The novel, chelating C, N-bidentate 2,6-bis(dimethylamino)phenyl ligand (R②), showing ambidentate N,N′-character in $M(R)_2$ (M = Ge, Sn, Pb) and Sn(R)X [X = $N(SiMe_3)_2$, $CH(SiMe_3)_2$, Cl]†

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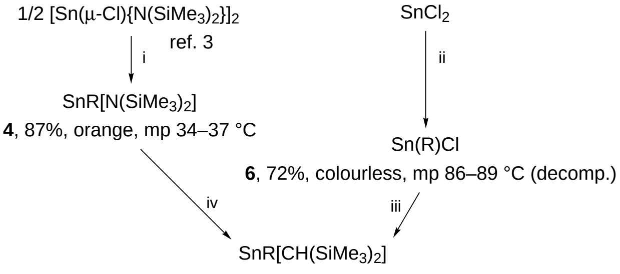
Treatment of MCl_2 or $[Sn(\mu\text{-}Cl)\{N(SiMe_3)_2\}]_2$ with $[Li(\mu\text{-}R)]_3$ [R = $C_6H_3(NMe_2)_2$-2,6] under mild conditions and in appropriate stoichiometry affords MR_2 (M = Ge 1, Sn 2, Pb 3) or Sn(R)X [X = $N(SiMe_3)_2$ 4, Cl 6], while 4 or 6 with $LiCH(SiMe_3)_2$ give $SnR[CH(SiMe_3)_2]$ 5; compounds 1–6 are characterised by their multinuclear NMR and MS spectra and 1–3 by X-ray crystal structures.

We draw attention to the chelating, C,N-bidentate, monoanionic terminal ligand ②$C_6H_3(NMe_2)_2$-2,6 (R②) having ambidentate N,N′-character which promises to find a useful role in organometallic chemistry. It was previously known only as the lithium complex $[Li(\mu\text{-}R)]_3$ in which R② was C,N-chelating and N′-bridging.[1] The ligand R② differs from the well established ②$C_6H_3(CH_2NMe_2)_2$-2,6, which is tripodal, as in $Sn[C_6H_3(CH_2NMe_2)_2\text{-}2,6]X$ (X = Cl, C_6H_4Me-4).[2]

At this time, we report the synthesis and characterisation of (*i*) the monomeric homoleptic 2,6-bis(dimethylamino)phenylmetal(II) heavy group 14 metal carbene analogues MR_2 (M = Ge **1**, Sn **2**, Pb **3**), (*ii*) the first monomeric heteroleptic aryltin(II) amide and alkyl $SnR[N(SiMe_3)_2]$ **4** and $SnR[CH(SiMe_3)_2]$ **5** and (*iii*) Sn(R)Cl **6**.

The yellow, crystalline complexes **1** (65%, mp 142–145 °C), **2** (90%, mp 85–90 °C) and **3** (70%, mp 126–130 °C [decomp.]) were prepared from $[Li(\mu\text{-}R)]_3$[1] and MCl_2 in appropriate stoichiometry at *ca.* 25 °C in diethyl ether for **2** and **3**, but preferably in tetrahydrofuran (thf) for **1**. An alternative procedure, from 2 RH + $Sn[N(SiMe_3)_2]$, proved unsuccessful; despite the fact that aromatic stannation using this tin(II) amide and $C_6H_4[N(SiMe_3)H]_2$-2,6 had readily yielded $Sn_3[\{1,3\text{-}(Me_3Si)N\}_2C_6H_3\text{-}2]_2$.[3]

The syntheses, in good yields and under mild conditions, of compounds **4**–**6** are illustrated in Scheme 1. Treatment of $1/3[Li(\mu\text{-}R)]_3$ and $1/2[Sn(\mu\text{-}Cl)\{N(SiMe_3)_2\}]_2$[4] or $SnCl_2$ afforded the colourless, crystalline **6** or the orange **4**, (Scheme 1, steps i or ii). From either **4** or **6** and 1/3 $[Li(\mu\text{-}R)]_3$, the orange–red **5** was obtained, (Scheme 1, steps iii or iv). Pure, crystalline compounds **4** and **5** were isolated after vacuum distillation.



