Variation of bonding modes in homoleptic tin(II) 1-azaallyls†

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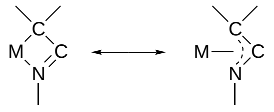
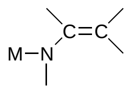
The homoleptic tin(II) compounds Sn[N(R)C(Bu^t)C(H)C$_6$H$_3$Me$_2$-2,5]$_2$ 1, Sn[N(R)C(Bu^t)C(H)R]$_2$ 2 and R$_2$CC(Ph)N(R)Sn[N(R)C(Ph)CR$_2$] 3 (R = SiMe$_3$) are prepared and structurally characterised.

The important series of first-row triatom-centred, monoanionic ligands [XYZ]$^-$ include allyl, triazenide and amidinate, with the carboxylate probably the archetype. Open-chain, structurally characterised 1-azaallyl ligands are of recent date.[1] In [Li(LL′)]$_2$,[1] *rac*-[Zr(LL′)$_2$Cl$_2$][2] and *rac*-[Yb(LL′)$_2$],[3] the [LL′]$^-$ ligand behaved in an η^3-chelating bridging (Li) or terminal (Zr, Yb) fashion [LL′ = N(R)C(Bu^t)C(H)R, R = SiMe$_3$]. We now report that the latter reflects on only one possible mode of terminal 1-azaallyl–metal (M) bonding (**MA**, η^3-iminoalkyl), while another, **MB**, represents an η^1-enamidometal isomer. This is illustrated by reference to the three homoleptic 1-azaallyltin(II) complexes, having the structures Sn**B**$_2$ **1**, Sn**A**$_2$ **2** and Sn(**A**)**B** **3**, the variation in structural types being due to changing the substituents on the NCC skeleton: Sn[N(R)C(Bu^t)C(H)C$_6$H$_3$Me$_2$-2,5]$_2$ **1**, Sn[N(R)C(Bu^t)C(H)R]$_2$ **2** and R$_2$CC(Ph)N(R)Sn[N(R)C(Ph)CR$_2$] **3** (R = SiMe$_3$).



MA



MB

The yellow (**1**, **2**) and orange (**3**) tin complexes were readily synthesised (78–84%) from SnCl$_2$ and 2 equiv. of Li[N(R)C(Bu^t)C(H)Ar] [obtained[4a] from LiCH(R)$_2$ + Bu^{t}CN, Ar = C$_6$H$_3$Me$_2$-2,5], K(LL′),[1] or Li[N(R)C(Ph)CR$_2$] [prepared[4b] from LiCR$_3$(thf)$_2$ + PhCN] in diethyl ether or pentane solution at ambient temperature. A single-crystal X-ray diffraction study‡ shows that **1** (Fig. 1) is coordinated by two η^1-enamido ligands with the free electron pair pointing away from the ligands. The N(1)–Sn–N(1′) angle of 111.2° is only slightly larger than in the mononuclear tin(II) amides Sn[N(SiMe$_3$)$_2$]$_2$[5] (104.7°) or Sn[N(Me)$_2$(CH$_2$)$_3$CMe$_2$]$_2$[6] (109.7°). The arrangement of the ligands is such that the aromatic rings are within the van der Waals range above and below the Sn atom [Sn–C(2) 3.151, Sn–C(7) 3.188 Å]. A similar interaction has been reported in 1,2-C$_6$H$_4$[N(CH$_2$Bu^t)]$_2$Sn.[7] The enamido character of the 1-azaallyl ligand in **1** is evident from the short Sn–N(1), long N(1)–C(1) and a short C(1)–C(2) distance (Table 1), as well as ^{13}C NMR shifts which are consistent with N(1)–C(1) being a single and C(1)–C(2) a double bond.

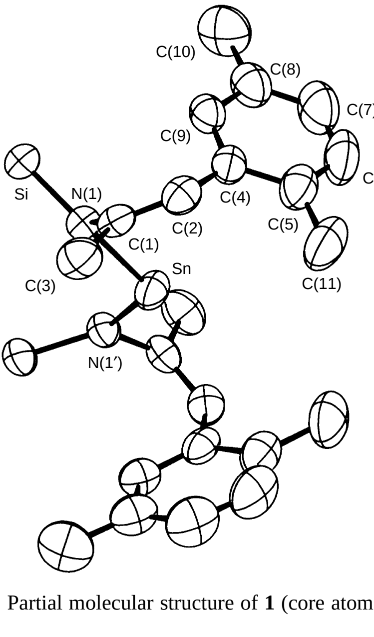


Fig. 1 Partial molecular structure of **1** (core atoms only)

