2(4)

Results

The work outlined herein shows that the reaction between Lewis acidic main group halides and trimethylsilyl substituted ether or amine reagents is a versatile route to a range of intramolecular base-stabilised main group halides (as shown in Chart 2 and Schemes 1 and 2 below).

This synthetic approach with concomitant evolution of the trimethylsilyl halide, has several advantages over possible alternative routes, such as the corresponding reaction with the parent amine or alcohol, or with alkali metal alkoxides or amides. Firstly, the solubility of the trimethylsilyl derivatives in weakly coordinating organic solvents allows the reaction to be carried out in a single-phase toluene or hexanes medium. This was found not only to lead to improved reaction rates, but also to a much cleaner product distribution, especially in the synthesis of complexes such as **10** and **12** that require the formation of two O–B linkages. In addition, formation of the trimethylsilyl derivatives, by reaction of the corresponding alcohol or amine with a large excess of trimethylsilyl chloride and extraction into hexanes, effectively constitutes a simple method for removal of water. Any moisture present is simply converted by the excess of trimethylsilyl chloride into hexamethyldisiloxane, which is removed *in vacuo*. By contrast *physical* methods of drying polyhydroxy species such as *N*-methyldiethanolamine are much less efficient, such that direct reaction with a boron trihalide, for example, inevitably leads to contamination of the product with $B(OH)_3$ and other species formed by hydrolysis of B–X bonds.

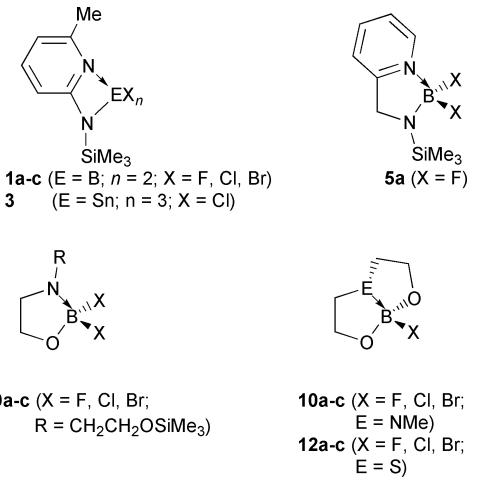


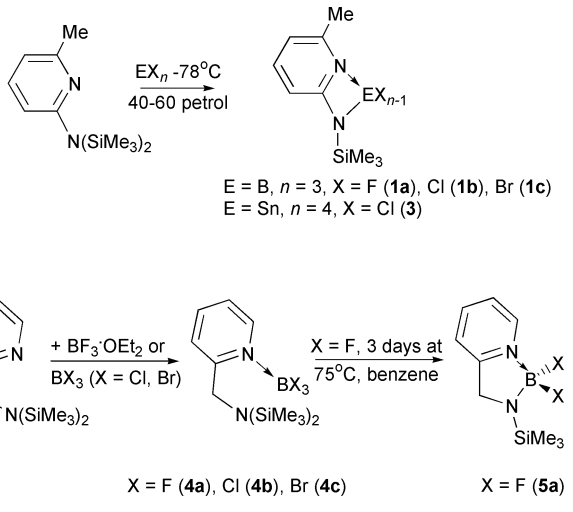
Chart 2

We have sought to establish the scope of this synthetic methodology for the formation of main group halides containing either alkoxo or amido ligands, and stabilised by the coordination of a tethered nitrogen or sulfur donor (see Schemes 1 and 2).

Synthesis of main group halides stabilised by pyridyl donors

Although the chelating properties of amido ligands bearing pendant pyridyl donors have been employed extensively in the chemistry of early transition metals,[6,7,25–33] their use in stabilising analogous main group derivatives remains little exploited.[8–18] We have therefore sought to extend the coordination chemistry of the 6-amido-2-picolyl ligand framework by using it to stabilise otherwise highly Lewis acidic main group halides (exemplified by halides of boron and tin).

