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Syntheses and crystal structures of [Sn{2-[$(Me_3Si)_2C]C_5H_4N$}R] [R = $C_6H_2Pr^i_3$-2,4,6 **1** or $CH(PPh_2)_2$ **2**], two novel heteroleptic tin(II) compounds derived from [Sn-{2-[$(Me_3Si)_2C]C_5H_4N$}Cl], and for [{Sn($C_6H_2Pr^i_3$-2,4,6)$_2$}$_3$] **3**, a structural redetermination

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Two novel, monomeric heteroleptic tin(II) derivatives, [Sn{2-[$(Me_3Si)_2C]C_5H_4N$}R] [R = $C_6H_2Pr^i_3$-2,4,6 **1** or $CH(PPh_2)_2$ **2**], have been prepared, characterised by multinuclear NMR spectroscopies and their molecular structures determined by single crystal X-ray diffraction. Both compounds were prepared from the corresponding heteroleptic tin(II) chloro-analogue, [Sn{2-[$(Me_3Si)_2C]C_5H_4N$}Cl], and thus demonstrate the utility of this compound as a precursor to further examples of heteroleptic tin(II) derivatives: such compounds are often unstable with respect to ligand redistribution. In each case, the central tin(II) is three-co-ordinate. Crystals of trimeric [{Sn($C_6H_2Pr^i_3$-2,4,6)$_2$}$_3$] **3** were found to undergo a solid state phase transition, which may be ascribed to ordering of the ligand isopropyl groups. At 220 K the unit cell is orthorhombic, space group $Pna2_1$, compared with monoclinic, space group $P2_1/c$, for the same crystals at 298 K, in which there is an effective tripling of the now *b* (originally *c*) axis. This result illustrates the extreme crowding generated by this bulky aryl ligand.

Thermally stable, divalent compounds of Ge, Sn and Pb have been available for *ca.* twenty years. In recent years an increasingly large number of such compounds (ER_2; E = Ge, Sn or to a much lesser extent, Pb) have been reported, the great majority of which are homoleptic. Since the first examples to appear (E = Ge or Sn) which employed the bulky, monodentate alkyl ligand, $CH(SiMe_3)_2$,[1,2] other ER_2 compounds (E = Ge, Sn or Pb) have subsequently been reported and their molecular structures determined. For example, [ER_2] where E = Ge, R = 2-{$(Me_3Si)_2C$}C_5H_4N,[3] 2-{Ph(Me_3Si)C}C_5H_4N,[4] $C_6H_2Bu^t_3$-2,4,6[5] or $C_6H_3(C_6H_2Me_3$-2,4,6$)_2$-2,6;[6] E = Sn, R = $C_6H_2(CF_3)_3$-2,4,6,[7] $C_6H_2Bu^t_3$-2,4,6,[8] $C(PMe_2)_3$,[9] $CH(PPh_2)_2$,[10] $N(SiMe_3)_2$,[11] C_6H_3-($C_6H_2Me_3$-2,4,6)$_2$-2,6,[6] 2-{$(Me_3Si)_2C$}C_5H_4N,[12] 2-{Ph(Me_3Si)C}C_5H_4N or 8-{(Me_3Si)HC}C_9H_6N;[4] E = Pb, R = $CH(PPh_2)_2$, C($SiMe_3$)(PPh_2)$_2$,[10,13] $C_6H_2(CF_3)_3$-2,4,6,[14] $Si(SiMe_3)_3$,[15] C_6H_3-($C_6H_2Me_3$-2,4,6)$_2$-2,6,[6] or 8-{(Me_3Si)HC}C_9H_6N.[4] A number of examples, determined by single crystal X-ray diffraction to exhibit dimeric structures, further to [E_2R_4] [E = Ge or Sn, R = $CH(SiMe_3)_2$],[2] have also been reported. For example, E = Ge, R = Si($SiMePr^i_2$)$_3$, Si($SiPr^i_3$)$_3$[16] or $C_6H_3Et_2$-2,6;[17] E = Sn, R = $Si(SiMe_3)_3$.[15]

Of the heteroleptic derivatives, [Ge{$CH(SiMe_3)_2$}{C-($SiMe_3$)$_3$}][18] and [Sn{$C_7H_5(NPr^i)_2$-1,2}Cl][19] are monomeric, whilst [{E[$C_6H_3(C_6H_2Me_3$-2,4,6$)_2$-2,6]Cl}$_2$] (E = Ge or Sn) are both dimeric but feature terminal (Ge) and bridging (Sn) Cl ligands.[6] However, utilising chelating ligands with *N*-donor atoms has allowed the isolation and structural characterisation of a number of other monomeric, heteroleptic SnR_2 compounds, *e.g.* [Sn{2-[$(Me_3Si)_2C]C_5H_4N$}R] [R = $Sn(SiMe_3)_3$,[20] Cl or $N(SiMe_3)_2$][12] and [Sn{$C_6H_3(NMe_2)_2$-2,6}{Si[C_6H_3-(NCH_2Bu^t)$_2$-1,2][$C_6H_3(NMe_2)_2$-2,6]}].[21] The $Sn(SiMe_3)_3$-containing compound is the first structurally characterised example of a compound possessing a bond between divalent Sn and tetravalent Sn.[20] Similarly, the use of amide ligands has permitted the preparation and structural characterisation of two binuclear tin(II) derivatives, RSn–R′–SnR [R = $N(SiMe_3)_2$; R′ = $C_6H_n(NSiMe_3)_2$-1,4, *n* = 4 or 8].[22] With the planes of the trigonal arylamido N atoms parallel to those of the Sn atoms, stabilisation in these compounds results from N atom lone pair donation into empty tin 5p orbitals.

Recently, we have reported on our interest in divalent compounds of Ge, Sn and Pb as components of mixed-metal clusters.[23–27] For example, [$Ru(CO)_{12}$] was shown to react at low temperatures with SnR_2 (R = $C_6H_2Pr^i_3$-2,4,6), or at higher temperatures with its corresponding cyclic trimer, [$(SnR_2)_3$],[28] to give both [$Ru_3(CO)_{10}$(μ-SnR_2)$_2$] and [$Ru_3(CO)_9$(μ-SnR_2)$_3$].[27] Furthermore, reaction of the pentametallic species [$Ru_3(CO)_{10}$(μ-SnL_2)$_2$] [L = R′ = $CH(SiMe_3)_2$ or R] with SnR'_2 or SnR_2 afforded the hexametallic clusters [$Ru_3(CO)_9$(μ-SnR'_2)$_n$(μ-SnR_2)$_{3-n}$] (*n* = 1 or 2): in the reaction of [$Ru_3(CO)_{12}$] with SnR'_2 the hexametallic cluster [$Ru_3(CO)_9$(μ-SnR'_2)$_3$] was isolated in addition to the previously reported Ru_3Sn_2 cluster. The trimer [$(SnR_2)_3$] also reacted with the phosphine-co-ordinated cluster, [$Ru_3(CO)_{10}${$CH_2(PPh_2)_2$}], to give [$Ru_3(CO)_8$(μ-SnR_2)$_2${CH_2-(PPh_2)$_2$}], whilst with SnR'_2 [$Ru_2(CO)_6$(μ-SnR'_2){μ-CH_2-(PPh_2)$_2$}] resulted. Surprisingly, reaction of [$Ru_3(CO)_{12}$] with [E{$CH(PPh_2)_2$}][10] (E = Sn or Pb) did not yield a mixed-metal cluster, but provided a rapid and quantitative route (96%) to [$Ru_3(CO)_{10}${$CH_2(PPh_2)_2$}]: to obtain this compound from the reaction of the 'free' phosphine, $CH_2(PPh_2)_2$, with [$Ru_3(CO)_{12}$] requires harsh conditions and does not proceed as cleanly!

We have now utilised the stability conferred on the tin(II) centre arising from additional, intramolecular, *N*-donor co-ordination using the 2-{$(Me_3Si)_2C$}C_5H_4N ligand, in the preparation and characterisation of two novel, monomeric and heteroleptic tin(II) derivatives [Sn{2-[$(Me_3Si)_2C]C_5H_4N$}R] [R = $C_6H_2Pr^i_3$-2,4,6 **1** or $CH(PPh_2)_2$ **2**]. These compounds have been characterised by single crystal X-ray diffraction and

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multinuclear NMR spectroscopies. It is expected that: (*i*) **1** and **2** should allow access to further examples of mixed-metal clusters (see above), (*ii*) in the case of **2** the SnR{CH(PPh$_2$)$_2$}-incorporating cluster will be accessible [providing, by means of the two pendant donor P atoms, a further route to cluster expansion].

