

## Monomeric Bivalent Group 4B Metal Dialkylamides $M[\overline{\text{NCMe}_2(\text{CH}_2)_3\text{CMe}_2}]_2$ ( $M = \text{Ge}$ or $\text{Sn}$ ), and the Structure of a Gaseous Disilylamide, $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ , by Gas Electron Diffraction†

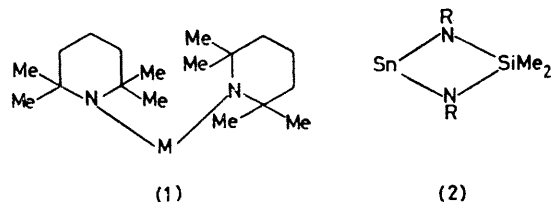
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**Summary** Reaction of  $\text{Li}[\overline{\text{NCMe}_2(\text{CH}_2)_3\text{CMe}_2}]$  ( $\text{LiNR}_2$ ) in  $n\text{-C}_5\text{H}_{12}$  at  $20^\circ\text{C}$  with  $\text{GeCl}_2\cdot\text{dioxan}$  or  $\text{SnCl}_2$  affords the corresponding coloured crystalline diamagnetic metal(II) dialkylamide,  $M(\text{NR}_2)_2$ , which is monomeric (cryoscopy in  $\text{C}_6\text{H}_{12}$ ), has a low first ionisation potential (6.90 eV for  $M = \text{Ge}$ , 6.80 eV for  $M = \text{Sn}$ ), and furnishes the 2,2,6,6-tetramethylpiperidyl radical  $\cdot\dot{\text{N}}\text{R}_2$  upon photolysis; electron diffraction analysis of gaseous  $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$  shows only the monomer at *ca.*  $100^\circ\text{C}$  and  $10^{-2}$  atm, which has  $\text{C}_{2v}$  symmetry,  $\angle\text{NSnN} = 96.0^\circ$ , and  $\text{Sn-N}$  (av.) =  $2.09 \text{ \AA}$ .

THE orange diamagnetic title  $\text{Sn}^{\text{II}}$  bis(silyl)amide<sup>1,2</sup> is monomeric in both cyclohexane and benzene,<sup>1,3</sup> as are some related compounds having at least one  $\beta$ -silicon or  $\beta$ -germanium atom per ligand molecule, *e.g.*  $M[\text{N}(\text{M}'\text{R}_3)_2]_2$  ( $M = \text{Ge}$  or  $\text{Sn}$ ;  $\text{M}' = \text{Si}$  or  $\text{Ge}$ ;  $\text{R} = \text{Me}$ ,  $\text{Et}$ , or  $\text{Ph}$ ),<sup>3</sup>  $\text{Pb}[\text{N}(\text{SiMe}_3)_2]_2$ ,<sup>1,3</sup>  $M[\text{N}(\text{CMe}_3)\text{SiMe}_3]_2$  ( $M = \text{Ge}$ ,  $\text{Sn}$ , or  $\text{Pb}$ ), and compound (2), which in solution is a monomer ( $\text{R} = \text{Bu}^t$ ) or dimer

( $\text{R} = \text{Pr}^t$ ) and in the crystal for  $\text{R} = \text{Bu}^t$  has both a monomeric and a dimeric phase (*X*-ray).<sup>4</sup> The amides (1) are monomeric in cyclohexane (cryoscopy) and are related to the as yet unknown carbon compounds,  $M[\text{N}(\text{CMe}_3)_2]_2$ . By contrast, tin(II) dimethylamide is a colourless dimer, probably with a  $\mu\text{-(NMe}_2)_2$ -bridged structure.<sup>5</sup>



The amides (1) (the tin compound has been mentioned at a conference<sup>6</sup>) were prepared from  $\text{GeCl}_2\cdot\text{dioxan}$  or  $\text{SnCl}_2$  and  $\text{LiNCMe}_2(\text{CH}_2)_3\text{CMe}_2$  at *ca.*  $20^\circ\text{C}$  in  $n\text{-C}_5\text{H}_{12}$ , and analysed satisfactorily. The lead(II) amide is markedly less stable and decomposed below  $0^\circ\text{C}$ , in contrast to  $\text{Pb}[\text{N}(\text{SiMe}_3)_2]_2$ .<sup>3</sup>

† No reprints available.

