Synthesis and characterisation of the first stable, heteroleptic silylstannylenes†

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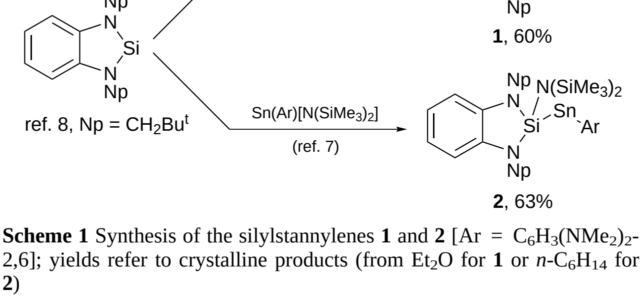
Treatment of the silylene $Si[C_6H_4(NCH_2Bu^t)_2\text{-}1,2]$ with $SnAr_2$ or $SnAr[N(SiMe_3)_2]$ yields the thermally stable (silyl)stannylene $SnAr[Si\{C_6H_4(NCH_2Bu^t)_2\text{-}1,2\}X]$ [X = Ar 1 or $N(SiMe_3)_2$ 2], having δ [$^{119}Sn\{^1H\}$] 412 [$^1J(^{29}Si\text{–}^{117/119}Sn)$ 715/749 Hz] (1) and δ 621 (2); crystalline 1 has a V-shaped Si–Sn–C skeleton, *l*(Sn–Si) = 2.636(2) Å and two remote Sn···N contacts, av. 2.75 Å (to one NMe_2 group of each of the aryl groups).

Homoleptic heavier group 14 metal(II) (M = Ge, Sn or Pb) compounds in which M is bound to a more electropositive element than carbon (*e.g.*, Si, Ge or a metal) are rare. Two types of group 6 metal complexes are known, $[Pb\{Mo(\eta^5\text{-}C_5Me_5)(CO)_3\}_2(thf)]$[1a] [and $\eta^5\text{-}C_5H_5$ or $\eta^5\text{-}C_5H_3(SiMe_3)_2\text{-}1,3$ analogues] and $[Ge\{C_6H_3(C_6H_2Me_3\text{-}2',4',6')_2\text{-}2,6\}\{Mo(\eta^5\text{-}C_5H_5)(CO)_2\}]$,[1b] as well as some tin(II) phosphides[2a,b] and arsenides,[2b,c] but especially relevant to the present work are three silyl derivatives: $[Sn\{Si(SiMe_3)_3\}_2]_2$,[3] $[Sn\{Si(SiMe_3)_3\}_2(\mu\text{-}Cl)Li(thf)_3]$[4] and $Pb[Si(SiMe_3)_3]_2$[3] (thf = OC_4H_8). Each of these five X-ray characterised compounds was prepared by a metathetical exchange reaction, using an alkali metal salt of the appropriate ligand and $M'Cl_2$ (M′ = Ge or Pb) or[3] $M'[N(SiMe_3)_2]_2$ (M′ = Sn or Pb). Two transient heterobinuclear complexes have been identified spectroscopically or by trapping experiments, $Ge(C_6H_2Me_3\text{-}2,4,6)_2M'X_2$ [$M'X_2$ = $Si(C_6H_2Me_3\text{-}2,4,6)_2$[5] or $Sn(C_6H_2Pr^i_3\text{-}2,4,6)_2$],[6] each obtained from tetravalent precursors.

Thermally stable mononuclear heavier group 14 metal(II) compounds MX_2 (M = Ge, Sn or Pb and X^- is a mono- or bidentate ligand) are highly reactive, but insertion reactions into M–X bonds leading to new M^{II} complexes MX'_2 or M(X)X′ have not previously been reported. The latter (heteroleptic) type is in any event rare.[7]

We now describe the synthesis (Scheme 1) and characterisation of the first heteroleptic (silyl)stannylenes, the crystalline, yellow–orange, diamagnetic $SnAr[Si\{C_6H_4(NCH_2Bu^t)_2\text{-}1,2\}Ar]$ **1** and the red–brown $SnAr[Si\{C_6H_4(NCH_2Bu^t)_2\text{-}1,2\}\{N(SiMe_3)_2\}]$ **2** [Ar = $C_6H_3(NMe_2)_2\text{-}2,6$]. They were obtained by treatment of the yellow silylene $Si[C_6H_4(NCH_2Bu^t)_2\text{-}1,2]$[8] with for **1** the yellow $SnAr_2$[7] in *n*-hexane at ambient temperature in a slow reaction, or for **2** with the yellow $SnAr[N(SiMe_3)_2]$[7] under the same conditions but in a faster reaction.