Additionally, we present newly determined X-ray crystallographic data for [(SnR$_2$)$_3$] **3** (R = C$_6$H$_2$Pr$^i_3$-2,4,6): a room temperature structure determination of this compound using standard diffractometric methods has been previously reported by three of us (C. J. C., D. J. C., M. A. C.).[28] During a data collection at 220 K (on a crystal also used for a data collection at 298 K) it became clear that there had been a phase transition to a more ordered form. We now report this result in detail because of the light it throws on the genesis of the room temperature structure, which exhibited perfect long-range order with an asymmetric unit of *three* trimer molecules and negligible side-chain disorder. The present result provides evidence of one consequence of steric crowding caused by the C$_6$H$_4$Pr$^i_3$-2,4,6 ligand, suggesting that some conformational freezing out occurs at room temperature.

Experimental

Equipment

All experiments were carried out under an inert atmosphere of argon. All chemical manipulations were performed, either using standard Schlenk line techniques employing a dual manifold vacuum/argon line fitted exclusively with Young's type greaseless taps, or in a Miller–Howe glove-box under an inert atmosphere of dinitrogen operating at <1 ppm O$_2$ and <5 ppm H$_2$O. Solvents were predried by distillation over the appropriate drying agent under an atmosphere of dinitrogen for 72 h prior to use, freeze-thaw degassed and stored in ampoules under dinitrogen or argon, either in the presence of a potassium mirror (Et$_2$O, hexane or toluene) or a sodium mirror (thf).

Multinuclear NMR spectroscopy

The ^{1}H and ^{13}C-{^{1}H} NMR spectra were recorded using a Bruker WM 250 instrument (operating at a field strength of 5.872 T with observational frequencies of 250.00 and 62.86 MHz respectively), ^{29}Si-{^{1}H}, ^{31}P-{^{1}H} and ^{119}Sn-{^{1}H} spectra on either a Bruker DPX 250 or DMX 400 (variable temperature spectra for **2** only) instrument (operating at field strengths of 5.872 and 9.395 T with observational frequencies of 49.662, 101.202, 93.181 and 79.46, 161.923, 149.089 MHz respectively). The ^{1}H, ^{13}C-{^{1}H} and ^{29}Si-{^{1}H} spectra were referenced externally to SiMe$_4$, ^{31}P-{^{1}H} spectra externally to H$_3$PO$_4$ and ^{119}Sn-{^{1}H} spectra externally to SnMe$_4$. Low resolution CI and EI mass spectra were recorded on a Fisons 'Autospec' double focusing mass spectrometer.

X-Ray crystallography

The structures of compounds **1**, **2** and **3** were determined from image plate X-ray diffraction data, **1** and **2** from a Mar 180 cm plate using ambient temperature data and capillary-mounted crystals, **3** from a Stoe 180 cm image plate at 220 K and a crystal frozen in an oil drop; Mo-Kα radiation with a graphite monochromator (λ = 0.710 73 Å) was used for all measurements. Data collection and structure refinement parameters are shown in Table 3. For **1** and **2**, 95 images having a 2° rotation per image were collected using a data collection time of 5 min per frame and a crystal-to-plate distance of 75 mm. The XDS program[29] was used for all data processing and merged together with MARSCALE, the MarResearch version of XSCALE.[29] Final cell constants were determined using the GLOREF routine within XDS, using refined diffraction spots collected over 190° of rotation. Each structure was solved using the direct methods routine in SHELXS and refined using the SHELXL 97 version of SHELXL.[30] Hydrogen atoms were placed in calculated positions and the final cycles of refinement were full-covariance least squares. For **3**, data were measured using a 3° rotation angle per frame and a 15 min exposure, processed using the proprietary Stoe software supplied with the IPDS system and otherwise treated similarly. The structure plots (Figs. 2–4) were drawn using the ZORTEP program.[31]

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Materials

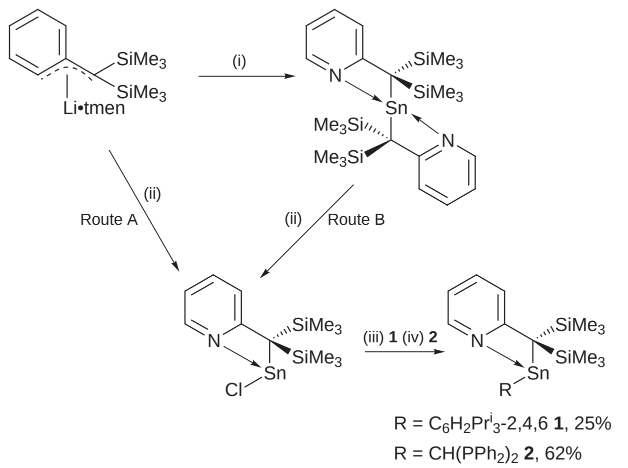
The compounds LiBu^n (2.5 mol dm^{-3} in hexane), CH$_2$(PPh$_2$)$_2$, 2-MeC$_5$H$_4$N, SiMe$_3$Cl, 1-BrC$_6$H$_2$Pr$^i_3$-2,4,6 and SnCl$_2$ (97%) from Aldrich Chemical Co. were used as received. The Li reagents, [Li(tmen){2-[(Me$_3$Si)$_2$C]C$_5$H$_4$N}],[32] Li(Et$_2$O)(C$_6$H$_2$-Pr$^i_3$-2,4,6),[28] Li(Et$_2$O)[CH(PPh$_2$)$_2$][33] and [{Sn(C$_6$H$_2$Pr$^i_3$-2,4,6)$_2$}$_3$][28] **3** were prepared and characterised according to literature methods.

Syntheses

[Sn{2-[(Me$_3$Si)$_2$C]C$_5$H$_4$N}Cl].[12] To a Schlenk tube charged with a stirred slurry of 2 equivalents of SnCl$_2$ (15.38 g, 80.96 mmol) in Et$_2$O (50 ml) was added a stirred orange solution of [Li(tmen){2-[(Me$_3$Si)$_2$C]C$_5$H$_4$N}] (14.56 g, 40.48 mmol) in Et$_2$O (50 ml) over a 30 min period, resulting in an immediate change from white to intense yellow which, after complete addition of the lithium reagent, became orange. The mixture was stirred for 2 d, cooled, the solution filtered and the Et$_2$O removed *in vacuo*. The resulting intensely yellow solid was washed with freezing-cold hexane (2 × 30 ml) and separated from LiCl with hot hexane (3 × 50 ml). This hexane was removed *in vacuo* to afford [Sn{2-[(Me$_3$Si)$_2$C]C$_5$H$_4$N}Cl] as a yellow-orange crystalline solid in 71% yield (11.18 g, 28.62 mmol). ^{1}H NMR (C$_6$D$_6$, 298 K): δ 7.42 (d, 1 H), 6.95 (t, 1 H), 6.39 (d superimposed on t, 2 H) and 0.26 (s, 18 H). ^{13}C-{^{1}H} NMR (C$_6$D$_6$, 298 K): δ 175.36 [C$_5$H$_4$N, C(2)], 144.23, 138.46, 129.20, 119.29, 43.34 {*C*[Si(CH$_3$)$_3$]$_2$} and 1.98 {C[Si(*C*H$_3$)$_3$]$_2$}.

[Sn{2-[(Me$_3$Si)$_2$C]C$_5$H$_4$N}(C$_6$H$_2$Pr$^i_3$-2,4,6)] 1. To a Schlenk tube containing [Sn{2-[(Me$_3$Si)$_2$C]C$_5$H$_4$N}Cl] (3.30 g, 8.45 mmol), a stirrer-bar and Et$_2$O (50 ml), cooled to −78 °C using a solid CO$_2$–acetone slush bath, was added a stirred slurry of Li(Et$_2$O)(C$_6$H$_2$Pr$^i_3$-2,4,6) (1.97 g, 6.94 mmol) over a 30 min period; no change was observed. The mixture was allowed to warm slowly to ambient temperature (*ca.* 8 h) and stirred for 24 h. The solution was filtered and the Et$_2$O removed *in vacuo*. After *ca.* 4 d the viscous orange oil had solidified into a crystalline material; this was redissolved in hexane to afford a saturated solution from which, after a period of 2 d at ambient temperature, O$_2$- and water-sensitive, orange cubes of compound **1** were obtained in 25% yield (0.97 g, 1.74 mmol). ^{1}H NMR (C$_6$D$_6$, 298 K): δ 7.85 (d, 1 H), 7.15 (s, 2 H), 6.98 (t, 1 H), 6.68 (d, 1 H), 6.36 (t, 1 H), 3.01 (br, *ca.* 2 H), 2.86 (sept, *ca.* 1 H), 1.46–1.28 (overlapping doublets, 18 H), 0.33 (s, 9 H) and 0.04 (s, 9 H). ^{13}C-{^{1}H} NMR (C$_6$D$_6$, 298 K): δ 171.53 (C$_5$H$_4$N), 168.12 (*C*$_6$H$_2$Pr$^i_3$-2,4,6), 154.37 (*C*$_6$H$_2$Pr$^i_3$-2,4,6), 148.38 (*C*$_6$H$_2$Pr$^i_3$-2,4,6), 146.74 (C$_5$H$_4$N), 137.30 (C$_5$H$_4$N), C$_5$H$_4$N resonance obscured by solvent, 121.26 (*C*$_6$H$_2$Pr$^i_3$-2,4,6), 118.58 (C$_5$H$_4$N), 42.63 {*C*[Si(CH$_3$)$_3$]$_2$}, 35.69 and 34.82 [(CH$_3$)$_2$*C*H], 25.88 (br) and 24.55 [(*C*H$_3$)$_2$CH], 2.49 and 2.30 {C[Si(*C*H$_3$)$_3$]$_2$}. ^{29}Si-{^{1}H} NMR (C$_6$D$_6$, 298 K): δ 0 and −3. ^{119}Sn-{^{1}H} NMR (C$_6$D$_6$, 298 K): δ 474. Mass spectrum (CI, NH$_3$): m/z = 559 ($M^{\cdot+}$ and 321 {$M^{\cdot+}$ − 2-[(Me$_3$Si)$_2$C]C$_5$H$_4$N} [Found (Calc. for C$_{27}$H$_{43}$-NSi$_2$Sn): C, 57.55 (58.27); H, 7.84 (7.79); N, 2.53 (2.52)%].