Synthesis of amido boron dihalide complexes **1a–c**, in which the coordination sphere of the boron centre is augmented by interaction with a tethered pyridyl donor, can be accomplished by the reaction of the corresponding bis(trimethylsilyl) substituted ligand framework 6-[$(Me_3Si)_2N$]-2-Me-C_5H_3N with the appropriate boron trihalide (Scheme 1). Low temperature (−78 °C) and slow addition of the boron trihalide are required in order to prevent further reaction leading to elimination of a second equivalent of trimethylsilyl halide and the formation of bifunctional adducts of the type reported by Raston, Junk and colleagues.[14] In the case of the fluoride and chloride derivatives **1a** and **1b**, spectroscopic and analytical data are in agreement with the proposed formulation, although it proved impossible to grow single crystals of sufficient quality of either compound in order to probe the structural properties of the complexes.[14] In the case of the bromide derivative, **1c**, the EI mass spectrum rather surprisingly features a predominant peak corresponding to the ion $[M + Br]^+$. In order to ascertain whether this relates to some degree of oligomerisation or significant secondary interaction in the solid state (rather than being an artefact of the EI-MS experiment), an X-ray crystal structure analysis was therefore desirable. Single crystals of **1c** proved to be accessible *via* slow cooling to −30 °C of solutions in hexanes, and the crystal structure, depicted in Fig. 1, shows the compound to be monomeric, featuring no unusual secondary intermolecular interactions. **1c** possesses a rather strained four-membered ring composed of one boron, one carbon and two nitrogen atoms. That the chelate ring is planar is demonstrated by the sum of the internal angles being 360°. In addition, the two N–C distances within the ring are virtually identical [N(1)–C(1) = 1.367(8) Å, N(2)–C(1) = 1.368(8) Å], indicating that the structure can almost certainly be described in terms of near equal contributions from two resonance forms, consistent with



Scheme 1

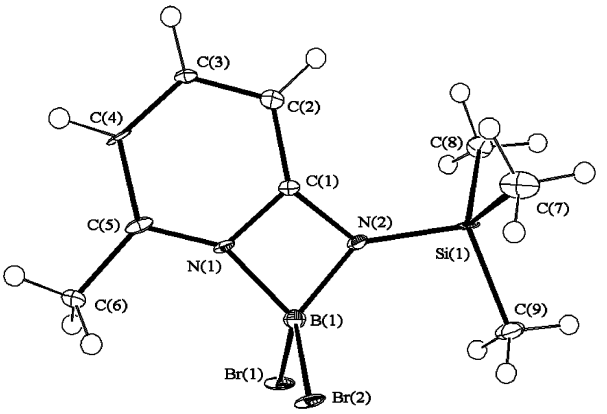


Fig. 1 Molecular structure of **1c**, with ellipsoids drawn at the 50% probability level.

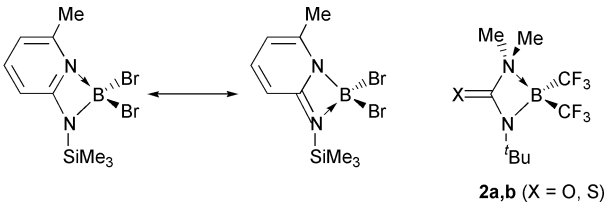


Fig. 2 Proposed 'diaza-allyl' formulation for **1c**.

a diaza-allyl formulation (see Fig. 2). This is also reflected in the scarcely significant differences between N–B distances [N(1)–B(1) = 1.577(9) Å, N(2)–B(1) = 1.547(9) Å]. A similar situation is found for the Li–N and N–C distances in the lithium compound [6-(Me_3SiN)-2-Me-C_5H_3N]Li(tmeda).[10] By means of comparison, the N–B distances found in compound **2a** synthesised by Bürger and co-workers and featuring discrete amido and amino functionalities within an analogous four-membered ring are 1.535(8) Å and 1.635(8) Å (for the N–B single and coordinative bonds, respectively).[34] To our knowledge **1c** represents the first structurally characterised example of a boron complex containing ligand **I** and the first example of a 1 : 1 complex for any of the group 13 elements.[13a] Boron dihalide fragments stabilised by a nitrogen donor as part of a four-membered chelate ring are also rare; bond lengths and angles for the four-membered ring are similar to those found for the amidinate derivative $CpMn(CO)_2$=C=C(Me)C($N^tBu)_2BCl_2$[35] and for [2-(Cl_2BN)-6-Me-C_5H_3N]BCl_2 synthesised by Raston *et al.*, which contains a similar picolyl framework to **1c**.[14]