Changing the 2,5-dimethylphenyl group of the η^1-ligand system in **1** by a trimethylsilyl group alters the ligand bonding mode to η^3. Thus the X-ray structure of **2** (Fig. 2)‡ shows that, in contrast to **1**, C(2) and N(1) are both within bonding range of the tin atom but compared to **1** the Sn–N(1) distances are longer (Table 1). The C(1)–C(2) and C(1)–N(1) distances and the ^{13}C NMR spectral chemical shifts show iminoalkyl rather than enamido character, as evident by comparison with Sn[NC$_5$H$_4$C(SiMe$_3$)$_2$-2]$_2$.[8] It is interesting to note that C(1) is bent towards the metal [the angle between the adjacent planes SnN(1)C(2) and N(1)C(1)C(2) is 37°] leading to a Sn–C(1) distance of 2.729(2) Å. Therefore an alternative description of **2** is as a bent sandwich complex similar to Sn(η-C$_5$Me$_5$)$_2$.[9]

The X-ray structure of crystalline **3**‡ shows that introducing a second trimethylsilyl group at C(2) or C(5) probably increases the steric demand of the ligand to such an extent that the bis(chelate) arrangement is no longer viable; thus, an intermediate situation between that of **1** and **2** is observed, wherein one ligand is η^3- and the other is η^1-coordinated. Table 1 shows relevant interatomic distances and NMR spectral chemical shifts. Important differences for the η^3-coordinated ligand in **3** compared with **2** are a shorter Sn–N(1) and a longer Sn–C(2) distance in **3** and a much smaller dihedral angle between the planes N(1)SnC(2) and N(1)C(1)C(2) of only 12.7°. That a higher coordination number than three in **3** is probably avoided by the increased bulk of the ligand (compared with that in **2**) is also supported by variable-temperature ^{1}H and ^{13}C NMR

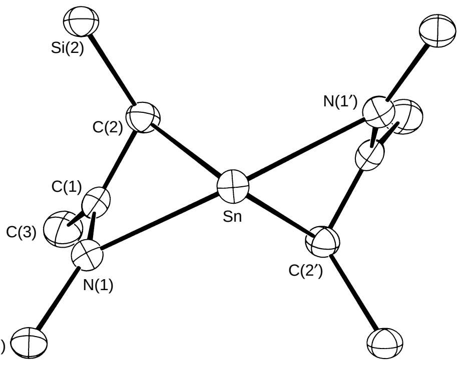


Fig. 2 Partial molecular structure of **2** (core atoms only) with selected bond angles (°): N–Sn–N′ 146.98(6), N–Sn–C(2) 57.99(6), N–Sn–C(2′) 97.25, C(2)–Sn–C(2′) 89.44(8)

spectroscopic experiments which show the two ligands to be equivalent in solution down to −90 °C, indicating that there is a rapid intramolecular exchange between the η^1- and η^3-coordinated ligand. Comparing **2** and **3** with **1** it may be that the preference for the enamido structure in **1** is due to electronic rather than steric reasons.

In conclusion, we believe that the following features (*i*) and (*ii*) are particularly noteworthy. (*i*) Compounds **1–3** serve as a good example to demonstrate how comparatively small differences in the backbone of a 1-azaallyl ligand may significantly influence their metal complex bonding modes. (*ii*) Enamido–metal bonding now shown in the tin(II) complexes **1** and **3** has only recently been crystallographically established for some alkali-metal 2-methylpyridine or related derivatives,[10,11] *e.g.*[11] $Li[NC_5H_4\{C(SiMe_3)Ph\}\text{-}2](tmen)$; such structures are widely postulated for group 1 and 2 metal complexes, which when prepared *in situ* are valuable C–C bond-forming synthons;[12] there is NMR spectroscopic structural evidence for $[M\{N(H)C(Bu^t)CHPr^n\}\{OP(NMe_2)_3\}_x]_n$ (M = Li, $x = 1$ or M = Na, $x = 2$)[13a] and $[Li\{N(Ph)\overline{C{=}CH(CH_2)_3C}H_2\}(thf)_x]_n$ ($x = 0$, or $x = 1 = n$).[13b] The $[NC_5H_4C(SiMe_3)_2\text{-}2]^-$ ligand has been found in an η^1-mode in the homoleptic mercury(II) complex, but it is the tautomeric (*cf.* **MB**) iminoalkyl ligated species.[14]

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Table 1 Some important structural and NMR spectroscopic data on the (1-azaallyl)tin(II) complexes **1**–**3**

	Complex		
Property	**1**	**2**	**3**
CN[a]	2	4	3
d(Sn–N, η^1)[b]/Å	2.130(3)	—	2.153(4)
d(Sn–N, η^3)[b]/Å	—	2.510(2)	2.288(4)
d[Sn–C(1)]/Å	(2.791)	2.729(2)	2.775(4)
d[Sn–C(2)]/Å	(3.151)	2.295(2)	2.531(5)
C–C(η^1)[b]/Å	1.349(5)	—	1.365(6)
C–C(η^3)[b]/Å	—	1.463(3)	1.461(6)
C–N(η^1)[b]/Å	1.435(4)	—	1.432(5)
C–N(η^3)[b]/Å	—	1.298(3)	1.317(6)
$\delta[^{119}Sn\{^1H\}]$	61.5	−387.2	−37.3
$\delta[^{13}C\{^1H\}, C(1)]$	152.6	202.5	185.7
$\delta[^{13}C\{^1H\}, C(2)]$	104.4	50.0	100.6

[a] CN = coordination number. [b] The designations of η^1 and η^3 relate to the enamido or chelate mode of the ligand-to-metal bonding, respectively.