[Sn{2-[(Me$_3$Si)$_2$C]C$_5$H$_4$N}{CH(PPh$_2$)$_2$}] 2. To a Schlenk tube containing [Sn{2-[(Me$_3$Si)$_2$C]C$_5$H$_4$N}Cl] (4.02 g, 10.29 mmol), a stirrer-bar and Et$_2$O (50 ml) was added a stirred slurry of Li(Et$_2$O)[CH(PPh$_2$)$_2$] (4.78 g, 10.29 mmol) over a 30 min



Scheme 1 Preparation of [Sn{2-[(Me$_3$Si)$_2$C]C$_5$H$_4$N}R] {R = Cl, 2-[(Me$_3$Si)$_2$C]C$_5$H$_4$N, C$_6$H$_2$Pr$^i_3$-2,4,6 **1** or CH(PPh$_2$)$_2$ **2**} from [Sn{2-[(Me$_3$Si)$_2$C]C$_5$H$_4$N}Cl].[12] (i) Et$_2$O, $\frac{1}{2}$ SnCl$_2$, hexane extraction, hexane wash; (ii) Et$_2$O, SnCl$_2$, hexane extraction, hexane wash; (iii) Et$_2$O, −78 °C, LiR, hexane extraction, concentration, crystallisation; (iv) Et$_2$O, LiR, toluene extraction, recrystallisation from hot toluene

period, resulting in a change from orange to intense yellow. The mixture was stirred for 2 d, filtered and the Et$_2$O removed *in vacuo*. The resulting intensely yellow solid was separated from LiCl with hot toluene and the solvent was removed subsequently *in vacuo* to afford compound **2** as an intensely yellow solid. Yield 62% (4.71 g, 6.38 mmol). Redissolution in hot toluene afforded, upon cooling, **2** as large intensely yellow needles which could be handled in air for a number of minutes without any visible signs of decomposition. ^{13}C-{^{1}H} NMR (C$_4$D$_8$O, 245 K): δ 173.70 [C$_5$H$_4$N, C(2)], 146.50 (C$_5$H$_4$N), 141.80–127.40 {C$_5$H$_4$N and CH[P(C_6H$_5$)$_2$]$_2$}, 118.54 (C$_5$H$_4$N), 38.70 {C[Si(CH$_3$)$_3$]$_2$}, 4.10 and 1.40 {C[Si(CH$_3$)$_3$]$_2$}. ^{13}C-{^{1}H} NMR (C$_6$D$_6$, 298 K): δ 173.93 [C$_5$H$_4$N, C(2)], 146.50 (C$_5$H$_4$N), 137.71 (C$_5$H$_4$N), 118.54 (C$_5$H$_4$N), 38.70 {C[Si(CH$_3$)$_3$]$_2$}, 26.79 {CH[P(C$_6$H$_5$)$_2$]$_2$, t, ^1J(^{31}P–^{13}C) 114 Hz], 4.40 and 2.14 {C[Si(CH$_3$)$_3$]$_2$, br}. ^{29}Si-{^{1}H} NMR (C$_4$D$_8$O, 245 K): δ −1.6 and −1.9. ^{31}P-{^{1}H} NMR (C$_4$D$_8$O, 245 K): δ −0.6 (s, 1 P) and −9.5 [s, 1 P, ^2J($^{119(117)}$Sn–^{31}P) 200 Hz]. ^{31}P-{^{1}H} NMR (C$_4$D$_8$O, 298 K): δ 0.9 (s, 1 P) and −8.5 [s, 1 P, ^2J($^{119(117)}$Sn–^{31}P) 212 Hz]. ^{31}P-{^{1}H} NMR (C$_4$D$_8$O, 330 K): δ 1.3 (s, 1 P) and −8.2 (s, 1 P). ^{119}Sn-{^{1}H} NMR (C$_4$D$_8$O, 245 K): δ 390.3. ^{119}Sn-{^{1}H} NMR (C$_4$D$_8$O, 265 K): δ 391.7 (d, 209 Hz). ^{119}Sn-{^{1}H} NMR (C$_6$D$_6$, 300 K): δ 397.4 [2 d, ^2J(^{31}P-$^{119(117)}$Sn) 173, 252 Hz]. Mass spectrum (CI, NH$_3$): m/z = 740 ($M^{\cdot +}$, 503 {$M^{\cdot +}$ − 2-[(Me$_3$Si)$_2$C]C$_5$H$_4$N}, 385 [CH$_2$(PPh$_2$)$_2$], 356 [$M^{\cdot +}$ − CH(PPh$_2$)$_2$] and 238 {2-[(Me$_3$Si)$_2$CH]C$_5$H$_4$N} [Found (Calc. for C$_{37}$H$_{43}$NP$_2$Si$_2$Sn): C, 60.05 (60.17); H, 5.87 (5.87); N, 2.15 (1.90)%].‡

[{Sn(C$_6$H$_2$Pr$^i_3$-2,4,6)$_2$}$_3$] 3. This compound was prepared according to our previously reported method.[28]

Results and Discussion

The precursor [Sn{2-[(Me$_3$Si)$_2$C]C$_5$H$_4$N}Cl] was prepared in high yield (*ca.* 70%) *via* the reaction of [Li(tmen){2-[(Me$_3$Si)$_2$C]C$_5$H$_4$N}][32] with a one molar excess of SnCl$_2$ in Et$_2$O at ambient temperature (Scheme 1, route A); an alternative route B which was not employed in this work is by the ligand redistribution between [Sn{2-[(Me$_3$Si)$_2$C]C$_5$H$_4$N}$_2$] and SnCl$_2$,[12] analogous to that employed in the preparation of heteroleptic tin(II) cyclopentadienyl derivatives.[34,35]

Synthesis of [Sn{2-[(Me$_3$Si)$_2$C]C$_5$H$_4$N}R]

[Sn{2-[(Me$_3$Si)$_2$C]C$_5$H$_4$N}(C$_6$H$_2$Pr$^i_3$-2,4,6)] 1. Compound **1** was prepared by the treatment of a stirred solution of a slight excess of [Sn{2-[(Me$_3$Si)$_2$C]C$_5$H$_4$N}Cl] in Et$_2$O at −78 °C with a solution of 1 equivalent of Li(Et$_2$O)(C$_6$H$_2$Pr$^i_3$-2,4,6) also in Et$_2$O (Scheme 1) and was obtained as oxygen- and moisture-sensitive orange cubes in 25% yield, recrystallised from concentrated hexane solution.

[Sn{2-[(Me$_3$Si)$_2$C]C$_5$H$_4$N}{CH(PPh$_2$)$_2$}] 2. Compound **2** was prepared by the treatment of a stirred solution of [Sn{2-[(Me$_3$Si)$_2$C]C$_5$H$_4$N}Cl] in Et$_2$O at ambient temperature with a stirred slurry of Li(Et$_2$O)[CH(PPh$_2$)$_2$] also in Et$_2$O (Scheme 1) and was obtained as an intensely yellow powder in 62% yield. Redissolution of this solid in hot toluene afforded, upon cooling, **2** as intensely yellow needles which did not show any visible signs of decomposition upon exposure to air for a period of minutes.