Scheme 1 Synthesis of the heteroleptic aryltin(II) complexes **4**–**6** [R = $C_6H_3(NMe_2)_2$-2,6]. *Reagents and conditions*: i, LiR, hexane, 0 °C, 12 h; ii, LiR, Et_2O, 0 °C, crystallisation from Et_2O–hexane; iii, LiR + $SnCl_2$, Et_2O, 25 °C, 12 h, (*in situ*) $LiCH(SiMe_3)_2$, hexane; iv, $LiCH(SiMe_3)_2$, hexane, 0 °C, 12 h, Et_2O.

Each of the hydrocarbon-soluble compounds **1**–**6** gave satisfactory microanalytical, as well as ^1H, $^{13}C\{^1H\}$, $^{29}Si\{^1H\}$ (**4**, **5**), $^{119}Sn\{^1H\}$ (**2**, **4**–**6**) and $^{207}Pb\{^1H\}$ (**3**) NMR‡ and EI (70 eV) mass spectra (each giving, as the highest *m/z* peak,the parent monomeric molecular ion in significant intensity: from 8% for **4** to 35% for **2**). Additionally, single-crystal X-ray diffraction data established the molecular structures of the isomorphous, isostructural complexes **1**, **2** (Fig. 1) and **3**;§ the structures of **1** and **3** will be discussed in the full paper.

The ^1H NMR spectra of each of the homoleptic complexes MR_2 **1**–**3** in C_6D_6 (**1**, **3**) or [$^2H_8$]toluene (**2**)‡ showed singlets for both the NMe_2 and the 3,5-aromatic protons at 298 K, but for **2** each split into two separate signals at 178 K. This indicates that at the higher temperature there is a rapid exchange process involving $2\text{-}Me_2N\cdots M \rightleftharpoons 6\text{-}Me_2N\cdots M$ exchange; while at the lower temperature, the spectra are consistent with the solid-state structures,§ having each ligand R② bonded in a bidentate chelating fashion, with one of the NMe_2 groups being non-bonding. This analysis is supported by the ^{119}Sn NMR spectra for **2**.‡ Thus, the magnitude of the $^{119}Sn\{^1H\}$ chemical shift in PhMe–C_6D_6, δ 442.2 at 298 K (similarly, δ $^{207}Pb\{^1H\}$ 3919 in **3**) reflects a higher than two-coordinate metal(II) environment,[5] and moreover was similar to the CP MAS value of δ 492. The $^{119}Sn\{^1H\}$ NMR spectral chemical shifts in the heteroleptic complexes Sn(R)X **4**–**6** (δ 422 **4**, 758 **5** and 380 **6**) are consistent with their having three-coordinate tin(II), being intermediate between the values for the homoleptic SnR_2 **2** and SnX_2 [X = $N(SiMe_3)_2$, δ 776; X = $CH(SiMe_3)_2$, δ 2310 at 373 K[6a] (or 2315 at 375 K[6b]) for $Sn[CH(SiMe_3)_2]_2$ in [$^2H_8$]toluene and δ 725, 745 by CP MAS for the dimer[6b]]. The ^1H NMR solution spectra of **4**–**6**‡ also showed single NMe_2 and identical 3- and 5-aromatic proton environments at 298 K; low-temperature data are not yet to hand for **1** or **3**–**6**. The low-temperature ^1H NMR solution spectra of both **2** (containing the C,N-chelating R②) and $Sn[C_6H_3(CH_2NMe_2)_2\text{-}2,6]Cl$[2] (having the C,N,N′-tripodal ligand) were consistent with their solid-state structures, but at higher temperatures each showed fluxional behaviour.