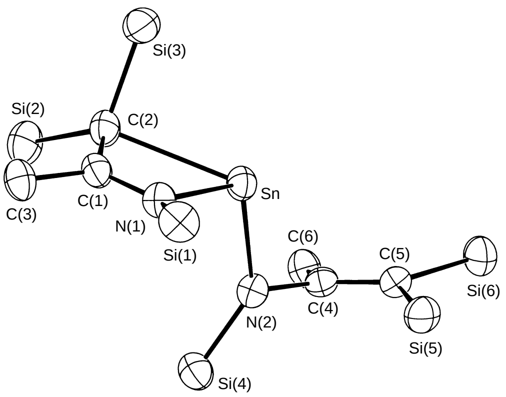

Fig. 3 Partial molecular structure of **3** (core atoms only) with selected bond angles (°): N(1)–Sn–N(2) 109.9(1), N(1)–Sn–C(2) 59.33(1), N(2)–Sn–C(2) 113.2(2), C(4)–N(2)–Si(4) 116.4(3), C(4)–N(2)–Sn 105.0(3), Si(4)–N(2)–Sn 137.6(2)

Footnotes

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† No reprints available.

‡ *Crystal data* for **1**: $C_{34}H_{56}N_2Si_2Sn$, M = 667.68, monoclinic, space group $C2/c$ (no. 15), a = 13.006(4), b = 15.957(3), c = 17.735(10) Å, β = 98.74(3), U = 3638(2) Å^3, Z = 4, D_c = 1.22 g cm^{-3}, F(000) = 1408, λ(Mo-Kα) = 0.710 73 Å, μ = 0.79 mm^{-1}. Data were collected at 293(2) K on a Enraf-Nonius CAD4 diffractometer in the ω–2θ mode in the range $2 < \theta < 25°$. The structure was solved by direct methods (SHELXS 86) and refined by full-matrix least squares on all F^2 (SHELXL 93) with absorption correction by ψ-scans. All non-hydrogen atoms were anisotropic, and hydrogen atoms were included in the riding mode with U_{iso}(H) = 1.2 U_{eq}(C) or 1.5 U_{eq} for Me groups. Final residuals for 3190 independent reflections were R_1 = 0.057, wR_2 = 0.086 and for the 2442 with $I > 2\sigma(I)$, R_1 = 0.037, wR_2 = 0.077.

2: $C_{24}H_{56}N_2Si_4Sn$, M = 603.8, monoclinic, space group $C2/c$ (no. 15), a = 11.387(5), b = 16.675(6), c = 18.390(8) Å, β = 106.07(3), U = 3355.4 Å^3, Z = 4, D_c = 1.20 g cm^{-3}, F(000) = 1280, λ(Mo-Kα) = 0.710 73 Å, μ = 0.92 mm^{-1}. 3060 independent reflections were collected at 173(2) K on a Enraf-Nonius CAD4 diffractometer in the ω–2θ mode in the range $2 < \theta < 25°$. The structure was solved by heavy-atom methods (SHELXS 86) and refined by full-matrix least squares on F (Enraf-Nonius MolEN) with absorption correction by DIFABS. All non-hydrogen atoms were anisotropic, and hydrogen atoms were included in the riding mode with U_{iso}(H) = 1.2 U_{eq}(C) or 1.5 U_{eq} for Me groups. Final residuals for 2623 reflections [with $I > 2\sigma(I)$] were R = 0.025, R' = 0.030.

3: $C_{34}H_{64}N_2Si_6Sn$, M = 788.1, monoclinic, space group $P2_1/c$ (no. 14), a = 19.249(4), b = 12.400(3), c = 19.820(5) Å, β = 112.83(2), U = 4360(2) Å^3, Z = 4, D_c = 1.20 g cm^{-3}, F(000) = 1664, λ(Mo-Kα) = 0.71073 Å, μ = 0.77 mm^{-1}. Conditions for data collection and refinement were identical to those for **1**. Final residuals for 7663 independent reflections were R_1 = 0.096, wR_2 = 0.106 and for the 5008 with $I > 2\sigma(I)$, R_1 = 0.048, wR_2 = 0.088.

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 182/463.

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