[2 + 2] Cycloaddition derivatives of stiba(III)alkene (Sb=C) and arsa(III)imine (As=N) intermediates

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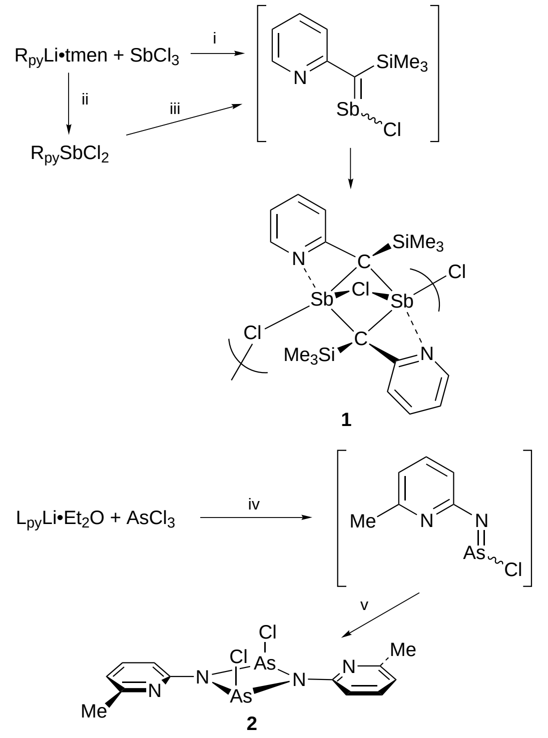
Mild thermolysis of (2-pyridyl)($SiMe_3$)$_2$C$SbCl_2$ and [2-(6-Me)pyridyl]($SiMe_3$)N$AsCl_2$ affords, respectively, the chloro-bridged polymeric geminal C-centred distibine(III) complex [(2-pyridyl)($SiMe_3$)CSbCl]$_\infty$ 1 and the geminal N-centred arsenic(III) amide [{2-(6-Me)pyridyl}NAsCl]$_2$ 2; the proposed mechanism involves the elimination of Me_3SiCl and a [2 + 2] stereospecific *cis*-cycloaddition of the stibaalkene (Sb=C) and arsaimine (As=N) intermediates.

In developing the main group chemistry of the bulky alkyl ligand, (2-pyridyl)($SiMe_3$)$_2$C$^-$, R_{py}, and the related amido ligand, {2-(6-Me)pyridyl}($SiMe_3$)N$^-$, L_{py}, the presence of the Me_3Si group has been important in the kinetic protection of any metal(loid) centre.[1] However another important aspect of this chemistry is the potential present for the low energy β-elimination of Me_3SiCl from substituted metal(loid) chloride complexes resulting in novel and/or rare multiply bonded species. As such the elimination of halosilane from $R_{py2}SbCl$ proved useful in synthesising the novel geminal Al^{III}/Sb^{III} bimetallic heterocycle[2] and has been important in the preparation of phosphaalkenes and alkynes.[3] In contrast to N, and to a lesser degree P, the multiply bonded species of the heavier group 15 elements have a tendency to oligomerise unless this thermodynamically favoured process is offset by the presence of bulky ligands.[4] However this can be utilised in the formation of C-centred geminal organodimetallics which are receiving increasing attention as a result of their potential in developing new synthetic routes to complex organic molecules.[5]

Herein, we report the synthesis and characterisation of the chloro-bridged polymeric C-centred geminal distibine, [(2-pyridyl)($SiMe_3$)CSbCl]$_\infty$ **1** and the dimeric N-centred amidoarsine, [{2-(6-Me)-pyridyl}NAsCl]$_2$ **2** derived from the doubly bonded intermediate species [(2-pyridyl)($SiMe_3$)C=SbCl] and [{2-(6-Me)pyridyl}N=AsCl] *via* the elimination of Me_3SiCl from $R_{py}SbCl_2$ and $L_{py}AsCl_2$.

In contrast to its As and P analogues, which undergo Me_3SiCl elimination at below −20 °C, $R_{py}SbCl_2$ can be prepared, as previously described,[6] from the 1 : 1 metathesis reaction of $R_{py}Li{\cdot}tmen$ and $SbCl_3$. However Me_3SiCl elimination can be achieved in two ways, as shown in Scheme 1, to give bright yellow rod-like crystals of **1**.† The crystals, which melt at 201–203 °C after gradually becoming opaque and then blackening, are relatively stable to air and atmospheric moisture, slowly becoming white and opaque, On melting further Me_3SiCl elimination occurs giving the appearance of effervescence.

