A *gem*-aluminium(III)/antimony(III) C centre incorporated in a bimetallic six-membered heterocycle

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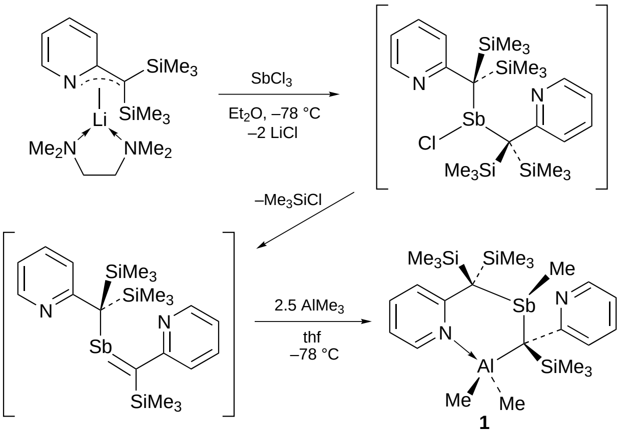
Reaction of $AlMe_3$ with the implied stibene intermediate (–Sb=C<) formed in the reaction of [(2-pyr)$(SiMe_3)_2$CLi·tmeda] with $SbCl_3$ affords the carboalumination product containing a *gem*-Al/Sb C centre as part of a six-membered heterocycle, [(2-pyr)$(SiMe_3)_2$C–Sb(Me)–(2-pyr)$(SiMe_3)$C–Al$(Me)_2$] 1, structurally authenticated as the (*RS,SR*) diastereoisomer.

The main-group complexes of the bulky alkyl ligand (2-pyr)$(SiMe_3)_2C^-$, R, have been extensively investigated.[1] Such bulky ligands, devoid of a β-hydrogen, are important in the search for unusual and novel main-group chemistry such as low-valent and multiply bonded species due to the kinetic protection offered to the element in question and the presence of a potentially stabilising internal N donor. Thus the variety of complexes isolated and characterised include monomeric, subvalent, hypervalent, electron-deficient and low-coordinate species. Studies by Cowley *et al.*[2] and others[3] have shown that it is possible to stabilise double-bonded species involving group 15 elements using the tri-*tert*-butyl substituted mesityl and $(SiMe_3)_2C^-$ ligands, *e.g.* E′=E, As=P, P=As, As=As, Sb=P. Multiply bonded complexes of this type involving As and P tend to be more stable to oligomerisation than those containing Sb which appear to require a higher degree of steric protection and stabilisation.[4]

We have previously reported that it is possible to synthesise the monomeric $RSbCl_2$ complex from the 1 : 1 metathetical exchange reaction of [RLi·$(Et_2O)_n$] and $SbCl_3$ in diethyl ether. However, as was also the case with the arsenic and bismuth complexes, the formation of the monochloride species from the 2 : 1 reaction was highly problematic with evidence for the low-temperature elimination of $SiClMe_3$ affording an intractable dark red oil.[5] Herein we now report on the synthesis and characterisation of a novel mixed group 13/15 complex **1** (Scheme 1) which was obtained *via* the addition of $AlMe_3$ to a thf solution of this red oil. Such *gem*-diorganometallics are attaining increasing recognition and importance in organic synthesis.[6]



Scheme 1

The dark red oil can be consistently generated from the specific 2 : 1 reaction of crystalline RLi·tmeda and $SbCl_3$ in thf at −78 °C. A red solution is formed over 12 h as the reaction mixture is allowed to warm to ambient temperature. The deep red oil is then obtained when all volatiles are removed *in vacuo* and LiCl removed by the addition of hexane and subsequent filtration. From initial one- and two-dimensional NMR studies it is clear that the red oil is a complex mixture of products; ^{13}C NMR revealed at least 5 $SiMe_3$ environments to be present. To date, attempts at obtaining a reproducible crystalline product directly from the oil have been unsuccessful despite varying the polarity of added solvents, *i.e.* hexane to thf, and cooling from 4 to −78 °C. Attempts at distilling any liquid or low-melting point products *in vacuo* (0.1 mmHg) have also been unsuccessful as decomposition to elemental antimony occurs readily above 80 °C. In an attempt to identify any of the products we have submitted the red oil to a series of reactions. One which has been successful is the addition of $AlMe_3$.