Similar chemistry can also be used to give access to the tethered-pyridyl stabilised amidotin trichloride species, **3** (Scheme 1). As in the case of **1**, the reaction proceeds smoothly at −78 °C, and the product is obtained as a pale yellow crystalline solid in yields of up to 75%. Attempts to synthesise the tin *dichloride* derivative [6-(Me_3SiN)-2-Me-$C_5H_3N]_2SnCl_2$ either by reaction of $SnCl_4$ with two or more equivalents of 6-[$(Me_3Si)_2N$]-2-Me-C_5H_3N, or by reaction of **3** with 6-[$(Me_3Si)_2N$]-2-Me-C_5H_3N merely led to the recovery of **3**. Interestingly this chemistry is indicative of the mild nature of trimethylsilyl substituted amine precursors as sources of amido ligands. Analogous chemistry using the corresponding lithium reagent 6-[Li(Me_3Si)N]-2-Me-C_5H_3N as the source of ligand **I**, leads exclusively to the 2 : 1 complex [6-(Me_3SiN)-2-Me-$C_5H_3N]_2SnCl_2$. In this way appropriate choice of reagent can be used to selectively give access to the required main group complex. Spectroscopic data for **3** are in accord with the proposed formulation, and are confirmed by the results of a single crystal X-ray diffraction study (Fig. 3 and Table 3).

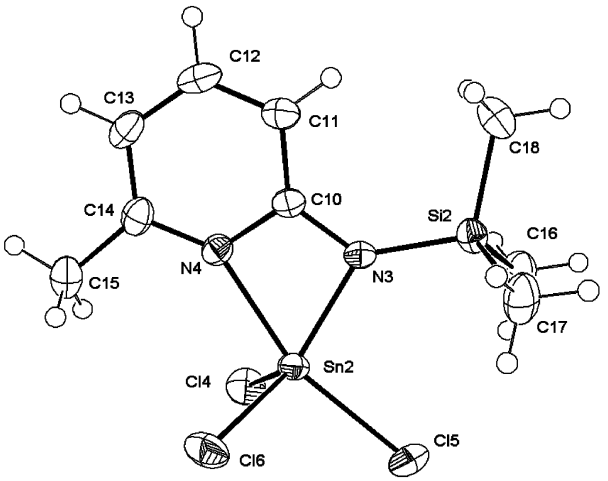


Fig. 3 Molecular structure of one of the two independent molecules of **3**, with ellipsoids drawn at the 50% probability level.

There are two independent molecules of **3** within the asymmetric unit, which differ only in minor details; the molecular structure consists of a five-coordinate tin centre bonded to three chloride ligands and one 6-(trimethylsilyl-amido)-2-picolyl ligand. The geometry at the tin centre is best thought of as being a distorted trigonal bipyramid, with the sum of the angles subtended at the tin centre by the three equatorial substituents [Cl(4), Cl(6) and N(3)] being 354.3(1)°. The geometry of the amidopicolyl chelate enforces an angle of 62.8(1)° for the N(3)–Sn(2)–N(4) unit (as opposed to 90° for an idealized trigonal bipyramid) and the same constraint is responsible for bending of the N(4)–Sn(2)–Cl(5) angle from linearity [161.5(1)°]. Interestingly, although the NCNSn chelate ring is planar (as was also found for **1c**) the bond lengths within the ring are more consistent with discrete amido and picolyl donors than with the delocalised diaza-allyl formulation proposed for **1c**. Thus, the N–C distances with the chelate ring (which were identical in the case of **1c**), are found to be 1.376(3) and 1.354(3) Å for N(3)–C(10) and N(4)–C(10), respectively. In addition, the distance from the tin centre to the amido nitrogen N(3) [2.075(2) Å] is markedly shorter than that to the picolyl nitrogen N(4) [2.209(2) Å]. Presumably the widely differing Sn–N distances reflect not only the asymmetry

Table 3 Selected bond lengths (Å) and angles (°) for **3**

C10–N4	1.354(3)	N3–Si2	1.770(2)
C10–N3	1.376(3)	N3–Sn2	2.075(2)
C10–Sn2	2.612(3)	N4–Sn2	2.209(2)
C14–N4	1.353(3)	Cl4–Sn2	2.3279(9)
C16–Si2	1.861(3)	Cl5–Sn2	2.3464(10)
C17–Si2	1.853(3)	Cl6–Sn2	2.3244(10)
C18–Si2	1.856(3)		
N4–C10–N3	109.8(2)	Cl6–Sn2–Cl4	108.33(3)
N4–C10–C11	119.0(2)	N3–Sn2–Cl5	98.82(6)
N3–C10–C11	131.2(2)	N4–Sn2–Cl5	161.45(6)
N4–C10–Sn2	57.70(13)	Cl6–Sn2–Cl5	97.40(4)
N3–C10–Sn2	52.14(12)	Cl4–Sn2–Cl5	97.33(4)
C11–C10–Sn2	176.35(19)	N3–Sn2–C10	31.56(8)
C10–N3–Si2	132.88(18)	N4–Sn2–C10	31.20(8)
C10–N3–Sn2	96.30(16)	Cl6–Sn2–C10	111.25(6)
Si2–N3–Sn2	130.69(11)	Cl4–Sn2–C10	110.03(6)
C14–N4–C10	123.3(2)	Cl5–Sn2–C10	130.32(6)
C14–N4–Sn2	145.54(19)	N3–Si2–C17	109.02(12)
C10–N4–Sn2	91.09(15)	N3–Si2–C18	111.36(12)
N3–Sn2–N4	62.76(8)	C17–Si2–C18	109.63(16)
N3–Sn2–Cl6	126.03(6)	N3–Si2–C16	108.36(13)
N4–Sn2–Cl6	92.58(6)	C17–Si2–C16	110.46(15)
N3–Sn2–Cl4	119.98(6)	C18–Si2–C16	108.00(14)
N4–Sn2–Cl4	94.28(6)		