Pale yellow prismatic crystals of **2** were obtained in a similar manner to the thermal elimination synthesis of **1**.† These crystals also decompose slowly in air, and melt in the range 187–189 °C.



Scheme 1 *Reagents and conditions*: i, thf, −78 °C to room temp., 3 days; ii, Et_2O, −78 °C; iii, toluene, 50 °C, 4 h; iv, Et_2O, −78 °C; v, toluene, 80 °C, 4 h

X-Ray diffraction studies on **1**‡ revealed a geminal distibine structure. Such geminal distibine complexes are extremely rare with only a few structurally authenticated Sb^V and Sb^{III} methylene bridged complexes.[7] The repeating unit of the polymer contains, as its core, an almost square, but buckled, C_2Sb_2 ring internally bridged by a single Cl lying on a 2-symmetry axis, as does the other Cl which provides the connecting points along the chain (Fig. 1). The geminal carbon is formally bonded to two Sb^{III} centres with bond distances of 2.180(9) and 2.219(9) Å. Furthermore each Sb centre is bound to a pyridyl N [2.220(8) Å] a ring bridging Cl(1), [2.850(3) Å] and a linking Cl(2) [3.054(2) Å] making each Sb five coordinate. The stereochemically active lone pairs occupy a position *trans* to one of the geminal C-centres. The Sb–Cl distances in **1** are much longer than those found in $R_{py}SbCl_2$, 2.373(2) and 2.469(2) Å, while the Sn–N distance is actually

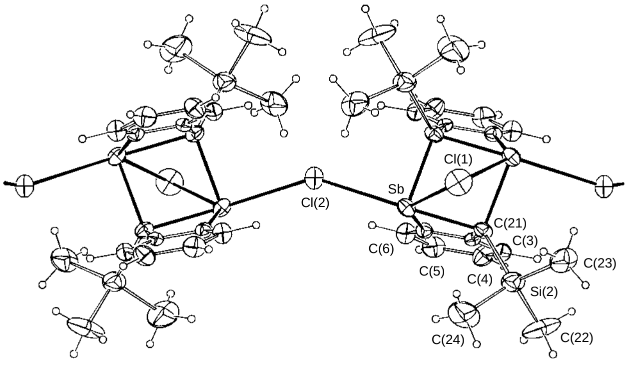


Fig. 1 Crystal structure of **1**

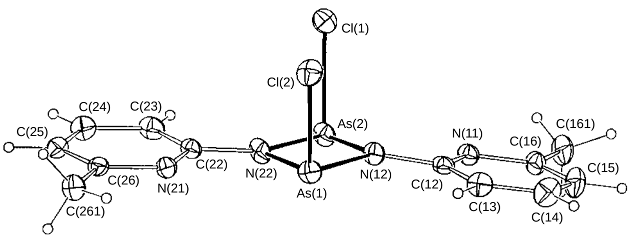


Fig. 2 Crystal structure of **2**

shorter, *cf.* 2.317(7) Å. The C(21)–Sb–N(1) angle of 63.1(3)° is comparable with that of 61.4(2)° found in $R_{py}SbCl_2$. The Sb–C distance of 2.213(5) Å in $R_{py}SbCl_2$[4] is only comparable with the longer Sb–C bond distance found in **1** despite the greater coordinative saturation at the Sb centre, *i.e.* five over four, while the Sb–C(–Al) distance in the recently reported Sb/Al geminal metallocycle,[2] in which Sb is only three coordinate, is shorter than both Sb–C bonds in **1**, being 2.167(7) Å. The bridging Cl(1) directly straddles the two Sb centres in the repeating unit at an angle of 67.4(1)° while the linking Cl(2) forms an angle of 149.3(1)° between the Sb centres of two different repeating units. Surprisingly the pyridyl rings are *cis* to the $(CSb)_2$ ring and almost eclipse each other.

The symmetry of bond distances and angles, and hence charge distribution, within the dimeric repeating unit must be the result of an initial [2 + 2] cycloaddition reaction of the stibene units, [(2-pyridyl)($SiMe_3$)C=SbCl], prior to polymerisation through the linking chlorides (Scheme 1). The concomitant stereochemical requirements of such a reaction may explain the *cis* arrangement of the pyridyl rings. However, it is noted that such reactions for alkenes are photolytically induced. The presence of the metal and thus some ionic character may render the cycloaddition more facile.