Complex $SnR[N(SiMe_3)_2]$ **4** is similar to the three-coordinate tin(II) compound $Sn[C(SiMe_3)_2C_5H_4N\text{-}2][N(SiMe_3)_2]$,[5] both with respect to its yellow colour and $^{119}Sn\{^1H\}$ chemical shift, δ 319; while δ [$^{119}Sn\{^1H\}$] for the four-coordinate SnR_2 **2** is at a higher frequency than for the similarly coordinated tin(II) complexes $Sn[C(SiMe_3)_2C_5H_4N\text{-}2]_2$ (δ 139),[5] $Sn[C_6H_3(CH_2NMe_2)_2\text{-}2,6]X$ (X = Cl, δ 155.6; X = C_6H_4Me-4, δ 209.5),[2] or $Sn(C_{10}H_6NMe_2\text{-}8)_2$ (δ 150.9 at ② 80 °C).[7]

The aryltin(II) chloride **6** was reasonably thermally stable, but in solution it slowly deposited metallic tin. Its stability is attributed to its three-coordinate nature, as in $Sn[C(SiMe_3)_2C_5H_4N\text{-}2]Cl$;[5] attempts to make $Sn[CH(SiMe_3)_2]Cl$ from $Sn[CH(SiMe_3)_2]_2$ + $SnCl_2$ afforded $Sn[CH(SiMe_3)_2]_2Cl_2$ + Sn.[8] However, **6** was clearly less robust than the four-coordinate tin(II) complex $Sn[C_6H_3(CH_2NMe_2)_2\text{-}2,6]Cl$.[2]

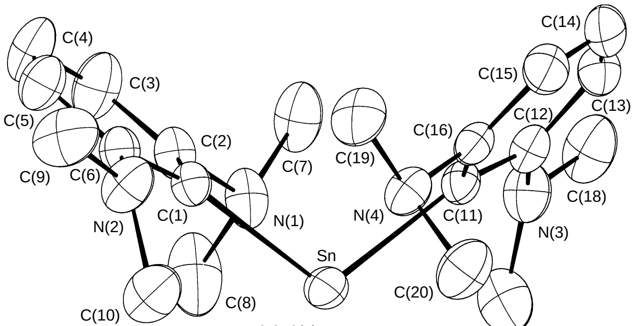
Crystalline SnR_2 **2**, illustrated in Fig. 1 and **2a**, is a mononuclear, four-coordinate tin(II) complex, the shortest Sn···Sn separation being 6.7 Å.§ The C(1)–Sn–C(11) angle of 105.6(2)° is typical of two-coordinate SnX_2 complexes, *e.g.* 103.6(1)° in $Sn(C_6H_2Bu^t{}_3\text{-}2,4,6)_2$,[9] but significantly different from those in the four-coordinate tin(II) complexes $Sn[C(SiMe_3)_2C_5H_4N\text{-}2]_2$ [125.0(2)°][5] or $Sn(C_{10}H_6NMe_2\text{-}8)_2$ [93.8(5)°];[7] the nature of the chelate bite-angle is clearly a major factor. The coordinating NMe_2 groups, one from each ligand, are arranged in a transoid fashion around the distorted trigonal-pyramidal tin centre, assuming that a lone pair of electrons occupies an equatorial site. The three CNC angles at each of the coordinating N atoms [N(1), N(4)] range from 108.9(5) to 114.1(5)° (av. 111.1°), while those at the more remote N atoms [N(2), N(3)] vary from 115.5(5) to 120.1(6)° (av. 117.7°), thus approximating to sp^3 and sp^2 N environments, respectively. The Sn···N(1) and Sn···N(4) distances (av. 2.64 Å) may be compared with an average of 2.42 Å in $Sn[C(SiMe_3)_2C_5H_4N\text{-}2]_2$[5] or 2.56 Å in $Sn[C_6H_3(CH_2NMe_2)(CH_2NMe_2)\text{-}2,6]_2Cl$.[2] To ensure optimal Sn···N(1) [or N(4)] donation, the Sn–C(1) and Sn–C(11) bonds are strongly tilted towards N(1) and N(4); hence, the C(2)–C(1)–Sn and C(16)–C(11)–Sn angles (av. 104.0°) and C(6)–C(1)–Sn and C(12)–C(11)–Sn (av. 138.2°) are severely distorted from sp^2 values.

