Alkylation of (As, Sb, Bi)Cl_3: Formation of [(As, Sb, Bi)RCl_2], (*E*)-[$BiR(CH_2CH{=}C)(SiMe_3)(C_5H_4N$-2)] and 2-$CH(SiMe_3)_2C_5H_4N$-5-R [R = $C(SiMe_3)_2C_5H_4N$-2]

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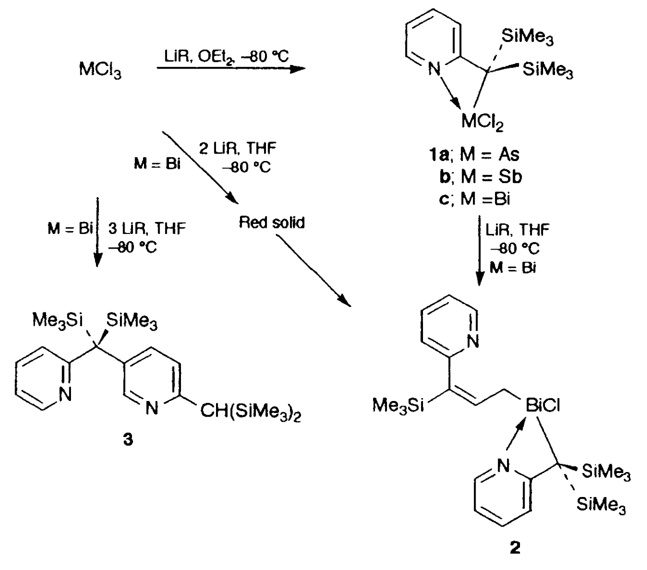
Monomeric alkyldichloro-antimony(III) and -bismuth(III) compounds [$MRCl_2$], R = $C(SiMe_3)_2C_5H_4N$-2′, and the thermally unstable arsenic(III) analogue are accessible from the appropriate group 15 trichloride and LiR in diethyl ether; treating $BiCl_3$ with two and three equivalents of LiR in tetrahydrofuran (THF) yields (*E*)-[$BiR(CH_2CH{=}C)(SiMe_3)(C_5H_4N$-2)] where the C_2 insertion–$SiMe_3$ elimination fragment originates from THF, and the 'head-to-tail' alkyl coupled species, 2-$CH(SiMe_3)_2C_5H_4N$-5-R.

Antimony(III) and bismuth(III) mixed hydrocarbyl–halide compounds tend to be oligomeric or polymeric with bridging halides as in MCl_3,[1–3] unless the hydrocarbyl group is bulky,[4] and for bismuth there are few studies on such compounds[3,4] unlike for the lighter group 15 elements where they have been of interest as precursors to lower valent/multiple bonded species.[5] As part of a systematic study of the main group chemistry of the highly hindered ligand $C(SiMe_3)_2C_5H_4N$-2[6,7] we have developed some antimony(III) and bismuth(III) chemistry, and for comparison, some arsenic(III) chemistry, and report the results herein.

Noteworthy features of our studies include (*i*) the formation of alkyldichloro metal–metalloid(III) species, [$MRCl_2$], M = As, **1a**, M = Sb, **1b**, M = Bi, **1c**, R = $C(SiMe_3)_2C_5H_4N$-2, which have monomeric structures in the solid, **1b** and **1c**; (*ii*) instability of **1a**, slowly eliminating $ClSiMe_3$, and rapid formation of $ClSiMe_3$ even at 0 °C while attempting to prepare the analogous P^{III} compound using the same procedure as for preparing (**1a–c**), *viz* LiR and MCl_3; (*iii*) instability of the dialkylchloro species, MR_2Cl, M = Sb and Bi, yielding for bismuth a substituted allyl, (*E*)-[$BiR(CH_2CH{=}C)$-($SiMe_3$)(C_5H_4N-2)], **2** (structurally authenticated) with THF as an implied reactant; and (*iv*) formation of the 'head-to-tail' coupled dialkyl, 2-$CH(SiMe_3)_2C_5H_4N$-5-R, **3**, while attempting to trialkylate $BiCl_3$.