This argument can also be proposed in explaining the dimeric structure of the amidoarsine, **2**. The sp^2 geometry at the amido N requires that the $(NAs)_2$ ring and the (Me)pyridyl fragments are coplanar (Fig. 2), dihedral angles 8.6(3) and 4.4(2)°, though from an examination of the bond lengths there is no evidence of delocalisation. The unusual *cis* orientation of the Cl atoms relative to the $(NAs)_2$ ring is most likely, once again, a result of the stereochemical outcome of the [2 + 2] cycloaddition. Olah and Oswald[8] noted that the reaction of Bu^tNH_2 with $AsCl_3$ resulted in the formation, *via* HCl elimination, of the imidochloroarsenite $Bu^tN{=}AsCl$. The subsequent crystal structure[9] showed the complex to be dimeric, $(Bu^tNAsCl)_2$ **3** sharing the same structural features as **2**; the geometry around N being essentially planar and the Cl atoms *cis* to the $(NAs)_2$ planar ring. There is a great deal of similarity in the bond distances and angles of the $As_2N_2Cl_2$ cores: As–N bond lengths in **2** range from 1.809(7)–1.857(7) Å compared with 1.799(5)–1.827(4) Å in **3**, however the As–Cl bond distances in **2** of 2.228(2) and 2.233(2) Å are shorter than those in **3**, 2.249(3) and 2.252(2) Å, while the As···As–Cl angles in**2** are 103.72(8) and 103.75(8)° and 111.1(1) and 110.5(1)° in **3**. To date the only structurally characterised compound containing an $As^{III}{=}N$ bond is [2,4,6-$Bu^tC_6H_2N$(H)–As=$NC_6H_2Bu^t_3$-2,4,6],[10] the aryl groups of which are significantly more bulky than L_{py}. Dimerisation in **2** is not unexpected given the loss of a bulky Me_3Si moiety.

At room temperature the ^1H and ^{13}C NMR spectra of **2** suggest one dominant species (> 95%) with only one other set of minor signals indicating other possible oligomeric species. At low temperature these two species integrate almost equally. No coalescence occurs so it is unlikely that there is restricted rotation around the C–N bond. A more reasonable assumption is the presence of either monomers or higher oligomers. The NMR spectra of **1** show no evidence of polymer disintegration in solution but reveal that the polymer crystals often retain residual solvents in their structure. The structure shown in Fig. 1 contains 0.5 toluene situated between layers of the polymeric chain in the interstices formed by four $R_{py2}Sb_2Cl_2$ units.

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Notes and References

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† (*i*) $R_{py}SbCl_2$ was prepared as previously described.[4] The *in vacuo* removal of Et_2O from this reaction, followed by the addition of toluene, subsequent filtration to remove LiCl and heating to 50 °C for 4 h leads to the precipitation of a pale yellow powder. Removal of toluene and recrystallisation at 4 °C from thf–toluene results in bright yellow rod-like crystals of **1**. (*ii*) Alternatively, the metathesis reaction of $R_{py}Li$ and $SbCl_3$ can be carried out in thf at −78 °C, allowed to warm slowly to room temp. and stirred for 3 days. The thf is removed *in vacuo* and a CH_2Cl_2 extraction of the remaining solids allows for the crystallisation of **1**, again at 4 °C. Yield 63% (not maximised). Mp 201.203 °C. ^1H NMR (300 MHz, CD_2Cl_2, 25 °C) δ 7.76 (d, br, 1 H), 7.57 (t, 1 H), 7.14 (br, d, 1 H), 6.73 (t, 1 H), 0.34 (s, 9 H), residual thf (0.25) 3.68 (m, 1 H), 1.80 (m, 1 H), residual toluene (0.33) 7.17 (m, 1.7 H) 2.11 (s, 1 H). ^{13}C NMR (100.6 MHz, CD_2Cl_2, 25 °C) δ 160.6, 144.1, 138.0, 128.1, 119.1, 45.7 (CH_2), 2.8. Satisfactory elemental analysis obtained.