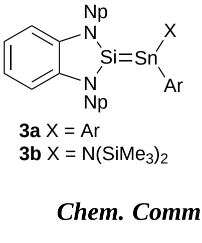


Scheme 1 Synthesis of the silylstannylenes **1** and **2** [Ar = $C_6H_3(NMe_2)_2\text{-}2,6$]; yields refer to crystalline products (from Et_2O for **1** or *n*-C_6H_{14} for **2**)

The crystalline aryl(silyl)stannylenes **1** and **2** were thermally robust, decomposing before melting only at *ca.* 120 °C. The orange (**1**) and orange–red (**2**) hexane solutions were more labile (**1** > **2**), the former slowly (days) depositing tin at ambient temperature. Their stability may, in part, be due to close contacts between tin and one or more *o*-nitrogen atoms of the Ar^- ligand(s), *cf.* ref. 7. Each of **1** and **2** gave satisfactory microanalytical results, as well as multinuclear NMR spectra.‡ The EI (70 eV) mass spectra showed the parent molecular ion in 2% intensity for **1** and 9% for **2**, as the highest *m/z* peak; the most intense fragment ion was $[Si\{C_6H_4(NCH_2Bu^t)_2\text{-}1,2\}Ar]^+$ for **1** and $[Si\{C_6H_4(NCH_2Bu^t)_2\text{-}1,2\}\{N(SiMe_3)_2\}]^+$ for **2**. Single crystal X-ray diffraction data established the molecular structure of **1**.§

The ^1H NMR spectrum of **1** in C_6D_6 at 298 K showed separate signals for each of the two CH_2CMe_3 groups and several for the eight NMe groups of the two Ar moieties.‡ The corresponding spectrum of **2** in [$^2H_8$]toluene at 298 K revealed two signals for the $SiMe_3$ groups but only one for the two CH_2CMe_3 groups and a broad feature for the NMe_2 protons. The latter split into two separate signals at 238 K. This indicates that at the higher temperature there is a rapid N → Sn exchange process involving the $Sn\cdots NMe_2\text{-}2 \rightleftharpoons Sn\cdots NMe_2\text{-}6$ fragments, while at the lower temperature only one of the two NMe_2 groups is bound to tin, as also found in the solid state for **1**, *vide infra*. This interpretation is consistent (at least for **1**) with the values found for the $^{119}Sn\{^1H\}$ NMR spectral chemical shifts: δ 412 (**1**) and δ 621 (**2**) in PhMe–C_6D_6 at 298 K, which may be compared with δ 442 for $SnAr_2$ and 422 for $SnAr[N(SiMe_3)_2]$ having four- and three-coordinate tin, respectively.[7] A comparison of these results with the two existing (silyl)tin(II) compounds is not possible; since attempts to detect ^{119}Sn or ^{29}Si NMR spectral signals in the range −60 to +30 °C for $[Sn\{Si(SiMe_3)_3\}_2]_2$ were unsuccessful,[3] while for $[Sn\{Si(SiMe_3)_3\}_2(\mu\text{-}Cl)Li(thf)_3]$ only the ^{29}Si chemical shifts were recorded, δ −6.23 for *Si*(SiMe$_3$)$_3$ and δ −22.14 for Si(*Si*Me$_3$)$_3$.[4] The SiSn $^{29}Si\{^1H\}$ NMR spectral chemical shifts in PhMe–C_6D_6 at 298 K were found at δ 48.8 for **1** and δ −27.8 for **2**. The former signal, unlike the latter, showed readily discernible coupling to tin: $^1J(^{29}Si\text{–}^{117}Sn)$ 715 Hz and $^1J(^{29}Si\text{–}^{119}Sn)$ 749 Hz; these values may be compared with $^1J(^{29}Si\text{–}^{119}Sn)$ of 580 Hz for $Sn(SiMe_3)Me_3$[9] and 515 Hz for $(SnPh_3)_2SiPh_2$.[10] The ^{29}Si–Sn coupling in **2** may have been obscured by coupling to the ^{14}N nucleus of the $N(SiMe_3)_2$ group.