Synthetic procedures for (**1a–c**)–**3** are summarised in



Scheme 1 R = $C(SiMe_3)_2C_5H_4N$-2

Scheme 1.† The alkyldichloro species have significantly different thermal stabilities; compound **1a** decomposes at *ca.* 20 °C over several hours and **1b** can be sublimed at 200–210 °C, *ca.* 0.2 mbar whereas **1c** decomposes under the same conditions and unlike the antimony compound is photosensitive yielding bismuth mirrors from THF solutions. The coordination environment of **1b**‡ is strongly affected by a stereochemically active lone pair of electrons, Fig. 1, and can be considered as a distorted trigonal bipyramid with the Cl(1), C(6), Sb and the lone pair of electrons approximating to a trigonal plane. The Sb–Cl, C distances are unexceptional[2] whereas the Sb–N distance at 2.371(7) Å is long,[8] reflecting the steric strain associated with a four-membered chelate ring. The bismuth analogue **1c** has a similar structure,[9] and the arsenic compound, **1a**, is most likely monomeric, albeit with a long metalloid–N distance based on electronegativity considerations; in a phosphorus(III) compound [$PCPh_2(C_5H_4N$-2)-(η^2-C_8H_8)] where the ligand closely resembles R there is no P···N interaction.[10]

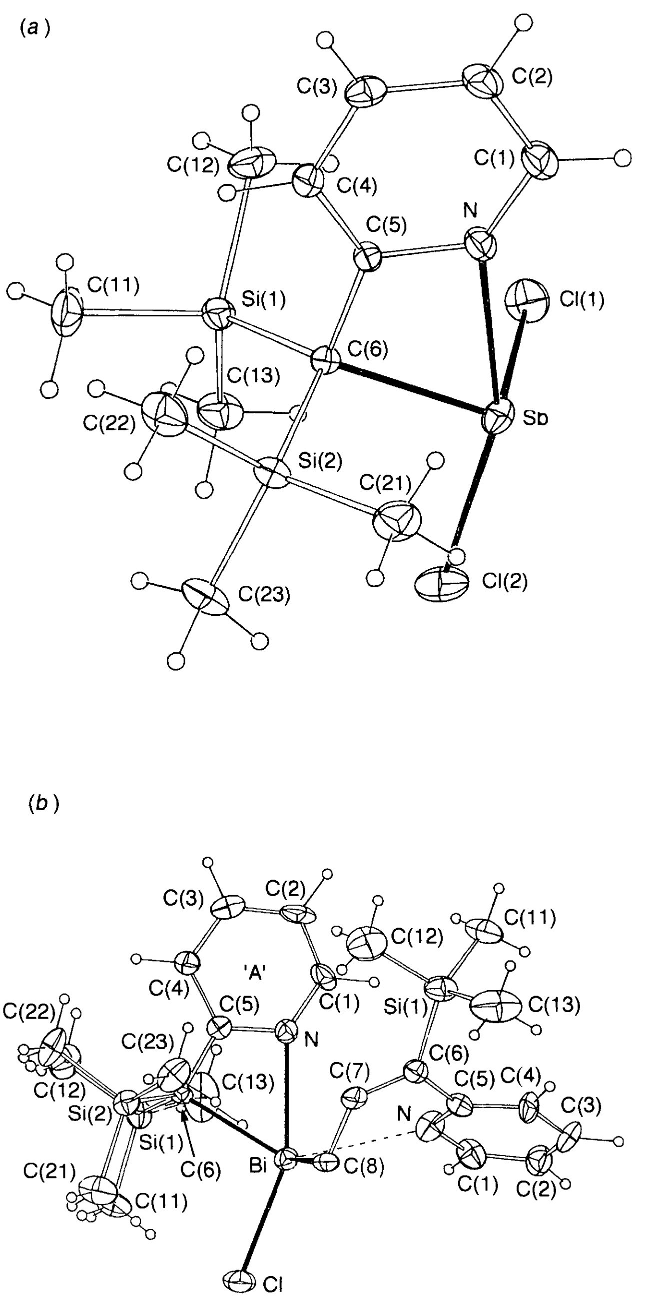


Fig. 1 Molecular projections of (*a*) [$SbRCl_2$], **1b** and (*b*) *E*-[$BiR(CH_2CH{=}C)(SiMe_3)(C_5H_4N$-2)], **2**, showing 20% thermal ellipsoids for the non-hydrogen atoms, and arbitrary radii for hydrogen atoms. Selected bond distances (Å) and angles (°): **1b** Sb–Cl(1,2) 2.373(2), 2.469(2); Sb–N 2.371(7); Sb–C(6) 2.213(5); Cl(1)–Sb–Cl(2) 92.89(8); Cl(1)–Sb–N 87.5(1); Cl(1)–Sb–C(6) 101.4(1); Cl(2)–Sb–N 159.4(2); Cl(2)–Sb–C(6) 98.4(2); N–Sb–C(6) 61.4(2). (**2**) Bi–Cl 2.646(4); Bi–N(A) 2.485(9); Bi–C(A6) 2.41(1); Bi–C(B8) 2.23(2); C(B7)–C(B8) 1.49(2); C(B7)–C(B6) 1.38(2); Cl–Bi–N(A) 156.7(3); Cl–Bi–C(A) 100.7(3); Cl–Bi–C(B8) 84.9(3); N(A)–Bi–C(A6) 58.5(4); N(A)–Bi–C(B8) 91.7(4); C(A6)–Bi–C(B8) 108.3(5); Bi–C(B8)–C(B7) 117.6(7); C(B8)–C(B7)–C(B6) 125(1); C(B7)–C(B6)–C(B5) 121(1); C(B7)–C(B6)–Si(B) 117.6(9); C(B5)–C(B6)–Si(B) 121(1).