2. A toluene solution of $L_{py}AsCl_2$, prepared from the metathesis reaction of $L_{py}Li{\cdot}Et_2O$ with $AsCl_3$, was heated at 80 °C for 4 h. The *in vacuo* reduction of the solution and cooling slowly from 50 °C to room temp. resulted in pale yellow prismatic crystals of **2**. Yield 94%. Mp 187–189 °C. ^1H NMR (300 MHz, C_7D_8, 25 °C) (major component, > 95%) δ 6.89 (m, 1 H), 6.45 (d, 1 H, J 8 Hz), 6.30 (d, 1 H, J 8 Hz), 2.26 (s, 3 H, Me), (minor component) 6.73 (t), 6.50 (d), 6.40 (d), 2.19 (s). ^{13}C NMR (100.6 MHz, C_7D_8, 25 °C) δ 169.0, 156.5, 139.0, 115.0, 105.6. 23.8. Satisfactory elemental analysis obtained.

‡ *Crystallographic data* for **1**. (CAD4 diffractometer, crystals mounted in capillaries) $(R_{py}SbCl)_2{\cdot}C_7H_8$, $C_{25}H_{34}Cl_2N_2Sb_2Si_2$, M = 733.15, orthorhombic, space group *Pnna* (D_{2h}^6, no. 52) a = 10.015(3), b = 15.746(13), c = 18.996(3) Å, U = 2996(3) Å^3, D_c = 1.625 g cm^{-3}, Z = 4, $F(000)$ = 1448. μ_{Mo} = 20.8 cm^{-1}, specimen 0.08 × 0.32 × 0.25 mm, $A^*_{min,max}$ = 1.35, 1.72. $2\theta_{max}$ = 50°, final R,R_w = 0.047, 0.039 (statistical weights). N_o = 1339 'observed' [$I > 3\sigma(I)$] reflections out of N = 2640 unique. Toluene disordered with a site occupancy factor of 0.5. **2**. $C_{12}H_{12}As_2Cl_2N_4$, M = 443.08, monoclinic, space group $P2_1/c$ (C_{2h}^5, no. 14), a = 9.926(4), b = 13.005(3), c = 14.224(4) Å, β = 122.61(2)°, U = 1546.6(9) Å^3, D_c = 1.859 g cm^{-3}, Z = 4, $F(000)$ = 848, μ_{Mo} = 46.6 cm^{-1}, specimen 0.58 × 0.24 × 0.28 mm, $A^*_{min,max}$ = 2.64, 3.60, $2\theta_{max}$ = 50°, final R,R_w = 0.055, 0.051 (statistical weights). N_o = 2144 'observed' [$I > 2\sigma(I)$] reflections out of N = 3540 unique. CCDC 182/724.

1 T. R. van den Ancker and C. L. Raston, *J. Organomet. Chem.*, 1995, **500**, 289; L. M. Engelhardt, G. E. Jacobsen, W. C. Patalinghug, B. W. Skelton, C. L. Raston and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1991, 2895.
2 P. C. Andrews, C. L. Raston, B. W. Skelton and A. H. White, *Chem. Commun.*, 1997, 1183.
3 A. C. Gaumont and J. M. Denis, *Chem. Rev.*, 1994, **94**, 1413.
4 N. C. Norman, *Polyhedron*, 1993, **20**, 2431.
5 I. Marek and J.-F. Normant, *Chem. Rev.*, 1996, **96**, 3241.
6 C. Jones, L. M. Engelhardt, P. C. Junk, D. S. Hutchings, W. C. Patalinghug, C. L. Raston and A. H. White, *J. Chem. Soc., Chem. Commun.*, 1991, 1560.
7 W. Kolandra, W. Schwarz and J. Weidlein, *Z. Anorg. Allg. Chem.*, 1983, **501**, 137; *J. Organomet. Chem.*, 1984, **260**, C1; H. Schmidbaur, B. Milewski-Mahrla, G. Muller and C. Kruger, *Organometallics*, 1984, **3**, 38; A. F. Chiffey, J. Evans, W. Levason and M. Webster, *Organometallics*, 1995, **14**, 1522.
8 G. A. Olah and A. A. Oswald, *Can. J. Chem.*, 1960, **38**, 1428.
9 R. Bohra, H. W. Roesky, M. Noltemeyer and G. M. Sheldrick, *Acta Crystallogr., Sect. C*, 1984, **40**, 1150.
10 P. B. Hitchcock, M. F. Lappert, A. K. Rai and H. D. Williams, *J. Chem. Soc., Chem. Commun.*, 1986, 1633.

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