The small yellow rod-shaped crystals† of **1**‡ were obtained from the reaction of a thf solution of the red oil with a 2.5-fold excess of $AlMe_3$ (based on the initial quantity of R used) in thf at −78 °C. The crystals cocrystallised with large colourless crystals of [$(Me_3Al)_2$(tmeda)] at 4 °C in hexane–thf over several days. That the tmeda complex is formed is indicative that all the tmeda is not removed *in vacuo* with other volatiles.

X-Ray diffraction studies on the yellow crystals revealed a novel monomeric mixed aluminium–antimony complex, space group $P2_1/n$, in which both Sb and Al are bound to the same carbon, Fig. 1. A search of the Cambridge Crystallographic Database§ confirms that this is the first mixed group 13/15 complex of its type. Importantly, a stibene (–Sb=C<) intermediate can be invoked to explain the formation of the complex as carboalumination, *viz.* the addition of $AlMe_3$ across the antimony–carbon double bond. A probable mechanism for the formation of **1** is outlined in Scheme 1.

The stibene intermediate contains a modified and an unmodified ligand as a result of $SiClMe_3$ elimination. It has to be assumed that this stibene complex is stable and present in a relatively significant quantity. ^{13}C NMR has been, as yet, of limited help in identifying the particular double-bonded carbon with the only markers by which to judge the chemical shift being: (*i*) stibabenzene in which the delocalised C–Sb appears at δ 178.3,[7]¶ which is coincident with both the delocalised C–N and quaternary carbon in the pyridyl ring, (*ii*) a study of several acyclic stibonium ylides[8]‖ reported the $Sb^+–C^- \leftrightarrow Sb=C$ shift to be in the region δ 74.6–93.2 which corresponds well with a lone signal at δ 78.0 in the ^{13}C (C_6D_6) NMR spectrum of the red oil. Very recently Nixon and co-workers reported[9] the first solid-state structurally characterised acyclic distibene complex, *trans*-1,4-bis(trimethylsiloxy)-1,4-bis(2,4,6-tri-*tert*-butylphenyl)-2,3-distibabutadiene, an interesting point being that the crystals are red.

The crystals of **1** are relatively air stable and melt with decomposition from 88 °C. The solid-state structure is dominated by a six-membered metallocycle [C(12)C(12′)Sb-

C(22′)AlN(11)], Scheme 1, with ring closure being secured by the dative pyridyl N–Al bond. Two chiral centres are present in the molecule, the Sb and the C centre which is *gem* with respect to the Sb^{III} and Al^{III} centres. These are respectively (R) and (S) or (S) and (R) in the same molecule with the solid comprised of an enantiomeric mixture.

The Sb–C(22′) distance of 2.167(7) Å is shorter than that of Sb–C(12′), *i.e.* C with two bound trimethylsilyls, which at 2.247(7) Å is longer than that found in RSbCl$_2$, 2.213(5) Å. TheAl–C(22′) bond length is 2.017(6) Å which is longer than those for the bound Me groups, av. 1.978(8) Å. The pyridyl N–Al distance of 2.062(6) Å is unremarkable. Despite the near planarity of the SbC(22′)C(22)N(21) atoms, there is little or no interaction between Sb and N(21) as confirmed by the separation of 2.914(6) Å and the close to tetrahedral angle at C(22′) [Sb–C(22′)–C(22) 106.7(4)°], which can be compared with the analogous bond angle of 94.45° in RSbCl$_2$ where there is a long but definite Sb–N [2.371(7) Å] interaction.