Noteworthy properties of the orange  $\text{Ge}^{\text{II}}$  and the dark-red  $\text{Pb}^{\text{II}}$  dialkylamides are (i) their colour, which clearly does not arise from an electronic transition into a vacant  $nd$ -orbital on  $\beta$ -Si or  $\beta$ -Ge [ $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) in  $n\text{-C}_6\text{H}_{14}$ : Ge, 426 (670), 250 ( $7.6 \times 10^3$ ), and 217 ( $1.16 \times 10^3$ ); Sn 475 (720) and 222 ( $8 \times 10^5$ )]; (ii) the exceptionally low first ionisation potentials (*ca.* 6.8 eV), compared with  $\text{M}[\text{N}(\text{SiMe}_3)_2]_2$  or  $\text{M}[\text{N}(\text{CMe}_3)\text{SiMe}_3]_2$ ,<sup>7</sup> and (iii) their photolysis in  $n\text{-C}_6\text{H}_{12}$  to afford the 2,2,6,6-tetramethylpiperidyl radical, identified by its e.s.r. spectrum  $g_{\text{av}} 2.006$ ,  $a(^{14}\text{N}) 1.525 \text{ mT}$ ,  $t_{1/2}$  *ca.* 0.5 min at 25 °C (*cf.* ref. 8). Observation (iii) shows that compounds (1) are among the most hindered amides; by contrast, photolysis of  $\text{M}[\text{N}(\text{SiMe}_3)_2]_2$  affords the persistent metal(III) amide.<sup>3</sup> Consistent with (ii), which strongly suggests significant  $\text{SiN}(d \leftarrow p)$   $\pi$ -bonding amides (1) are more responsive to oxidative addition (*e.g.*, with MeI) than  $\text{M}[\text{N}(\text{SiMe}_3)_2]_2$ .<sup>9</sup>

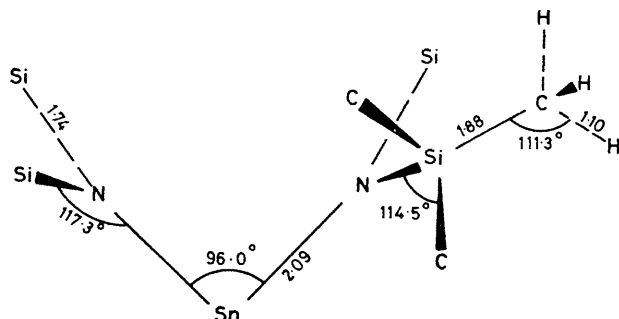


FIGURE. Schematic drawing showing important molecular parameters for gaseous  $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ , obtained from an electron diffraction study.

From their sharp  $^1\text{H}$  n.m.r. spectra, diamagnetism, and absence of e.s.r. signals, the monomeric amides are expected to have a singlet electronic ground state with an approximate  $p^2$  bonding at the metal. This model is essentially borne out by the electron diffraction results (obtained and analysed by techniques previously described; see ref. 10) on gaseous  $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$  at 100 °C and  $10^{-2}$  atm which are consistent with a wholly monomeric molecule of  $C_{2v}$  symmetry with planar bonding at nitrogen. It thus differs from the  $D_{2d}$   $\text{Be}[\text{N}(\text{SiMe}_3)_2]_2$ .<sup>11</sup> The essential molecular parameters are shown in the Figure,  $R = 9.6\%$ .

In the light of the size of the  $\text{N}(\text{SiMe}_3)_2$  ligand, it may be surprising to find the small angle at Sn,  $\angle \text{NSnN} = 96^\circ$ . This compares with  $95^\circ$  in gaseous  $\text{SnCl}_2$ .<sup>12</sup> The Sn-N bond length (2.089 Å) is unexceptional; *cf.*, 2.045 in  $\text{Sn}(\text{NMe}_2)_4$ ,<sup>13</sup> 2.033(5) in  $\text{Sn}[\text{N}(\text{Bu}^t)\text{SiMe}_2\text{NBu}^t]_2$ ,<sup>4</sup> and 2.09 Å in (2) ( $R = \text{Bu}^t$ , monomer; or 2.39 Å in the dimer).<sup>4</sup> The  $\text{N} \cdots \text{N}$  distance of *ca.* 3.1 Å makes  $\text{N} \cdots \text{N}$  interaction unlikely, as is also clear from the considerable torsional motion around the Sn-N bonds, which further indicates that there is little steric interaction between the  $\text{N}(\text{SiMe}_3)_2$  groups. Although electron diffraction data are not available on the isoelectronic compound  $\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$ , we note that the latter is a Sn-Sn-bonded dimer in the crystal,<sup>14</sup> and a monomer in cyclohexane solution or in the gas.

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