Multinuclear NMR spectroscopic data for [Sn{2-[(Me$_3$Si)$_2$C]-C$_5$H$_4$N}R]

[Sn{2-[(Me$_3$Si)$_2$C]C$_5$H$_4$N}(C$_6$H$_2$Pr$^i_3$-2,4,6)] 1. The assignments of the resonances in the ^{1}H and ^{13}C-{^{1}H} NMR spectra of compound **1** were made on the basis of their integral values (^{1}H spectrum), chemical shifts and by an analysis of the ^{1}H–^{13}C COSY NMR spectrum. The ^{1}H NMR spectrum of **1** in C$_6$D$_6$ at ambient temperature exhibits resonances with characteristic chemical shifts and integral values for both ligands. The resonances corresponding to the aromatic ^{1}H environments of 2-[(Me$_3$Si)$_2$C]C$_5$H$_4$N are observed at δ 7.85, 6.98, 6.68 and 6.36, whilst the observation of two chemically distinct SiMe$_3$ ^{1}H environments, at δ 0.33 and 0.04, indicates the persistence of the formally co-ordinate N–Sn bond in solution (at ambient temperature) thereby preventing rotation of the bidentate ligand about the C–Sn bond and equivalencing of the two SiMe$_3$ groups. This result is interesting since in [Sn{2-[(Me$_3$Si)$_2$C]C$_5$H$_4$N}R] [R = Cl or N(SiMe$_3$)$_2$] the SiMe$_3$ ^{1}H environments of the 2-[(Me$_3$Si)$_2$C]C$_5$H$_4$N ligand are found to be equivalent at ambient temperature: for R = Cl it was reported that the formally co-ordinate N–Sn bond dissociated at 220 ± 2 K and for R = N(SiMe$_3$)$_2$, 214 ± 2 K.[12] Furthermore, in the latter compound, the N(SiMe$_3$)$_2$ ^{1}H environments were found to be inequivalent at ambient temperature, with their coalescence at 368 ± 2 K corresponding to unrestricted rotation of the N(SiMe$_3$)$_2$ group about the (Me$_3$Si)$_2$N–Sn bond. The aromatic ^{1}H environments of the C$_6$H$_2$Pr$^i_3$-2,4,6 ligand are observed as a sharp singlet at δ 7.15, the two (CH$_3$)$_2$CH ^{1}H environments as a broad multiplet and well resolved septet at δ 3.01 and 2.86 respectively and the (CH_3)$_2$CH ^{1}H environments at δ 1.46–1.28 as one resolved doublet and a doublet overlapping a broad peak. In the ^{13}C-{^{1}H} NMR spectrum resonances for the aromatic ^{13}C environments of the 2-[(Me$_3$Si)$_2$C]C$_5$H$_4$N ligand are observed at δ 171.53, 146.74, 137.30 and 118.58 (one resonance is obscured by C$_6$D$_6$ solvent, but is apparent on the basis of a correlation peak in the ^{1}H-^{13}C COSY spectrum). The resonance for the quaternary ^{13}C environment of the 2-[(Me$_3$Si)$_2$C] moiety is observed at δ 42.63 and is very similar to that for [Sn{2-[(Me$_3$Si)$_2$C]C$_5$H$_4$N}Cl] (δ 43.34). As can be seen from Table 1, the chemical shift of this resonance is quite sensitive to the nature of the second R group at the tin centre and is thus generally a good ‘label’ for compound identification.

In agreement with the ^{1}H NMR spectrum, two distinct ^{13}C resonances are observed for the SiMe$_3$ groups, at δ 2.49 and 2.30. For the C$_6$H$_2$Pr$^i_3$-2,4,6 ligand four resonances in the aromatic region are observed, corresponding to four chemically distinct aromatic ^{13}C environments, at δ 168.12, 154.37, 148.38 and 121.26. The two chemically distinct (CH$_3$)$_2$CH ^{13}C environments are observed at δ 35.69 and 34.82, whilst resonances corresponding to the (CH_3)$_2$CH ^{13}C environments are

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‡ Similarly poor elemental analysis values for N were found for [Sn{2-[(Me$_3$Si)$_2$C]C$_5$H$_4$N}R] {R = 2-[(Me$_3$Si)$_2$C]C$_5$H$_4$N or Cl}: 5.2 (4.7) or 4.1 (4.7) and 3.4 (3.6) or 4.0 (3.6)% respectively.[12]

Table 1 Comparison of solution (δ) $^{13}C\text{-}\{^1H\}$ NMR chemical shift data for tin(II) compounds containing the $2\text{-}[(Me_3Si)_2C]C_5H_4N$ ligand

Compound	δ							Ref.
$[Sn\{2\text{-}[(Me_3Si)_2C]C_5H_4N\}_2]$	3.88	40.60	—	—	—	—	—	12
$[Sn\{2\text{-}[(Me_3Si)_2C]C_5H_4N\}\{N(SiMe_3)_2\}]$	5.88	46.60	—	—	—	—	—	12
$[Sn\{2\text{-}[(Me_3Si)_2C]C_5H_4N\}\{Sn(SiMe_3)_3\}]$	1.23, 3.26	35.60	118.70	127.10	136.81	148.23	173.30	20
$[Sn\{2\text{-}[(Me_3Si)_2C]C_5H_4N\}Cl]$	1.98	43.34	119.29	129.20	138.46	144.23	175.36	12
2 $[Sn\{2\text{-}[(Me_3Si)_2C]C_5H_4N\}\{CH(PPh_2)_2\}]$	2.14, 4.40	38.70	118.54	obsc.	137.71	146.50	173.93	This work
1 $[Sn\{2\text{-}[(Me_3Si)_2C]C_5H_4N\}(C_6H_2Pr^i_3\text{-}2,4,6)]$	2.30, 2.49	42.63	118.58	obsc.	137.30	146.74	171.53	This work

Table 2 Comparison of solution (δ) $^{119}Sn\text{-}\{^1H\}$ NMR chemical shifts for selected tin(II) compounds $\{2\text{-}[(Me_3Si)_2C]C_5H_4N$-containing derivatives italicised}

Compound	δ	Ref.
$[Sn\{C_7H_5(NPr^i)_2\text{-}1,2\}Cl]$	−68, $CDCl_3$	19
$[Sn\{2\text{-}[(Me_3Si)_2C]C_5H_4N\}_2]$	*140, C_6D_6*	*12*
$[Sn\{CH(PPh_2)_2\}_2]$	176	9
$[Sn\{2\text{-}[(Me_3Si)_2C]C_5H_4N\}\{N(SiMe_3)_2\}]$	*326, C_6D_6*	*12*
$[Sn\{2\text{-}[(Me_3Si)_2C]C_5H_4N\}Cl]$	*351, C_6D_6*	*12*
2 *$[Sn\{2\text{-}[(Me_3Si)_2C]C_5H_4N\}\{CH(PPh_2)_2\}]$*	*397, C_6D_6*	*This work*
$[Sn\{C_6H_3(NMe_2)_2\text{-}2,6\}\{Si[C_6H_4(NCH_2Bu^t)\text{-}1,2][C_6H_3(NMe_2)_2\text{-}2,6]\}]$	412, $C_6H_5CH_3$–C_6D_6	21
$[Sn\{C_6H_3(NMe_2)_2\text{-}2,6\}\{N(SiMe_3)_2\}]$	422	36
$[Sn\{C_6H_3(NMe_2)_2\text{-}2,6\}_2]$	442	36
1 *$[Sn\{2\text{-}[(Me_3Si)_2C]C_5H_4N\}(C_6H_2Pr^i_3\text{-}2,4,6)]$*	*474, C_6D_6*	*This work*
$[Sn\{C_6H_3(C_6H_2Me_3\text{-}2,4,6)_2\}Cl]$	562, C_6D_6	6
$[C_6H_4(N(SiMe_3)\{Sn[N(SiMe_3)_2]\})_2\text{-}1,4]$	606, C_6D_6	22
$[Sn\{C_6H_3(NMe_2)_2\text{-}2,6\}\{Si[C_5H_4(NCH_2Bu^t)\text{-}1,2][N(SiMe_3)_2]\}]$	621, $C_6H_5CH_3$–C_6D_6	21
$[Sn\{C_6H_3(C_6H_2Me_3\text{-}2,4,6)_2\text{-}2,6\}_2]$	635, C_6D_6	6
$[C_6H_8(N(SiMe_3)\{Sn[N(SiMe_3)_2]\})_2\text{-}1,4]$	694, C_6D_6	22
$[Sn\{C_6H_2(CF_3)_3\text{-}2,4,6\}_2]$	723, C_6D_{12}	7
$[Sn\{N(SiMe_3)_2\}_2]$	776	37
$[Sn\{2\text{-}[(Me_3Si)_2C]C_5H_4N\}\{Sn(SiMe_3)_3\}]$	*897, C_6D_6*	*20*
$[Sn(C_6H_2Bu^t_3\text{-}2,4,6)_2]$	980	8
$[Sn\{CH(SiMe_3)_2\}_2]$	2272	38

observed at δ 25.88 and 24.55 as a barely resolvable broad peak and a sharp peak respectively. The $^{29}Si\text{-}\{^1H\}$ NMR spectrum exhibits two sharp resonances, at δ 0 and −3, the $^{119}Sn\text{-}\{^1H\}$ NMR spectrum a single resonance at δ 474 (Table 2).