Attempts at preparing MR_2Cl species were unsuccessful; for arsenic and antimony there was rapid loss of $ClSiMe_3$

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† *Synthesis and characterization* Compound **1a**: LiR[7] (1.06 g, 6.58 mmol) in OEt_2 (20 ml) was added over 15 min with stirring to $AsCl_3$ (1.18 g, 6.50 mmol) in OEt_2 (50 ml) at −80 °C. On warming to room temperature the mixture was filtered and the volume reduced *in vacuo* (*ca.* 20 ml) and cooled overnight to −30 °C yielding colourless crystals (1.36 g, 55%); ^1H NMR (250 MHz, C_6D_6) δ 0.29 (18H, s, CH_3) 6.38, 6.73, 6.92, 7.73 (4 × 1H, m, $H_{4,3,5,6}$); ^{13}C NMR (62.8 MHz) δ 1.3 (CH_3) 50.9 (SiCC) 119.8, 122.6, 136.8, 145.2, 164.0 ($C_{5,3,4,6,2}$).

Compound **1b**: Details as for **1a** (70% yield, m.p. 137–139 °C); ^1H NMR (250 MHz, C_6D_6) δ 0.29 (18H, s, CH_3) 6.30, 6.67, 6.87, 7.47 (4 × 1H, m, $H_{4,3,5,6}$); ^{13}C NMR (62.8 MHz) δ 2.3 (CH_3) 51.3 (SiCC) 120.7, 125.9, 138.5, 145.0, 166.7 ($C_{5,3,4,6,2}$).

Compound **1c**: LiR (0.98 g, 4.03 mmol) in OEt_2 (100 ml) was added over 15 min with stirring to $BiCl_3$ (1.26 g, 4.0 mmol) in OEt_2 (100 ml) at −80 °C. On warming to room temperature the mixture was filtered, volatiles removed *in vacuo* and the product recrystallised from toluene as yellow prisms (0.91 g, 44% yield, m.p. 194 °C); ^1H NMR (80 MHz, C_6D_6) δ 0.3 (18H, s, CH_3) 6.8, 7.3, 8.1, 8.8 (4 × 1H, m, $H_{4,3,5,6}$); ^{13}C NMR (20.1 MHz) δ 3.3 (CH_3) 69.9 (SiCC) 116.7, 121.7, 136.3, 144.1, 175.5 ($C_{5,3,4,6,2}$); MS *m/z* 515 (M^+). Satisfactory elemental analyses were obtaind for compounds **1b** and **c**.