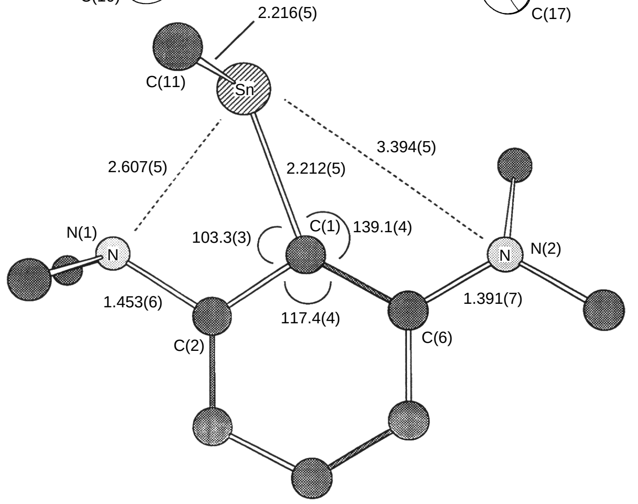
The Sn–C(1) and Sn–C(11) bond lengths (av. 2.214 Å) are similar to the $Sn–C_{aryl}$ bond lengths in $Sn(C_6H_2Bu^t{}_3\text{-}2,4,6)_2$ [av. 2.261(4) Å][9] and $Sn[C_6H_2(CF_3)_3\text{-}2,4,6]_2$ [av. 2.281(5) Å],[10] the latter having significant Sn···F contacts with each of the 2- and 6-CF_3 groups.

The average Li–C and Li–N(N′) bond distances in $[Li(\mu\text{-}R)]_3$ are rather similar, 2.17 and 2.12 Å, respectively,[1] whereas in **2** the Sn–C bonds are considerably (*ca.* 20%) shorter than the chelating Sn–N distances.

The data here presented, together with experiments in progress, including the formation of a thermally stable tin-centred radical and cation $^{\cdot}SnR_3$ and $[SnR_2\{CH(SiMe_3)_2\}]BPh_4$, respectively, and the borane adduct $SnR_2(BH_3)$, encourage us to regard this ligand as having considerable potential.

We thank the European Commission for fellowships for C. D. (category 30) and L. J.-M. P. (cat. 20), Mr J. Keates and Dr G. A. Lawless for the CP MAS spectra and Dr A. Abdul-Sada for the MS spectral data and the EPSRC for other support.





2a

Fig. 1 CAMERON representation of the molecular structure of $Sn[C_6H_3(NMe_2)_2\text{-}2,6]_2$ **2**. Selected bond lengths (Å) and angles (°) (see also **2a**): Sn···N(1) 2.607(5), Sn···N(4) 2.669(5); C(1)–Sn–C(11) 105.6(2), Sn–C(11)–C(16) 104.7(3), Sn–C(11)–C(12) 137.4(4).

Footnotes

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† No reprints available.

‡ *NMR spectroscopic data* [^1H NMR at 250.0 MHz in C_6D_6 or (for **2**) $[^2H_8]$toluene; $^{13}C\{^1H\}$ NMR at 62.9 MHz, $^{29}Si\{^1H\}$ at 49.7 MHz and $^{119}Sn\{^1H\}$ at 93.2 MHz, all in PhMe with C_6D_6; ^{119}Sn CPMAS NMR at 11.5 kHz]. **1**: ^1H δ 2.62 (s, 12 H, NMe_2), 6.61 (d, 2 H, 3-CH) (^3J 8 Hz), 7.14 (t, 1 H, 4-CH) (^3J 8 Hz). **2**: ^1H δ 2.70 (s, 12 H, NMe_2), 6.63 (d, 2 H, 3-CH) (^3J 8 Hz), 7.22 (t, 1 H, 4-CH) (^3J 8 Hz);$^{119}Sn\{^1H\}$ δ 442 [$^1J(^{119}Sn^{13}C)$ 432 Hz], $^{119}Sn\{^1H\}$ CP MAS δ 492. **3**: ^1H δ 2.71 (s, 12 H, NMe_2), 7.00 (d, 2 H, 3-CH) (^3J 7 Hz), 7.27 (t, 1 H, 4-CH) (^3J 7 Hz); $^{207}Pb\{^1H\}$ δ 3919. **4**: ^1H δ 0.27 (s, 18 H, $SiMe_3$), 2.52 (s, 12 H, NMe_2), 6.38 (d, 2 H, 3-CH) (^3J 8 Hz), 7.12 (t, 1 H, 4-CH) (^3J 8 Hz); $^{29}Si\{^1H\}$ δ ② 1.0; $^{119}Sn\{^1H\}$ δ 422. **5**: ^1H δ 0.09 (s, 1 H, CH), 0.29 (s, 18 H, $SiMe_3$), 2.51 (s, 12 H, NMe_2), 6.38 (d, 2 H, 3-CH) (^3J 8 Hz), 7.14 (t, 1 H, 4-CH) (^3J 8 Hz); $^{29}Si\{^1H\}$ δ ② 2.37; $^{119}Sn\{^1H\}$ δ 758. **6**: ^1H δ 2.45 (s, 12 H, NMe_2), 6.28 (d, 2 H, 3-CH) (^3J 8 Hz), 7.09 (t, 1 H, 4-CH) (^3J 8 Hz); $^{119}Sn\{^1H\}$ δ 380.