$[Sn\{2\text{-}[(Me_3Si)_2C]C_5H_4N\}\{CH(PPh_2)_2\}]$ 2. The $^{13}C\text{-}\{^1H\}$ NMR spectrum of compound **2** in C_6D_6 at 298 K exhibits *inter alia* six sharp resonances and two broad resonances, at δ 173.93, 146.50, 137.71, 118.54, 38.70, 4.40, 2.14 and 26.79. These correspond, respectively, to seven of the eight ^{13}C environments of the $2\text{-}[(Me_3Si)_2C]C_5H_4N$ ligand and the ^{13}C environment of the central C atom of the $CH(PPh_2)_2$ ligand [a triplet with $^1J(^{31}P\text{–}^{13}C)$ 114 Hz]. The two very broad resonances at δ 4.40 and 2.14 (which sharpen at low temperature, see below) are assigned on the basis of their chemical shifts to the $SiMe_3$ ^{13}C atom environments. The broadness of nearly all of the resonances in the spectrum suggests that, at ambient temperature, a coalescence point corresponding to unrestricted rotation about the $Sn\text{–}CH(PPh_2)_2$ bond is being closely approached. This is in agreement with the observation of *sharp* peaks for all of the resonances at *ambient temperature* in the $^{13}C\text{-}\{^1H\}$ NMR spectrum (C_4D_8O) of the germanium analogue, $[Ge\{2\text{-}[(Me_3Si)_2C]C_5H_4N\}\{CH(PPh_2)_2\}]$;[39] rotation about the shorter $Ge\text{–}CH(PPh_2)_2$ bond is very much more restricted. The resonance at δ 173.93 is assigned to the ^{13}C environment in the 2 position of the C_5H_4N ring on the basis of its intensity with respect to the intensities of the other C_5H_4N resonances. The resonances corresponding to the remaining ^{13}C environments of the $2\text{-}[(Me_3Si)_2C]C_5H_4N$ and $CH(PPh_2)_2$ ligands were not resolvable and as previously mentioned, for the most part, extremely broad. However, that the two resonances to lowest frequency (δ 4.40 and 2.14) correspond to chemically distinct ^{13}C environments is evidence that the formally co-ordinate N–Sn bond of **2** persists in solution at ambient temperature. The resonance corresponding to the C atom of the $2\text{-}[(Me_3Si)_2C]$ substituent appears at δ 38.70. The resonance corresponding to the central C atom of the $CH(PPh_2)_2$ ligand appears at δ 26.79 as an apparent triplet (see below) with $^1J(^{31}P\text{–}^{13}C)$ 114 Hz. This chemical shift is to slightly lower frequency with respect to that for 'free' bis(diphenylphosphino)-methane [C_6D_6, δ 28.86, t, $^1J(^{31}P\text{–}^{13}C)$ 48 Hz], but to significantly higher frequency than the corresponding resonances for $Li(Et_2O)[CH(PPh_2)_2]$ (C_6D_6, br, δ 17.71) and $[Sn\{CH(PPh_2)_2\}_2]$ [C-bound ligand, δ 17.87, t, $^1J(^{31}P\text{–}^{13}C)$ 62 Hz; P-bound ligand, δ 24.15, t, $^1J(^{31}P\text{–}^{13}C)$ 57 Hz].[9] This would suggest therefore that in solution the $CH(PPh_2)_2$ ligand of **2** is η^2 bound to the central Sn atom *via* the two P atoms. The $^{13}C\text{-}\{^1H\}$ NMR spectrum of **2** was also recorded in C_4D_8O at 245 K and exhibits a much greater number of resolved resonances in comparison to the spectrum in C_6D_6 at ambient temperature. The resonances in the region δ 141.80–127.40 (singlets and multiplets) correspond to the large number of chemically distinct Ph ^{13}C environments of the $CH(PPh_2)_2$ ligand at very low temperature. Additionally, the two resonances corresponding to the two $SiMe_3$ ^{13}C environments are considerably sharper than in the spectrum recorded at ambient temperature. A similar observation was made in the $^{31}P\text{-}\{^1H\}$ NMR spectra recorded in C_4D_8O at 245, 298 and 330 K (Fig. 1), each of which exhibited two resonances with equal integral values and similar intensities {δ −0.6 and −9.5 [$^2J(^{119(117)}Sn\text{–}^{31}P)$ 200 Hz], δ 0.9 and −8.5 [$^2J(^{119(117)}Sn\text{–}^{31}P)$ 212 Hz], δ 1.3 and −8.2 [$^2J(^{119(117)}Sn\text{–}^{31}P)$ not observed]}, with increasing peak widths ($\omega_{\frac{1}{2}}$ = 16 and 14, 50 and 46, 140 and 168 Hz).

The chemical shift and $^2J(^{119(117)}Sn\text{–}^{31}P)$ coupling constant values of *ca.* δ −9 and 200 Hz respectively are similar to the corresponding values of the C-bound ligand of $[Sn\{CH(PPh_2)_2\}_2]$ (273 K, δ −10.3 and *ca.* 300 Hz; P-bound ligand, δ −15.9 and *ca.* 1100 Hz).[10] Furthermore, the $^{31}P\text{-}\{^1H\}$ NMR spectrum of $[Sn\{CH(PPh_2)_2\}_2]$ recorded at 183 K exhibits *inter alia* resonances for two chemically distinct ^{31}P environments for the C-bound ligand (δ −9.5 and −16.1).[9] This suggests that the $CH(PPh_2)_2$ ligand in compound **2** is C-bound, at odds with the

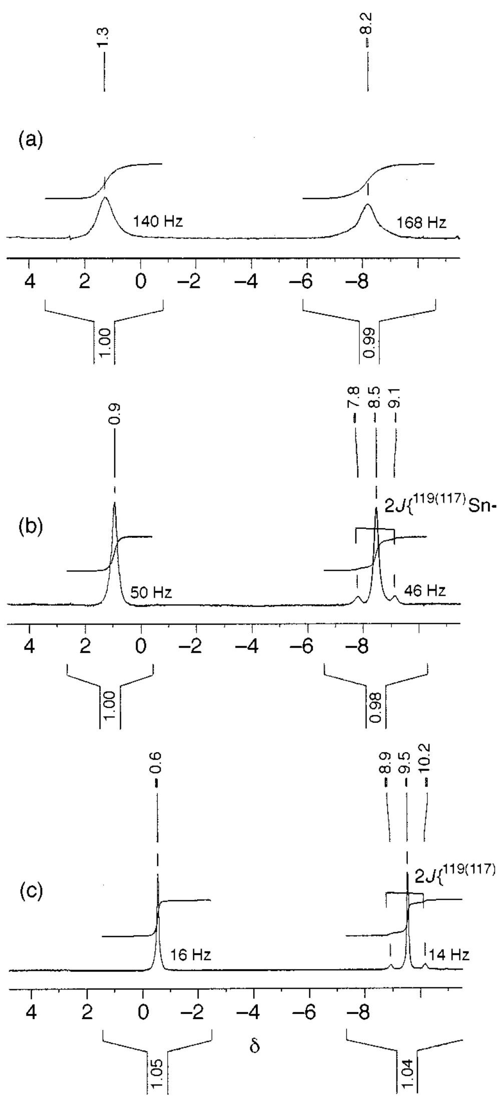

Fig. 1 Variable temperature ^{31}P-{^1H} NMR spectra of compound **2** [(a) 330, (b) 298 and (c) 245 K; C_4D_8O, 9.395 T]