Compound **3**: LiR (2.57 g, 14.7 mmol) in OEt_2 (30 ml) was added over 15 min with stirring to $BiCl_3$ (1.55 g, 4.9 mmol) in OEt_2 (100 ml) at −80 °C. The resulting red solution was brought to −15 °C, filtered, the volume reduced *in vacuo* (*ca.* 20 ml) and cooled overnight to −30 °C yielding colourless crystals (0.58 g, 25%, m.p. 85–89 °C); ^1H NMR (250 MHz, C_6D_6) δ 0.10, 0.18 (2 × 18H, s, CH_3) 1.45 (1H, s, SiCH) 6.8–8.6 (7H, m, CH); ^{13}C NMR (62.8 MHz) δ 0.29, 0.46 ($SiCH_3$) 32.2, 42.5 ($CSiMe_3$) 119.4, 120.2, 123.4, 124.3, 135.5, 137.1, 148.2, 149.2, 160.5, 163.1 ($C_{aromatic}$).

CAUTION: The toxicity of these compounds and any degradation products is unknown.

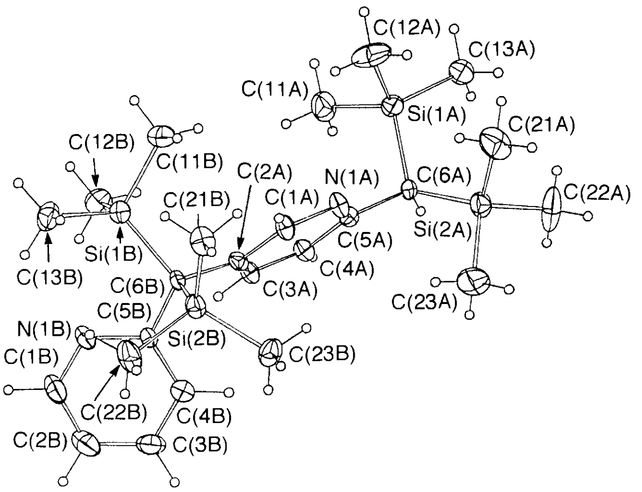

Fig. 2 Molecular projection of **3**

yielding intractable oils but for bismuth a red crystalline solid was isolated from THF solutions below 0 °C. Above 0 °C it decomposes over several minutes yielding orange crystals of compound **2** in low yield which proved difficult to separate from black powder, and recrystallisation from THF or toluene resulted in further deposition of black powder. Single crystals of **2** were characterised using mass spectrometry {*m*/*z* 190[$CH_2C(H){=}C(SiMe_3)(C_5H_4N)^+$], 209 [$Bi^+$], 236 [$R^+$], 426 [M − $BiCl^+$]} and a structure determination using diffraction data.‡ Here the metal centre also has a distorted trigonal bipyramidal structure with a stereochemically active lone pair, Bi, C((A6), C(B8) in the trigonal plane, Fig. 1, and is thus related to the structure of **1b** by interchanging Cl(1) with C(B8). The N(B) to Bi interaction is minimal, Bi–N 2.95(2) Å, which is at odds with the tendency for bismuth compounds to achieve high coordination numbers with pyridine ligands, *e.g.* seven coordination in [$BiI_2(NC_5H_5)_3(S_2CNEt_2)$],[11] and must arise from the geometrical constraints of the pyridyl group itself and of the allyl plane of the potentially bidentate ligand. The Bi–N(A) distance, 2.485(9) Å, is much shorter than in [$BiI_2(NC_5H_5)_3(S_2CNEt_2)$],[11] 2.663(3)–2.728(3) Å, as expected for a lower coordination number in **1b**, but is longer than for anionic *N*-centred ligands such as in [$Bi(NPh_2)_3$], 2.12(2)–2.28(2) Å.[12] The Bi–C distance for the chelate ring, 2.41(1) Å, is long and is more akin to Bi–C distances for the π-system, $BiEtCl_2$,[3] and reflects the steric hindrance of R-strain in the four-membered chelate ring; metal–carbon distances in the related compound bearing bulky groups, [$Bi\{CH(SiMe_3)_2\}_3$], are 2.31(1)–2.35(1) Å.[13] The Bi–C distance for the allyl group, 2.23(2) Å, is at the lower limit for less congested metal centres.[4] The Bi–Cl distance is unexceptional,[3] as is the geometry of the allyl moiety. The origin of the modified ligand in **2** involves THF, most likely *via* loss of $CH_2{=}C(H)OSiMe_3$ possibly associated with a Bi^V intermediate, for example, derived from oxidative addition of Bi^{III} across C–O of THF.