The pathway leading to **1** or **2** may have implicated an initial transient heterodinuclear tin–silicon 'double-bonded' complex **3**, which was rapidly isomerised by a 1,2-shift of X [X = Ar or $N(SiMe_3)_2$] from tin to silicon. Evidence for **3** rests on the



3a X = Ar
3b X = $N(SiMe_3)_2$

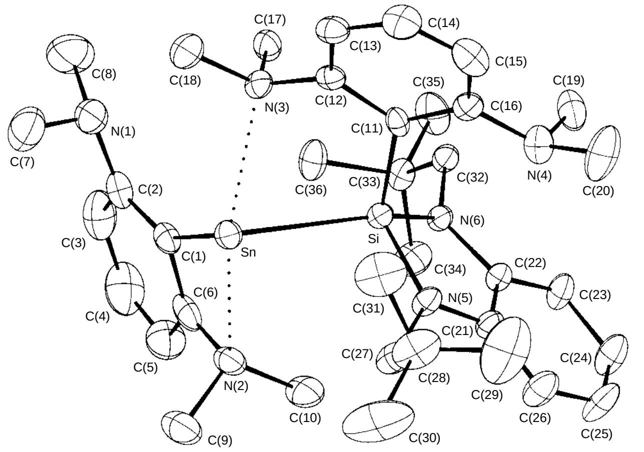


Fig. 1 CAMERON[16] representation (50% thermal vibration ellipsoids) of the molecular structure of $\mathrm{SnAr[\overline{Si\{C_6H_4(N}CH_2Bu^t)_2\text{-}1,2\}Ar]}$ **1** [Ar = $C_6H_3(NMe_2)_2$-2,6]. Selected bond lengths (Å) and angles (°): Sn–C(1) 2.210(8), Sn–Si 2.636(2), Sn···N(3) 2.569(6), Sn···N(2) 2.580(6), Si–C(11) 1.904(8); C(1)–Sn–Si 107.0(2), N(5)–Si–N(6) 91.0(3), C(6)–C(1)–Sn 102.5(6), C(2)–C(1)–Sn 140.0(6).

existence of related kinetically inert homonuclear complexes such as $[Sn\{CH(SiMe_3)_2\}_2]_2$,[11] $[Sn\{Si(SiMe_3)_3\}_2]_2$[3] and $X''_2SnSnCl_2$ [X'' = $CH(SiMe_3)C_9H_6N$-8][12] and the labile heterodinuclear analogue $X'_2SiGeX'_2$ (X' = $C_6H_2Me_3$-2,4,6) **4**.[5] Precedents for a 1,2-aryl shift in group 14 element chemistry include Wagner–Meerwein rearrangements, the photolytic scrambling between $Si_2X'_4$ and $Si_2X'''_4$ (X''' = $C_6H_3Me_2$-2,6),[13] and the trapping of **4** with $Si(H)Et_3$ generating $GeH(SiEt_3)(SiX'_3)X'$ with $GeX'(SiX'_3)$ as the presumed intermediate.[5]

The molecular structure of the crystalline aryl(arylsilyl)-stannylene **1**, illustrated in Fig. 1, shows it to be mononuclear with a V-shaped Si–Sn–C(1) skeleton but with Sn having further remote contacts to N(2) and N(3) (from an NMe_2 of each aryl group). The tin bonding environment may thus be regarded as approximating to a distorted trigonal bipyramid, N(2) and N(3) being axial and Si, C(1) and the lone pair in equatorial sites. The Si–Sn–C(1) angle of 107.0(2)° is similar to the 105.6(2)° in $SnAr_2$,[7] and the Sn–C(1) distance of 2.108(2) Å in **1** is likewise close to the av. of 2.214 Å in $SnAr_2$.[7] The Sn–Si bond length of 2.636(2) Å is comparable to the av. 2.672 Å in $[Sn\{Si(SiMe_3)_3\}_2]_2$[3] and the 2.681(2) Å in $[Sn\{Si(SiMe_3)_3\}_2(\mu\text{-}Cl)Li(thf)_3]$.[4] The Sn···N(2) and Sn···N(3) contacts in **1**, av. 2.75 Å, are slightly more remote than in $SnAr_2$ (av. 2.64 Å)[7] or $\overline{\mathrm{Sn[C_6H_3(CH_2N}}\mathrm{Me_2)(CH_2NMe_2)\text{-}2,6]Cl}$ (2.56 Å).[14] The aromatic ring containing C(1) is strongly tilted about the Sn–C(1) vector so as to allow N(2) to approach Sn, as evident from the significant deviations from the sp^2 values of the C(6)–C(1)–Sn [102.5(6)°] and C(2)–C(1)–Sn [140.0(6)°] angles; these are close to those found in $SnAr_2$, 104.0 and 138.2°.[7] The Sn···N(3) contact from the SiAr group does not involve strain, as shown by the more typical sp^2 values for the C(12)–C(11)–Si [118.3(6)°] and C(16)–C(11)–Si [123.5(6)°] angles.