conclusion drawn from the ^{31}C-{^1H} NMR spectrum and that the two P atoms are chemically inequivalent. This notion is supported, however, by the ^{119}Sn-{^1H} NMR spectrum in C_6D_6 at ambient temperature, which exhibits two doublets [$^2J(^{31}P{-}^{119(117)}Sn)$ 173 and 252 Hz] with partial superposition, centred at δ 397 (Table 2): the ^{119}Sn-{^1H} spectrum of [Sn{CH(PPh_2)$_2$}$_2$] at ambient temperature exhibits a triplet of triplets, centred at δ 176, with $^1J(^{31}P{-}^{119(117)}Sn)$ 1172 and $^2J(^{31}P{-}^{119(117)}Sn)$ 163 Hz.[9] Furthermore, the corresponding spectrum recorded at 183 K exhibits a triplet of doublet of doublets, with $^1J(^{31}P{-}^{119(117)}Sn)$ 1136 and $^2J(^{31}P{-}^{119(117)}Sn)$ 193 and 122 Hz [P-bound ligand and (inequivalent) C-bound ligand P atoms respectively]. Interestingly, the ^{119}Sn-{^1H} NMR spectrum of **2** recorded in C_4D_8O at 265 K exhibits a doublet centred at δ 392 with $^2J(^{31}P{-}^{119(117)}Sn)$ 209 Hz, whilst at 245 K this resonance is shifted to δ 390 and significantly broadened [$^2J(^{31}P{-}^{119(117)}Sn)$ no longer resolvable]. This broadening is attributed to an increased (quadrupolar) coupling of the ^{119}Sn to the ^{14}N nucleus. There is one feature of the multinuclear NMR spectroscopic data for compound **2** that is surprising. The ^{31}P-{^1H} NMR spectra exhibit two distinct resonances, at *ca.* δ 0 and −9. A similar observation is made in the corresponding spectra of the germanium analogue (298 K, C_6D_6, δ −0.1 and −11.1)[39] and [E{CH(PPh_2)$_2$}$_2$] (E = Sn, 273 K, δ −10.3 and −15.9; E = Pb, 253 K, δ −4.7 and −11.6).[10] On the basis of the relative magnitudes of the $^{119(117)}Sn{-}^{31}P$ coupling constant values the higher frequency resonance of the homoleptic tin compound was assigned to the P atoms of the C-bound ligand; for the lead analogue the opposite was the case. (In both cases, the ^{31}P chemical shift for the C-bound ligand is *ca.* δ −10.) However, the higher frequency resonance of **2** *does not* exhibit any (resolvable) $^{119(117)}Sn{-}^{31}P$ coupling. The ^{31}P-{^1H} NMR chemical shifts of $CH_2(PPh_2)_2$ and Li(Et_2O)[CH(PPh_2)$_2$] are δ −21.0 and −2.9 respectively (298 K, C_6D_6). However, we propose that the CH(PPh_2)$_2$ ligand of **2** is η^1 bound, through the central C atom, and that the two P atoms are chemically inequivalent (in the temperature range 245–330 K). This postulation is made on the basis of: (*i*) the 1 : 1 ratio of the two resonances in the ^{31}P-{^1H} spectra, (*ii*) the absence of a resonance to lower frequency than *ca.* δ − 9 in the ^{31}P-{^1H} spectra, (*iii*) the coupling constant values in the ^{31}P-{^1H} and ^{119}Sn-{^1H} spectra. Furthermore, this requires that the resonance in the ^{13}C-{^1H} NMR spectrum (C_6D_6, 298 K) corresponding to the central C atom of the CH(PPh_2)$_2$ ligand be an overlapping pair of doublets rather than a triplet (*i.e.* the C atom couples to two P atoms, each in a slightly different environment with respect to each other); this is in agreement with the relatively large $^1J(^{31}P{-}^{31}C)$ value observed (114 *vs.* 62 Hz for the C-bound ligand in [Sn{CH(PPh_2)$_2$}$_2$][9]).

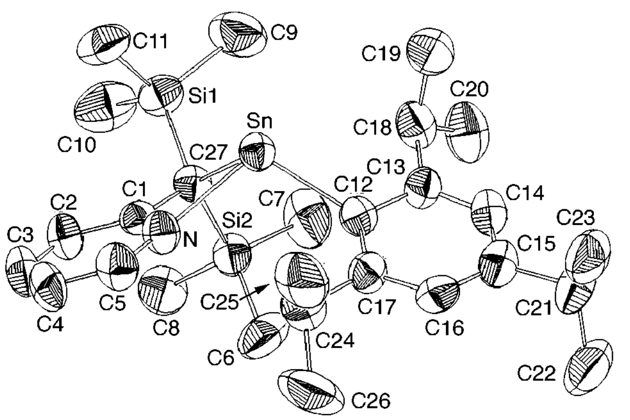

Fig. 2 Molecular structure of [Sn{2-[(Me_3Si)$_2$C]C_5H_4N}($C_6H_2Pr^i_3$-2,4,6)] **1** (thermal ellipsoids drawn at the 50% probability level)

The ^{29}Si-{^1H} NMR spectrum of compound **2** was also recorded in C_4D_8O at 245 K and exhibits two sharp and barely resolvable resonances, centred at δ −2.

Crystal structures of [Sn{2-[(Me_3Si)$_2$C]C_5H_4N}R] 1 and 2 and [{Sn($C_6H_2Pr^i_3$-2,4,6)$_2$}$_3$] 3

The molecular structures of compounds **1–3** are presented in Figs. 2, 3 and 4 respectively. Table 3 contains a summary of cell constants and data collection; important intramolecular distances and angles are listed in Tables 4, 5 and 6 respectively.

[Sn{2-[(Me_3Si)$_2$C]C_5H_4N}($C_6H_2Pr^i_3$-2,4,6)] 1. An examination of the molecular structure presented in Fig. 2 reveals **1** to be monomeric in the solid state. The central Sn^{II} is η^1 co-ordinated by the $C_6H_2Pr^i_3$-2,4,6 ligand and η^2 by the 2-[(Me_3Si)$_2$C]C_5H_4N ligand. The Sn atom is therefore formally three-co-ordinate, with a geometry similar to both that of the precursor [Sn{2-[(Me_3Si)$_2$C]C_5H_4N}Cl] and of the amide derivative [Sn{2-[(Me_3Si)$_2$C]C_5H_4N}{N($SiMe_3$)$_2$}],[12] *i.e.* a trigonal pyramid. The Sn atom is bound to the 2-[(Me_3Si)$_2$C]C_5H_4N ligand *via* the central C atom [C(27)] of the 2-[(Me_3Si)$_2$C] substituent and by a formally co-ordinate bond with the N atom of the C_5H_4N ring. The Sn–C(27) bond length of 2.372(7) Å (Table 4) is longer than the corresponding value in the precursor [2.32(2) (both molecules) Å] and the related [Sn{2-[(Me_3Si)$_2$C]C_5H_4N}$_2$] and [Sn{2-[(Me_3Si)$_2$C]C_5H_4N}-{N($SiMe_3$)$_2$}] [2.334(6)–2.377(7) and 2.356(8) Å respectively]. The Sn atom is bound to the C atom of the phenyl ring of the $C_6H_2Pr^i_3$-2,4,6 ligand [C(12), 2.254(7) Å]. This Sn–C distance is longer than that in *four-co-ordinate* [Sn{C_6H_3(NMe_2)$_2$-2,6}{Si[C_6H_3(NCH_2Bu^t)-1,2][C_6H_3(NMe_2)$_2$-2,6]}] [2.210(8) Å][21]

Table 3 Summary of crystal data and intensity collection parameters for compounds **1–3**

	1	**2**	**3**
Empirical formula	$C_{27}H_{42}NSi_2Sn$	$C_{37}H_{43}NP_2Si_2Sn$	$C_{90}H_{120}Sn_3$
M	703.21	738.54	1557.93
T/K	293(2)	293(2)	220
Habit	Orange cubes	Yellow cubes	Orange rhombs
Crystal system	Orthorhombic	Triclinic	Orthorhombic
Space group	*Pbca* (no. 61)	$P\bar{1}$	$Pna2_1$
a/Å	16.103(9)	11.035(11)	23.859(9)
b/Å	19.362(10)	13.114(13)	14.687(7)
c/Å	20.018(12)	13.564(14)	24.084(10)
α/°		95.958(10)	
β/°		108.110(10)	
γ/°		91.217(10)	
U/Å^3	6241.3(50)	1853(3)	8439.4(27)
Z	8	4	4
D_c/Mg m^{-3}	1.182	1.324	1.24
μ/mm^{-1}	0.885	0.866	0.92
F(000)	1380	760	3240
θ range/°	2.74 to 25.00	2.56 to 25.92	3.5 to 24.1
Index ranges, *hkl*	0 to 18, 0 to 22, 0 to 23	0 to 12, −14 to 14, −15 to 14	−26 to 23, −16 to 14, −27 to 27
Reflections collected	28 740	5612	27 148
Independent reflections	5154 (R_{int} = 0.0776)	5612	11 190 (R_{int} = 0.0733)
Structure refinement	Full matrix least squares on all F^2	Full matrix least squares on all F^2	Full matrix least squares on all F^2
Number of parameters refined	278	395	841
Final *R*, *R′* indices (observed data)	0.078, 0.245	0.0743, 0.2223	0.0796, 0.2150
Goodness of fit on F^2	1.774	0.969	1.314