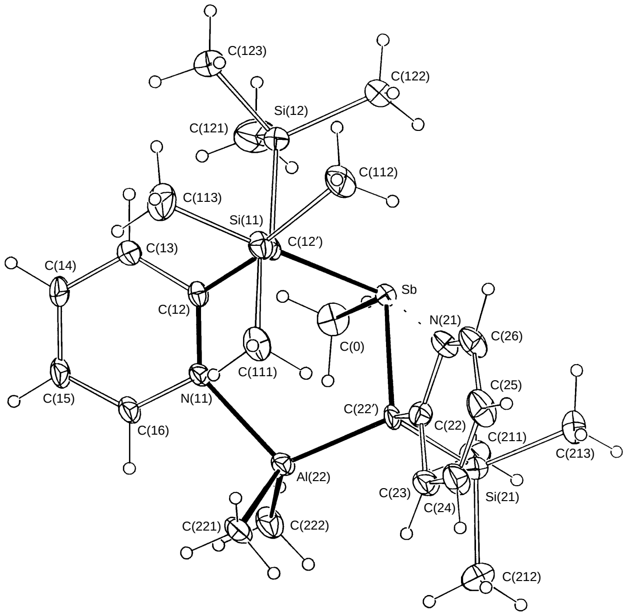


Fig. 1 Crystal structure of **1** with selected distances (Å) and angles (°): Sb–C(0,12′,22′) 2.178(7), 2.247(7), 2.167(7); Al(22)–N(11), C(22′,221,222) 2.062(6), 2.017(6), 1.975(8), 1.982(8); C(0)–Sb–C(12′,22′) 93.0(3), 97.2(3); C(12′)–Sb–C(22′) 105.3(2); Sb–C(12′)–C(12), Si(11,12) 112.6(4), 117.1(3), 99.9(3); Sb–C(22′)–C(22), Si(21), Al(22) 106.7(4), 108.3(3), 106.7(3); N(11)–Al(22)–C(22′,221,222) 109.6(2), 102.7(3), 102.7(3); C(22′)–Al(22)–C(221,222) 118.3(3), 114.1(3); C(221)–Al(22)–C(222) 107.7(3); Al(22)–N(11)–C(12,16) 137.8(4), 106.6(4); Al(22)–C(22′)–C(22), Si(21) 114.6(4), 115.3(3).

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Footnotes

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† Approximate yield based on separation of sample of crystals, 32% (yield not maximised and based on consumption of ligand R). mp 88 °C (decomp.). ^{1}H NMR (300 MHz, C$_6$D$_6$, 25 °C) δ 7.78 (d, br, 1 H), 7.67 (d, br, 1 H), 7.52 (d, 1 H), 7.05 (m, 2 H), 6.78 (t, 1 H), 6.40 (t, 1 H), 6.22 (t, 1 H), 1.08 (s, 3 H, MeSb), 0.45 (s, 9 H, SiMe$_3$), 0.25 (s, 9 H, SiMe$_3$), 0.09 (s, 9 H, SiMe$_3$), -0.37 (s, 6 H, Me$_2$Al). ^{13}C NMR (100.6 MHz, C$_6$D$_6$, 25 °C) δ 168.1 (quat-C), 148.0 (CH), 145.5 (CH), 136.8 (CH), 136.2 (CH), 127.2 (CH), 125.6 (CH), 118.5 (CH), 117.7 (CH), 5.7 (SiMe$_3$), 4.8 (MeSb), 2.7, 2.1 (SiMe$_3$)$_2$, 1.2 (Me$_2$Al).

‡ *Crystallographic data* for **1**: (CAD4 diffractometer, crystals mounted in a capillaries) C$_{24}$H$_{44}$AlN$_2$SbSi$_3$, M = 593.62; monoclinic, space group $P2_1/n$, a = 11.585(6), b = 14.595(13), c = 18.035(12) Å, β = 102.03(5), U = 2982(4) Å^3, D_c (Z = 4) = 1.322 g cm^{-3}; F(000) = 1232. μ_{Mo} = 10.9 cm^{-1}, specimen 0.10 × 0.28 × 0.33 mm, $A^*_{min,max}$ = 1.11, 1.34. $2\theta_{max}$ = 50°, final R, R_w = 0.044, 0.042. N_o = 3279 'observed' [$I > 3\sigma(I)$] reflections out of N = 5245 unique. Al assignment based on geometry (bond lengths) and refinement of population and charge balance. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/451.

§ Search carried out January 1997.

¶ NMR solvent CDCl$_3$ with 10% diglyme; measured at -10 °C.

‖ NMR solvent CD$_2$Cl$_2$.

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