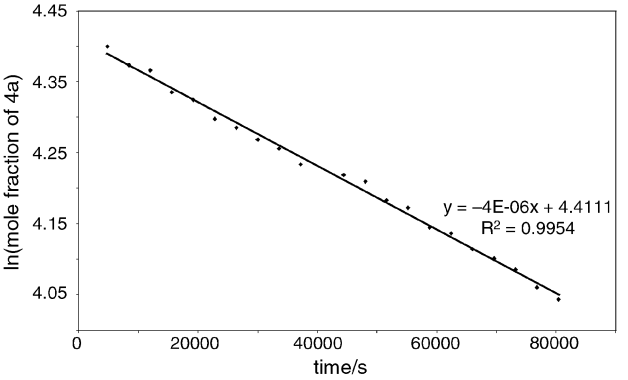


Fig. 4 Plot of ln(mole fraction of **4a**) *vs.* time for the thermolysis of **4a** at 75 °C, as determined from integration of ^{1}H NMR signals.†

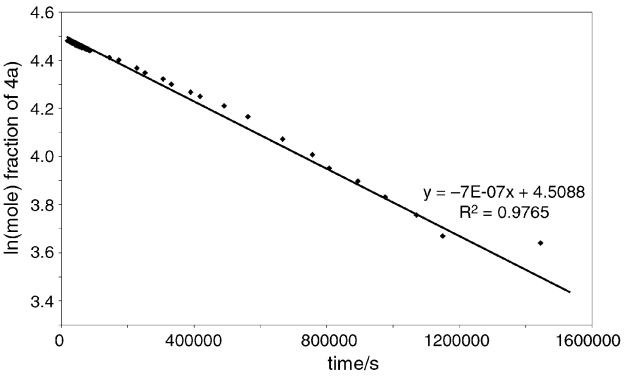


Fig. 5 Plot of ln(mole fraction of **4a**) *vs.* time for the thermolysis of **4a** at 55 °C, as determined from integration of ^{1}H NMR signals.†

of the ligand but also the occupation of distinct axial and equatorial sites by the picolyl and amido donors, with the bulky trimethylsilyl substituent attached to the amido function ensuring that it occupies the equatorial site. Thus, for example, even in $[(Ph_3P{=}N)SnCl_3]_2$[36] and $[Me_3SiNC(Ph)NSiMe_3]$-$SnCl_3$[37] which contain *equivalent* nitrogen donors occupying both axial and equatorial sites within a trigonal biyramidal complex, the axial Sn–N bond is longer than the equatorial linkage {*e.g.*, 2.092 and 2.039 Å for $[(Ph_3P{=}N)SnCl_3]_2$}. As expected there is also a small but significant lengthening of the Sn–Cl_{ax} distance [2.346(1) Å] compared to the Sn-Cl_{eq} bonds [2.324(1) and 2.328(1) Å]. In many respects the structure of **3** resembles that of $[6\text{-}(Cl_2AsN)\text{-}2\text{-}Me\text{-}C_5H_3N]AsCl_2$, which is described by Raston and co-workers as having an analogous trigonal bipyramidal geometry at As(1) (with one of the equatorial sites occupied by the As lone pair), and which possesses similar asymmetry in the As(1)–N distances.[12]