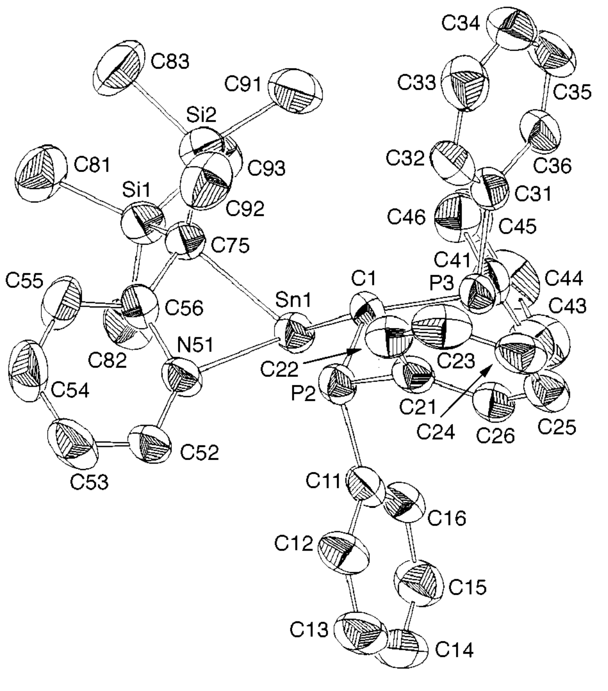

Fig. 3 Molecular structure of [Sn{2-[(Me$_3$Si)$_2$C]C$_5$H$_4$N}{CH(PPh$_2$)$_2$}] **2**: details as in Fig. 2

Table 4 Selected distances (Å) and angles (°) for compound **1** [estimated standard deviations (e.s.d.s) in parentheses]

Sn–C(12)	2.254(7)	N–C(5)	1.375(10)
Sn–N	2.345(6)	C(12)–C(17)	1.445(11)
Sn–C(27)	2.372(7)	C(12)–C(13)	1.447(10)
Si(1)–C(27)	1.890(7)	C(17)–C(24)	1.525(12)
Si(2)–C(27)	1.899(7)	C(13)–C(18)	1.526(11)
C(27)–C(1)	1.488(10)	C(15)–C(21)	1.575(11)
N–C(1)	1.354(9)		
C(12)–Sn–N	107.6(3)	C(17)–C(12)–Sn	123.2(5)
C(12)–Sn–C(27)	111.8(2)	Si(1)–C(27)–Sn	118.0(3)
N–Sn–C(27)	60.5(2)	Si(2)–C(27)–Sn	106.3(4)
Sn–N–C(1)	93.3(4)	Si(1)–C(27)–C(1)	109.0(5)
C(1)–C(27)–Sn	88.9(4)	Si(2)–C(27)–C(1)	112.9(5)
N–C(1)–C(27)	113.4(6)	Si(1)–C(27)–Si(2)	118.2(4)
C(13)–C(12)–Sn	118.2(5)		

Table 5 Selected distances (Å) and angles (°) for compound **2** (e.s.d.s in parentheses)

Sn(1)–C(1)	2.306(6)	Sn(1)–N(51)	2.300(6)
Sn(1)–C(75)	2.359(7)	P(2)–C(1)	1.835(6)
P(2)–C(11)	1.845(7)	P(2)–C(21)	1.860(7)
P(3)–C(31)	1.839(7)	P(3)–C(41)	1.858(7)
P(3)–C(1)	1.861(6)	Si(1)–C(81)	1.861(9)
Si(1)–C(82)	1.871(9)	Si(1)–C(75)	1.882(6)
Si(1)–C(93)	1.891(9)	Si(2)–C(92)	1.848(10)
Si(2)–C(91)	1.866(10)	Si(2)–C(75)	1.893(7)
C(55)–C(56)	1.392(10)	C(56)–C(75)	1.493(9)
C(1)–Sn(1)–N(51)	93.0(2)	C(1)–Sn(1)–C(75)	100.8(2)
N(51)–Sn(1)–C(75)	61.1(2)	C(1)–P(2)–C(11)	105.8(3)
C(1)–P(2)–C(21)	106.4(3)	C(11)–P(2)–C(21)	99.5(3)
C(31)–P(3)–C(41)	102.4(3)	C(31)–P(3)–C(1)	101.7(3)
C(41)–P(3)–C(1)	106.5(3)	C(81)–Si(1)–C(82)	104.0(5)
P(2)–C(1)–Sn(1)	110.8(3)	P(3)–C(1)–Sn(1)	114.2(3)
N(51)–C(56)–C(75)	112.6(6)		

and two-co-ordinate [Sn{C$_6$H$_3$(C$_6$H$_2$Me$_3$-2,4,6)$_2$-2,6}$_2$] [2.225(5) Å][6] and very much longer than any of the corresponding distances in **3** [range 2.15(1) to 2.21(1), Table 6]. In the case of [Sn{C$_6$H$_3$(C$_6$H$_2$Me$_3$-2,4,6)$_2$-2,6}$_2$], despite the large steric bulk of the aryl ligand involved, the two ligands are able to achieve a conformation which minimises unfavourable steric interactions.§ The Sn–C(12) distance is significantly longer than the average corresponding distance of 2.215(5) Å in [Ru$_3$(CO)$_9${μ-Sn(C$_6$H$_2$Pr$^i_3$-2,4,6)$_2$}$_3$] [2.18(2) and 2.25(2), 2.23(2) and 2.22(2), 2.21(2) and 2.20(2) Å].[27] It is significantly shorter than the Sn–C(27) distance (a consequence of the formally co-ordinate Sn–N bond) and the corresponding distances in monomeric [Sn{C$_6$H$_2$(CF$_3$)$_3$-2,4,6}$_2$][7] (2.28 Å): for this compound, the authors state 'Despite the *electron-withdrawing* character of the trifluoromethyl group . . . . the *electron-donating* ability *via* the lone pairs at the fluorine atoms is clearly established.' Thus, lengthening of the Sn–C bond in this compound may also be due to additional tin–ligand interaction(s). In the second crystalline form of this fluoro-containing tin(II)

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§ The concept of *steric demand vs. steric bulk* has recently been discussed in the context of highly substituted η-bound cyclopentadienyl ligands.[40]

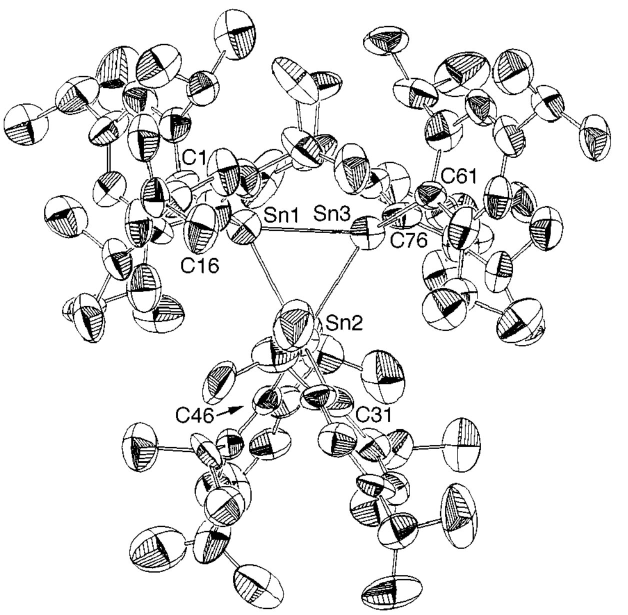

Fig. 4 Molecular structure of [{Sn($C_6H_2Pr^i_3$-2,4,6)$_2$}$_3$] **3**: details as in Fig. 1

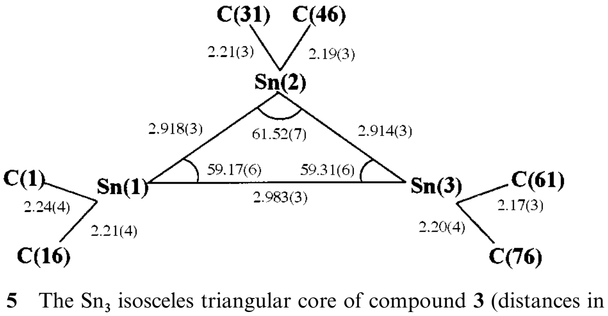

Fig. 5 The Sn_3 isosceles triangular core of compound **3** (distances in Å, angles in °)

derivative a dimer is found [Sn ··· Sn distance 3.639(1) Å], but the Sn–C distance is not significantly different [2.284(3) Å].[41] Similar distances to that in **1** are found in [Sn($C_6H_2Bu^t_3$-2,4,6)$_2$] [2.255(4) and 2.267(4) Å].[8] Tables 7 and 8 contain data for a comparison of the structures of **1** and **2** with those of other tin(II) 2-[$(Me_3Si)_2C$]C_5H_4N derivatives.