Similarly attempts at forming BiR_3 resulted in decomposition (> −30 °C) to a black solid and colourless crystals of **3**, characterised by NMR spectroscopy and an X-ray structure determination, Fig. 2.‡ Formation of **3** presumably arises from reductive elimination and/or nucleophilic attack of a coordinated R followed by rearrangement. It is unlikely that radical intermediates which subsequently associate–rearrange are involved since this would give 'tail-to-tail' coupling (4,4′ coupling of pyridyl rings)[6] rather than 'head-to-tail' as in the present case.

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‡ *Crystal structure determinations* (*T* = 295 K; Syntex $P2_1$ diffractometer, crystals mounted in capillaries). Compound **1b**: $C_{12}H_{22}NSbClSi_2$, *M* = 429.2, orthorhombic, space group $Pna2_1$, *a* = 13.702(3), *b* = 12.218(3), *c* = 10.782(3) Å, *U* = 1805 Å^3, *F*(000) = 856, *Z* = 4, D_c = 1.58 g cm^{-3}, μ(Mo-Kα) = 18.0 cm^{-1}, $A^*_{min,max}$ 1.29, 1.52, specimen 0.40 × 0.20 × 0.15 mm, 1682 unique reflections, 1492 with $I > 3\sigma(I)$ used in the refinement, $2\theta_{max}$ = 50°; *R* = 0.024, R_w = 0.026. Compound **2**: $C_{22}H_{38}N_2BiClSi_3$, *M* = 659.3, monoclinic, space group $P2_1/c$, *a* = 11.303(5), *b* = 15.380(4), *c* = 18.932(8) Å, β = 118.11(3)°, *U* = 2903 Å^3, *F*(000) = 1304; *Z* = 4, D_c = 1.51 g cm^{-3}, μ(Mo-Kα) =60 cm^{-1}, $A^*_{min,max}$ 3.5, 16.5, specimen 0.35 × 0.6 × 0.5 mm, 5108 unique reflections, 2914 with $I > 3\sigma(I)$ used in the refinement, $2\theta_{max}$ = 50°; *R* = 0.059, R_w = 0.044. Compound **3**: $C_{24}H_{44}N_2Si_4$, *M* = 473.1, monoclinic, space group $P2_1/c$,*a* = 13.29(1), *b* = 13.02(1), *c* = 17.826(5) Å, β = 105.75(8)°, *U* = 2968 Å^3, *F*(000) = 920, *Z* = 4, D_c = 1.06 g cm^{-3}, μ(Mo-Kα) = 1.8 cm^{-1} (no absorption correction), specimen 0.20 × 0.20 × 0.08 mm, 2556 unique reflections, 1533 with $I > 3\sigma(I)$ used in the refinement $2\theta_{max}$ = 40°; *R* = 0.043, R_w = 0.042.

Atomic coordinates, bond lengths and bond angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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