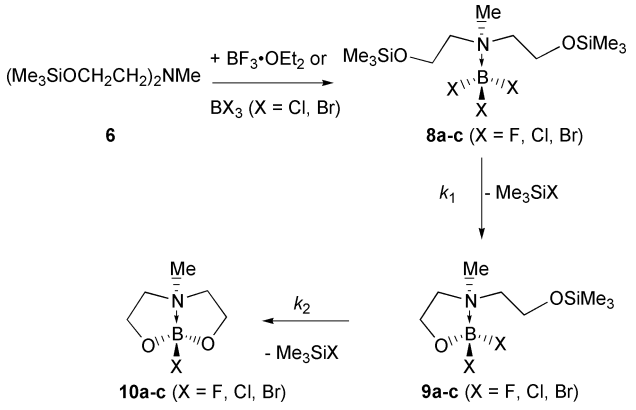
In contrast to the chemistry outlined above, reaction of bis(trimethylsilyl)aminomethyl pyridine, $2\text{-}[(Me_3Si)_2NCH_2]$-$C_5H_4N$, with BX_3 (X = F, Cl, Br) at room temperature leads not to the pyridyl stabilised amidoboron dihalides **5**, but to the simple adducts **4** (Scheme 1). The structures of **4a–c** have been deduced from spectroscopic data, with pyridyl rather than amine coordination at the boron centre being implied by ^{11}B and ^{1}H NMR data that are remarkably similar to those found for the analogous (pyridine)·BX_3 adducts.[38] Cyclisation from **4** to **5** with concomitant loss of trimethylsilyl halide requires extremely forcing conditions. Monitoring of the thermolysis of a solution of **4a** in benzene by ^{1}H NMR, for example, reveals that the cyclisation process is only complete after 3 days at 75 °C or 23 days at 55 °C. Furthermore, integration of the intensities of the ^{1}H NMR signals due to the methylene protons of **4a** and **5a** at intervals over the period of the reaction

(Figs. 4 and 5) demonstrates that the reaction is first order in **4a** and that the rate constant, k_1, for the cyclisation process is of the order of 4×10^{-6} s^{-1} at 75 °C and 7×10^{-7} s^{-1} at 55 °C. For the analogous chloride and bromide species **4b** and **4c** it proved impossible to drive the cyclisation reaction to completion, such that thermolysis invariably leads to inseparable mixtures of products.

Furthermore, although the pyridyl donor stabilised amidoboron and tin halides **1** and **3** can be synthesised in good to moderate yields by this route the analogous reactions to form alkoxoboron dihalides from 6-(Me_3SiO)-2-Me-C_5H_3N are much less straightforward. More forcing conditions are required in order to bring about the formation of the O–B bond (with elimination of the trimethylsilyl halide) and as a consequence inseparable mixtures of products are always formed. We have therefore sought alternative ligand frameworks for the stabilisation of alkoxo-substituted main group halides.

Synthesis of alkoxoboron halides stabilised by amine or thioether donors

Alkoxoboron mono- and di-halides containing a nitrogen or sulfur donor tethered by a two carbon aliphatic bridge (*e.g.*, **10** and **12**) can be synthesised from the bis(trimethylsilyl) ether derivatives of *N*-methyldiethanolamine or 2,2′-thiodiethanol according to the chemistry outlined in Scheme 2. Initial formation of the adduct **8** is followed by stepwise cyclisation to give successively the base-stabilised di- and mono-halides **9** and **10**. For X = F and E = NMe, formation of the adduct **8a** proceeds cleanly at room temperature, whereas the subsequent cyclisation steps require heating to 55 °C over a period of 48–72 h. Monitoring the reaction by ^{11}B and ^{19}F NMR it is possible to observe signals due to the intermediate **9a** and the final product **10a** even at relatively short reaction times (Fig. 6). Over a period of 96 h signals due to **8a** and **9a** completely disappear, leaving only the di-cyclised product **10a**. By measuring the intensities of the ^{11}B signals due to **8a**, **9a** and **10a** at hourly intervals it proved possible to obtain plots of concentration *vs.* time for these three species (see Fig. 7).‡



Scheme 2

‡ Estimates of the concentrations of **8a**, **9a** and **10a** in solution were made by integration of the respective signals in the ^{11}B NMR spectrum of the reaction mixture (Fig. 6). This approach makes the assumption of equal relaxation times for the ^{11}B nuclei in each of the three species. The error likely to be introduced by making this assumption is small; the similar chemical environments of the ^{11}B nuclei in each of the three species mean that the relaxation times in each case are likely to be similar (and short). There is considerable precedent for this type of approach in determining the concentrations of boron-containing species in solution.[39] A similar approach making use of the ^{19}F NMR data for the reaction mixture was complicated by the overlapping nature of two of the resonances.