§ *Crystal data*: **2**, $C_{20}H_{30}N_4Sn$; M = 445.2, monoclinic, space group $P2_1/c$ (no. 14), a = 11.608(2), b = 10.569(3), c = 17.393(3) Å, β = 98.85(1)°, Z = 4, U = 2108.5(8) Å^3, $F(000)$ = 912, D_c = 1.40 g cm②^3, μ(Mo-Kα) = 12.2 cm②^1, specimen 0.6 ③ 0.2 ③ 0.1 mm, 6386 reflections collected for $2 < \theta < 30°$, 3507 reflections with $I > 2\sigma(I)$, R_1 = 0.060, wR_2 = 0.161 (for all data) (T = 293K). Enraf-Nonius CAD4 diffractometer (λ = 0.710 73 Å). Full-matrix least-squares refinement with SHELXL-93, H atoms in riding mode and all non-H atoms anisotropic. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallograpic 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 182/438.

References

1 S. Harder, J. Boersma, L. Brandsma, J. A. Kanters, W. Bauer and P. v. R. Schleyer, *Organometallics*, 1989, **8**, 1696.
2 J. T. B. H. Jastrzebski, P. A. van der Schaaf, J. Boersma, G. van Koten, M. C. Zoutberg and D. Heijdenrijk, *Organometallics*, 1989, **8**, 1373.
3 H. Braunschweig, C. Drost, P. B. Hitchcock, M. F. Lappert and L. J.-M. Pierssens, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 261.
4 R. W. Chorley, P. B. Hitchcock, B. S. Jolly, M. F. Lappert and G. A. Lawless, *J. Chem. Soc., Chem. Commun.*, 1991, 1302.
5 B. S. Jolly, M. F. Lappert, L. M. Engelhardt, A. H. White and C. L. Raston, *J. Chem. Soc., Dalton Trans.*, 1993, 2653.
6 (*a*) S. J. Smith, D. Phil. thesis, University of Sussex, 1986; (*b*) K. W. Zilm, G. A. Lawless, R. M. Merrill, J. M. Millar and G. G. Webb, *J. Am. Chem. Soc.*, 1987, **109**, 7236.
7 J. T. B. H. Jastrzebski, P. A. van der Schaaf, J. Boersma, G. van Koten, D. Heijdenrijk, K. Goubitz and D. J. A. de Ridder, *J. Organomet. Chem.*, 1989, **367**, 55.
8 D. E. Goldberg, P. B. Hitchcock, M. F. Lappert, K. M. Thomas, A. J. Thorne, T. Fjeldberg, A. Haaland and B. E. R. Schilling, *J. Chem. Soc., Dalton Trans.*, 1986, 2387.
9 M. Weidenbruch, J. Schlaefke, A. Schäfer, K. Peters, H. G. von Schnering and H. Marsmann, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1846.
10 H. Grützmacher, H. Pritzkow and F. T. Edelmann, *Organometallics*, 1991, **10**, 23.

Received in Basel, Switzerland, 23rd January 1997; Com. 7/00528H