[Sn{2-[$(Me_3Si)_2C$]C_5H_4N}{CH(PPh_2)$_2$}] 2. An examination of the molecular structure presented in Fig. 3 reveals compound **2** to be monomeric in the solid state also and is not surprising in view of the high steric demand of the ligands employed. The central Sn atom is η^2 bound to the 2-[$(Me_3Si)_2C$]C_5H_4N ligand through the C atom of the 2-[$(Me_3Si)_2C$] substituent and the N atom of the C_5H_4N ring [Sn(1)–C(75) 2.359(7), Sn(1)–N(51) 2.300(6) Å; Table 5] and η^1 bound to the CH(PPh_2)$_2$ ligand through its central C atom, C(1) [Sn(1)–C(1) 2.306(6) Å]. The molecular structures of [E{CH(PPh_2)$_2$}$_2$] (E = Sn or Pb) have been reported and shown to be monomeric.[10] Furthermore, these compounds demonstrate two of the different bonding modes of the CH(PPh_2)$_2$ ligand, in that one ligand is η^1 co-ordinated through the central C atom and one η^2 through the two P atoms. The Sn–CH(PPh_2)$_2$ distances for **2** and [Sn{CH(PPh_2)$_2$}$_2$] [C-bound ligand, 2.286(16) Å] are not significantly different. However, in both [Sn{C(PMe_2)$_3$}$_2$][9] [the first structurally characterised Sn^{II}–P containing compound] and [Pb{C($SiMe_3$)(PPh_2)$_2$}$_2$],[13] in which there is tris substitution (and thus steric congestion) at the ligand central C atom, both ligands are η^2 bound to the central metal atom, through the two P atoms. It is unlikely that the η^2-bonding mode of *both* C(PMe_2)$_3$ ligands in [Sn{C(PMe_2)$_3$}$_2$] is a result of the less sterically demanding nature of the ligand with respect to CH(PPh_2)$_2$, since it would therefore be likely that *both* CH(PPh_2)$_2$ ligands in [Pb{CH(PPh_2)$_2$}$_2$] would also be η^2 bound. This implies therefore that: (*i*) in E^{II} chemistry the CH(PPh_2)$_2$ ligand is *preferably* alkyl type, bonding through the central C atom, (*ii*) the Sn{2-[$(Me_3Si)_2C$]C_5H_4N} fragment of **2** is less sterically demanding than the Sn[η^1-CH(PPh_2)$_2$] fragment of [Sn{CH(PPh_2)$_2$}$_2$] [since the second CH(PPh_2)$_2$ ligand in the latter is forced to bond η^2]. In **2** it was envisaged that there might be some competition between the electron-pair donor P atoms of the CH(PPh_2)$_2$ ligand and the N atom of the 2-[$(Me_3Si)_2C$]C_5H_4N ligand that would result in the latter being co-ordinated solely through the methyl C atom since P is a softer donor than N.

Table 6 Selected distances (Å) and angles (°) for compound **3** (e.s.d.s in parentheses)

Sn(1)–Sn(2)	2.918(3)	Sn(2)–Sn(3)	2.914(3)
Sn(3)–Sn(1)	2.983(3)	Sn(1)–C(1)	2.24(4)
Sn(1)–C(16)	2.21(4)	Sn(2)–C(31)	2.21(3)
Sn(2)–C(46)	2.19(3)	Sn(3)–C(61)	2.17(3)
Sn(3)–C(76)	2.20(4)		
Sn(1)–Sn(2)–Sn(3)	61.52(7)	Sn(2)–Sn(3)–Sn(1)	59.31(6)
Sn(3)–Sn(1)–Sn(2)	59.17(6)	C(1)–Sn(1)–C(16)	107.5(13)
C(31)–Sn(2)–C(46)	101.3(10)	C(61)–Sn(3)–C(76)	105.1(11)

The Sn(1)–C(1) distance of 2.306(6) Å is longer than that in the bis{CH(PPh_2)$_2$} analogue [2.286(16) Å],[10] though not significantly so, whilst the two Sn ··· P distances [Sn–P(3) 3.507 and Sn–P(2) 3.420 respectively] are longer than those in [Sn{CH(PPh_2)$_2$}$_2$] [3.403 and 3.353 Å (C-bound ligand), 2.676(5) and 2.659(5) Å (P-bound ligand)] and [Sn{C(PMe_2)$_3$}$_2$] [2.790(2) and 2.602(2), 2.839(2) and 2.598(2) Å].[9]

[{Sn($C_6H_2Pr^i_3$-2,4,6)$_2$}$_3$] 3. An examination of the molecular structure at 220 K presented in Fig. 4 reveals **3** to be a cyclic trimer of Sn($C_6H_2Pr^i_3$-2,4,6)$_2$ units, with one trimer molecule in the asymmetric unit, orthorhombic space group *Pna*2_1. This contrasts with our previously reported crystal data at 298 K in which the compound crystallised in the monoclinic space group, *P*2_1/*c*, with three trimer molecules present in the asymmetric unit and where it was stated that they were '. . . . differentiated from each other principally by the arrangement of the peripheral isopropyl ligands . . . .'. Also, there was an effective tripling of the now *b* (originally *c*) axis [14.687(7) *vs.* 43.357(7) Å respectively]. The three Sn atoms form an isosceles triangle [Fig. 5; Sn–Sn bond lengths of 2.918(3), 2.914(3) and 2.983(3) Å, average 2.938(5) Å] where before the molecular unit was a scalene triangular arrangement of Sn atoms.

Conclusion

We have prepared and structurally characterised two novel, monomeric heteroleptic tin(II) derivatives. Both were obtained from the corresponding heteroleptic tin(II) chloro-analogue, [Sn{2-[$(Me_3Si)_2C$]C_5H_4N}Cl], and thus the utility of this compound as a precursor to further tin(II) derivatives is demonstrated. The stabilising effect of the 2-[$(Me_3Si)_2C$]C_5H_4N ligand is demonstrated by a comparison of the molecular structures of **1** and **3**, monomeric and trimeric respectively. The greater steric demand of the (η^1-bound) CH(PPh_2)$_2$ ligand with respect to that of $C_6H_2Pr^i_3$-2,4,6 is illustrated by the comparative stability of **2** toward air and by the broad resonances in its ^{13}C-{^1H} NMR spectrum at ambient temperature. For both [Sn{2-[$(Me_3Si)_2C$]-C_5H_4N}Cl] and [Sn{2-[$(Me_3Si)_2C$]C_5H_4N}{N($SiMe_3$)$_2$}], in which the central Sn atoms are bound to electronegative ligands, Cl and N($SiMe_3$)$_2$ respectively, the ^1H NMR spectra at ambient temperature suggest a fluctional process involving the breaking and reforming of the formally co-ordinate N–Sn bond. Contrasting this, the ambient temperature ^1H NMR spectra of **1** and **2**, compounds in which the central Sn atom

Table 7 Comparison of bond angles (°) about the Sn^{II} of $[Sn\{2\text{-}[(Me_3Si)_2C]C_5H_4N\}R]$

R	Compound/Angle					
	R = $2\text{-}[(Me_3Si)_2Cl]C_5H_4N$	Cl	$N(SiMe_3)_3$	$Sn(SiMe_3)_3$	**1**	**2**
N–Sn–C_n	59.0(2), 60.7(2), 60.0(2)	61.4(6), 61.7(6)	61.1(2)	61.36(9)	60.5(2)	61.1(2)
N–Sn–R	102.1(2), 93.0(2), 94.2(2)	91.8(4), 89.1(4)	97.2(2)	89.68(6)	107.6(3)	93.0(2)
R–Sn–C_n	141.3(2), 134.6(2), 133.7(2)	101.6(4), 101.1(4)	105.4(2)	108.29(6)	111.8(2)	100.8(2)
Ref.	12	12	12	20	This work	This work

Table 8 Selected structural data for $2\text{-}[(Me_3Si)_2C]C_5H_4N$ derivatives of Sn^{II}

Compound	Co-ordination number	Sn–N/Å	Sn–C/Å	Ref.
$[Sn\{2\text{-}[(Me_3Si)_2]C_5H_4N\}\{Sn(SiMe_3)_3\}]$	3	2.288(2)	2.304(2)	20
$[Sn\{2\text{-}[(Me_3Si)_2C]C_5H_4N\}Cl]$	3	2.27(2), 2.26(2)	2.32(2), 2.32(2)	12
$[Sn\{2\text{-}[(Me_3Si)_2C]C_5H_4N\}_2]$	4	2.449(7), 2.384(6), 2.420(6)	2.377(7), 2.346(6), 2.334(6)	12
$[Sn\{2\text{-}[(Me_3Si)_2C]C_5H_4N\}\{N(SiMe_3)_2\}]$	3	2.299(5)	2.356(8)	12
2 $[Sn\{2\text{-}[(Me_3Si)_2C]C_5H_4N\}\{CH(PPh_2)_2\}]$	3	2.300(6)	2.359(7)	This work
1 $[Sn\{2\text{-}[(Me_3Si)_2C]C_5H_4N\}(C_6H_2Pr^i_3\text{-}2,4,6)]$	3	2.345(6)	2.372(7)	This work

is bound to more electropositive atoms, suggest that this fluctional process is not occurring up to 298 K.

We propose that, by their reaction with transition metal carbonyl compounds, *e.g.* $[M_3(CO)_{12}]$ (M = Ru or Os), **1** and **2** will allow access to several, further examples of mixed-metal clusters.

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