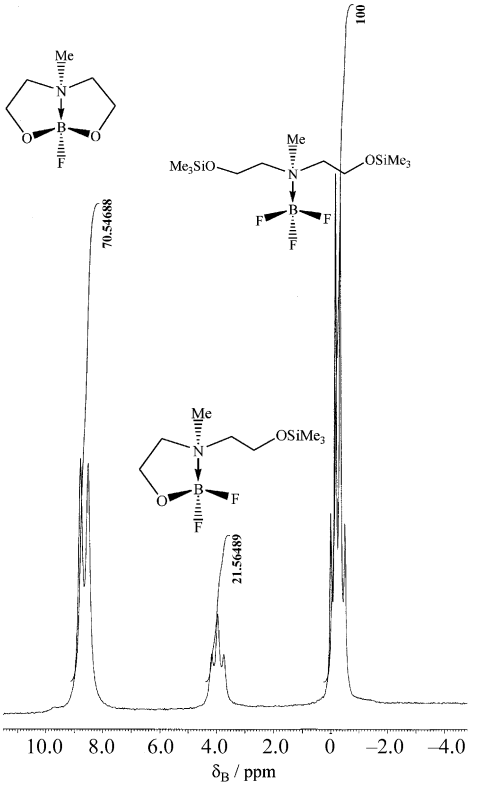


Fig. 6 ^{11}B{^{1}H} NMR signals for **8a**, **9a** and **10a** in benzene at 55° C.

After an initial induction period in which **8a** is formed from **6** and BF_3·OEt_2, the concentration of **8a** then displays the expected decay by a first-order process. A plot of ln(mole fraction) *vs.* time (for 5 h < t < 25 h) shows a linear relationship from which measurement of the gradient gives a first-order rate constant of $k_1 = 2.7 \times 10^{-5}$ s^{-1} for the conversion of **8a** into the mono-cyclised species **9a**.§ Complex **9a** shows the concentration/time behaviour expected of an intermediate species, with the final, di-cyclised product **10a** becoming the predominant species in solution for $t > 6$ h. The concentration *vs.* time behaviour for **9a** and **10a** could also be modelled using graph-fitting analysis.¶

§ A plot of ln(mole fraction) *vs.* time (h) for the adduct **8a** at 55 °C over the period 5 h < t < 25 h (Fig. 8) could be fitted to the linear relationship:

$$\ln(\text{mole fraction}) = -0.0984t - 0.3587 \ (R^2 = 0.9982)$$

from which it is possible to obtain a value for the first-order rate constant, k_1, of 9.8×10^{-2} h^{-1} or 2.7×10^{-5} s^{-1}. Data for t < 5 h were omitted from the calculation as NMR measurements indicated the presence of small quantities of BF_3·OEt_2 in the reaction mixture during this period. Consequently, for t < 5 h, **8a** is still being formed from BF_3·OEt_2 and **6** and the concentration of **8a** will be a more complex function of time over this period. Graph fitting was carried out using the program SigmaPlot.

¶ A plot of mole fraction *vs.* time (h) for the intermediate **9a** at 55 °C could be fitted to the expression:

$$\text{mole fraction} = 4.813(e^{-0.1759t} - e^{-0.1879t}) \ (R^2 = 0.9778)$$

from which values of 0.1879 and 0.1759 h^{-1} can be calculated for k_1 and k_2. Conversion to s^{-1} gives $k_1 = 5.2 \times 10^{-5}$ s^{-1} and $k_2 = 4.9 \times 10^{-5}$ s^{-1}. Similarly, the concentration *vs.* time (h) behaviour for the product **10a** is modelled by the expression

$$\text{mole fraction} = 0.5451(1 - e^{-0.1538t}) - 0.5177(1 - e^{-0.1524t}) \ (R^2 = 0.9959)$$

which yields $k_1 = 4.3 \times 10^{-5}$ s^{-1} and $k_2 = 4.3 \times 10^{-5}$ s^{-1}. Graph fitting was carried out using the program SigmaPlot.

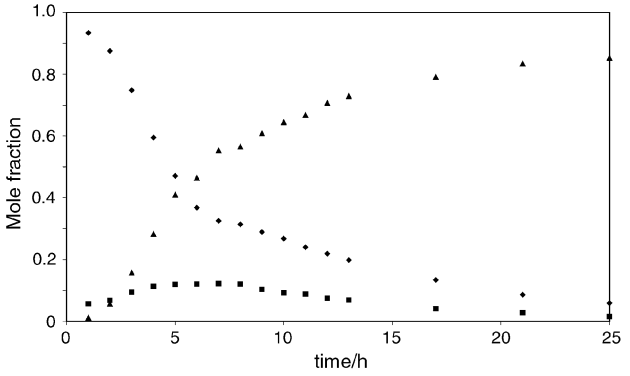


Fig. 7 Plot of mole fraction *vs.* time for compounds **8a** (diamonds), **9a** (squares) and **10a** (triangles) during the thermolysis of **8a** at 55 °C (as determined from integration of ^{11}B NMR signals).§