The reactions shown in Scheme 1 provide the first examples of insertion of (i) an unsaturated reagent into an M–Z bond of a carbene or a heavier group 14 element analogue MZ_2 generating a new metallene and (ii) a silylene into a metal–aryl or metal–amide bond. As to (ii), the reaction leading to **2** demonstrates that the migratory aptitude of $N(SiMe_3)_2$ is greater than that of Ar, as also evident from the faster rate of formation of **2** than **1**. Such reactions are likely to be antecedents of a wider series; for example involving the silylene and $M[N(SiMe_3)_2]_2$ (M = Ge, Sn or Pb).[15]

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Footnotes and References

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† No reprints available.

‡ *NMR spectroscopic data* [^1H NMR at 250.0 MHz in C_6D_6 for **1** or at 300.0 MHz in $[^2H_8]$toluene for **2**; $^{13}C\{^1H\}$ NMR at 75.47 MHz in C_6D_6, $^{29}Si\{^1H\}$ NMR at 99.33 MHz and $^{119}Sn\{^1H\}$ NMR at 93.2 MHz, all in PhMe with C_6D_6; at 298 K unless otherwise stated]. **1**: ^1H δ 0.78 and 1.02 (2s, 18 H, CMe_3), 2.39, 2.49 and 2.63 (3s, 18 H, NMe_2), 2.98 and 3.26 (2s, 6 H, NMe_2), 2.97–3.61 (AB-type, part. hidden, CH_2), 6.52–7.18 (m, 10 H, phenyl); ^{13}C δ 29.41 and 29.84 ($C\mathit{Me}_3$), 34.25 and 34.89 ($\mathit{C}Me_3$), 44.98, 46.56, 47.89 (broad, NMe_2), 57.04 and 59.77 (CH_2), 109.06, 109.50, 111.88, 114.61, 116.11, 116.46, 116.80, 131.76, 135.30, 144.92. 146.43, 151.97, 159.44, 161.03, 162.34 and 163.46 (arom. C); ^{29}Si δ 48.8 [$^1J(^{29}Si\text{–}^{117/119}Sn)$ 715, 749 Hz]; ^{119}Sn δ 412. **2**: ^1H (238 K) δ 0.1 and 0.45 (2s, 18 H, $SiMe_3$), 0.95 and 1.11 (2s, 18 H, CMe_3), 2.17 and 2.61 (2s, 12 H, NMe_2), 2.28, 2.48, 2.52, 3.04, 3.09, 3.51 and 3.56 (AB-type, one signal hidden, broad signals, 4 H, CH_2), 5.95, 5.98, 6.52–7.07 (m, phenyl); ^{13}C δ 5.16 and 5.67 ($SiMe_3$), 30.09 ($C\mathit{Me}_3$), 33.78 ($\mathit{C}Me_3$), 45 (vbr, NMe_2), 56.44 (CH_2), 109.24, 117.18, 119.44, 128.47, 144.06, 146.15 and 159.88 (arom. C); ^{29}Si δ 1.28 ($SiMe_3$), −27.65 (Si–Sn); ^{119}Sn δ 620.94.

§ *Crystal data*: **1**, $C_{36}H_{56}N_6SiSn$, M = 719.6, monoclinic, space group $P2_1/n$ (non-standard no. 14), a = 16.118(5), b = 11.124(3), c = 21.526(5) Å, β = 101.71(2)°, U = 3779(2) Å^3, $F(000)$ = 1512; Z = 4, D_c = 1.26 g cm^{-3}, μ(Mo-Kα) = 7.4 cm^{-1}, specimen 0.2 × 0.2 × 0.06 mm, 4802 reflections collected for $2 < \theta < 22°$, 4614 independent reflections [R(int) = 0.057], $R1$ = 0.049 for 2872 reflections with $I > 2\sigma(I)$, $wR2$ = 0.123 (for all data).

Intensities were measured on an Enraf-Nonius CAD4-diffractometer [T = 293(2) K] using monochromated Mo-Kα radiation (λ = 0.71073 Å); no crystal decay. Full-matrix least squares on all F^2 refinement with SHELXL-93, H atoms in riding mode and all non-H atoms anisotropic. CCDC 182/572.

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