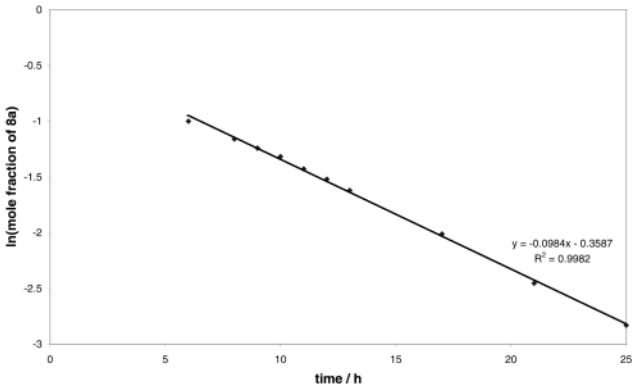


Fig. 8 Plot of ln(mole fraction of **8a**) *vs.* time for the thermolysis of **8a** at 55 °C, as determined from integration of ^{11}B NMR signals.§

The time dependence of the concentration of the intermediate **9a** could be fitted to a difference of exponentials expression for which values of 5.2×10^{-5} s^{-1} and 4.9×10^{-5} s^{-1} were obtained for the rate constants k_1 and k_2 for the two cyclisation steps. An analogous treatment of the concentration of the final product **10a** gives $k_1 = 4.3 \times 10^{-5}$ s^{-1} and $k_2 = 4.3 \times 10^{-5}$ s^{-1}. The kinetic data for the cyclisation reactions are therefore consistent with two-first order steps for which the rate constants are of the order of 4×10^{-5} s^{-1} and are identical within the error limits of the experiment.

Spectroscopic and analytical data for **10a** are in accord with the proposed structure, and these inferences were confirmed by the results of a single crystal X-ray diffraction study (see Fig. 9). The molecule is disordered about a crystallographically imposed mirror plane and although this was successfully modelled by assuming 50% occupancy for the disordered atoms, detailed discussion of the structural parameters for this part of the molecule is not possible. **10a** represents the first crystallographically characterised example of an alkoxo boron halide stabilised by the coordination of an amine nitrogen attached through a one- or two-atom tether. This form of chelate does find precedent, however, amongst aryl derivatives of group 13 elements, and the structural parameters for **10a** are broadly in agreement with those found for such analogous five-membered ring systems.[40]

Similar reaction chemistry can be used to give access to analogous derivatives containing other halides (*e.g.*, the chloride complexes **8b**, **9b** and **10b**). Formation of the adduct **8b** is easily accomplished from **6** and BCl_3, but the cyclisation processes leading to the dichloride **9b** and monochloride **10b** proceed much less readily than in the fluoride case. Higher

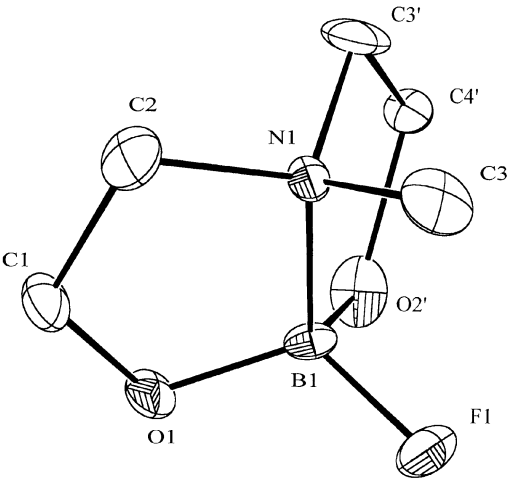


Fig. 9 Molecular structure of **10a**, with ellipsoids drawn at the 30% probability level.

temperatures are needed to complete the first cyclisation step, and despite prolonged reaction times (3–4 weeks) at elevated temperatures (120 °C) it proved impossible to drive the final cyclisation step to completion. Furthermore, the cyclisation steps, which required somewhat forcing conditions for X = F, and which could not be driven fully to completion for X = Cl, appear to be less favourable still for X = Br. In this case similar chemistry leads to a mixture of products in which the di-cyclised analogue **10c** is thought to be a very minor component.

By contrast, the analogous reaction chemistry involving stabilisation by a thioether (rather than amino) donor is much more facile. The thioether adduct $[(Me_3SiOCH_2CH_2)_2S{\cdot}BF_3]$ (**11a**) can be identified in the ^{11}B spectrum of the reaction mixture (formed by adding $BF_3{\cdot}OEt_2$ to **7**) after short times at room temperature ($t < 1$ h). However, cyclisation appears to occur rapidly under these conditions and after 6 h the only boron-containing species present in solution is the thioether stabilised dialkoxoboron fluoride **12a**. **12a** has been characterised by spectroscopic and analytical data, and although single crystals suitable for X-ray diffraction could not be obtained, a structure analogous to that found for **10a** is proposed.

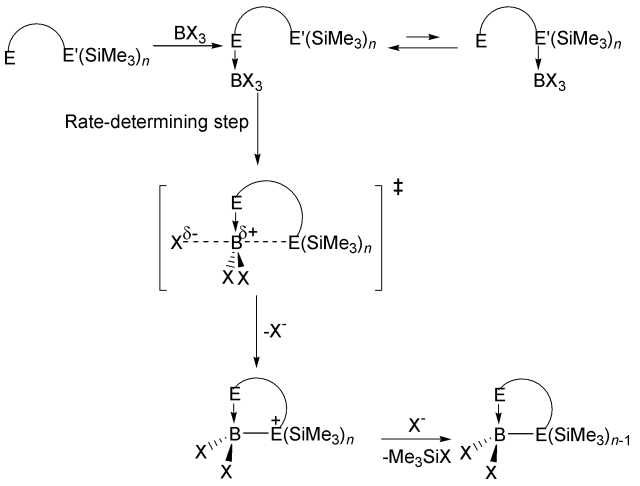
Discussion

Synthesis of intramolecular base-stabilised main group halides has been accomplished by the reaction of trimethylsilyl substituted amines or ethers with the corresponding halide precursor. This route has been shown to be applicable to a range of amido- and alkoxoboron and -tin halides stabilised by nitrogen or sulfur donors attached by one- or two-atom tethers. Structural details have been elucidated for compounds stabilised by bases tethered through either one (**1c** and **3**) or two arms (**10a**). Studies of kinetics and reactivity have also allowed us to reach several conclusions concerning the mechanism of such reactions.

(i) The synthesis of amido-substituted halides is more facile than the corresponding reaction used to make alkoxo derivatives, that is

$$R_nE\text{–}SiMe_3 + BX_3 \rightarrow R_nE\text{–}BX_2 + Me_3SiX$$

occurs more readily for $R_nE = R_2N$ than for $R_nE = RO$. Hence, for example, elimination of Me_3SiX from a reaction mixture containing 6-[$(Me_3Si)_2N$]-2-Me-C_5H_3N and BX_3 occurs readily at −78 °C, with careful control of temperature being required to prevent further reaction, whereas the



Scheme 3

corresponding reactions with 6-(Me_3SiO)-2-Me-C_5H_3N have proved impossible to drive to completion.

(ii) The synthesis of alkoxoboron halides by the elimination of trimethsilyl halide is more facile in the case of fluoride than for chloride or bromide, that is

$$RO–SiMe_3 + BX_3 \rightarrow RO–BX_2 + Me_3SiX$$

proceeds more readily in the case of X = F than for X = Cl or Br.

(iii) Cyclisation by elimination of trimethylsilyl halide occurs more readily for halides stabilised by sulfur donors than in the analogous amino systems, that is

$$(Me_3SiOCH_2CH_2)_2E{\cdot}BX_3 \xrightarrow{-2Me_3SiX} \overline{E(CH_2CH_2O)_2BX}$$

occurs more readily for E = S than for E = NMe.

(iv) Analysis of kinetic data for several systems has shown that the trimethylsilyl halide evolving cyclisation step is a first-order process, and that in the case of systems offering the possibility for two step-wise cyclisation reactions, there is no significant difference in the rates of these two steps.

These observations are consistent with a cyclisation mechanism in which the rate-determining step involves intramolecular nucleophilic attack at the boron centre by the nitrogen or oxygen centre of the trimethylsilyl substituted amine or ether (Scheme 3). That the rate of attack is faster for the formation of amido rather than alkoxo linkages [(i) above] is consistent with the greater nucleophilicity of amine rather than ether donors. In addition, the reduced rates observed for boron centres coordinated by nitrogen rather than sulfur donors [(iii) above] is consistent with the greater stabilisation of the pre-cyclised adduct by the more strongly electron-donating nature of the N → B interaction compared to S → B. The observation of enhanced rates for fluorides (compared to chlorides or bromides) may be due in part to the more favourable thermodynamics associated with the elimination of trimethylsilyl fluoride (rather than Me_3SiCl or Me_3SiBr).

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