

# A singly bonded amido-distannyne: H<sub>2</sub> activation and isocyanide coordination†

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**The first amido-distannyne,  $L^{\dagger}SnSnL^{\dagger}$  ( $L^{\dagger} = -N(Ar^{\dagger})(SiPr^i_3)$ ,  $Ar^{\dagger} = C_6H_2\{C(H)Ph_2\}_2Pr^i-2,6,4$ ), has been prepared and shown to possess a very long Sn–Sn single bond; the compound activates dihydrogen under ambient conditions to give  $L^{\dagger}Sn(\mu-H)_2SnL^{\dagger}$ , and reacts with  $Bu^iNC$  to give a stable adduct complex,  $L^{\dagger}(Bu^iNC)SnSn(CNBu^i)L^{\dagger}$ .**

The chemistry of the heavier group 14 alkyne analogues, REER (E = Si, Ge, Sn or Pb; R = bulky aryl or silyl), has rapidly expanded since the first example was reported in 2000.<sup>1</sup> The interest in these compounds was initially derived from their unusual structure and bonding. That is, they possess *trans*-bent structures, as opposed to linear alkynes, and their E–E bond orders can range from near three (E = Si) to one (E = Pb).<sup>2</sup> All examples of digermynes, RGeGeR, have intermediate Ge–Ge bond orders, and some are thought to possess significant singlet biradical character, which has been proposed to lead to the unusual “transition metal-like” reactivity displayed by these species.<sup>2a,3</sup> The most high profile manifestation of this was the first ambient temperature activation of H<sub>2</sub> by a main group complex,  $Ar'GeGeAr'$  ( $Ar' = C_6H_3(C_6H_3Pr^i-2,6)_2-2,6$ ), reported by Power and co-workers in 2005.<sup>4</sup> More recently, several distannynes, *e.g.*  $Ar'SnSnAr'$ , have also been shown to activate H<sub>2</sub> at room temperature.<sup>5</sup> Although these distannynes have either Sn–Sn single or multiple bonds in the solid state, calculations indicate that their electronic ground state is the multiply bonded form,<sup>6</sup> and therefore that they exist in this form in solution.<sup>7</sup> Consequently, the activation of H<sub>2</sub> by distannynes in solution is thought to involve multiply bonded species, in all cases. A recent theoretical study supports this view, but does show that the mechanism of activation by distannynes (and digermynes) may be more complex than originally thought.<sup>8</sup>

We have recently developed a series of extremely bulky amides<sup>9</sup> and have begun to explore their utility for the stabilisation of low oxidation state p-block compounds.<sup>10</sup> As part of that study, the first amido-digermynes,  $LGeGeL$  ( $L = -N(Ar^{\dagger})(SiMe_3)$   $L^*$ , or  $-N(Ar^{\dagger})(SiPr^i_3)$   $L^{\dagger}$ ,  $Ar^{\dagger} = C_6H_2\{C(H)Ph_2\}_2Me-2,6,4$ ;  $Ar^{\dagger} = C_6H_2\{C(H)Ph_2\}_2Pr^i-2,6,4$ ) have been prepared and shown to possess either a very long Ge–Ge single bond (*ca.* 2.71 Å,  $L^*GeGeL^*$ ),<sup>11</sup> or a short Ge–Ge multiple bond (*ca.* 2.36 Å,  $L^{\dagger}GeGeL^{\dagger}$ ).<sup>12</sup> The suppression of any Ge–Ge  $\pi$ -bonding character in  $L^*GeGeL^*$  is thought to result from significant N  $\rightarrow$  Ge  $\pi$ -donation within the planar SiCNGe<sub>2</sub> fragments of that compound. In contrast, the greater bulk of the amide ligands in  $L^{\dagger}GeGeL^{\dagger}$  prevents planarity of its SiCNGe<sub>2</sub> fragments, thereby circumventing N  $\rightarrow$  Ge  $\pi$ -overlap, and promoting Ge–Ge  $\pi$ -bonding. Despite the electronic differences between the two compounds, solutions of both were found to readily activate H<sub>2</sub> at temperatures as low as –10 °C in solution, while H<sub>2</sub> activation also occurs for  $L^*GeGeL^*$  in the solid state.<sup>11</sup>

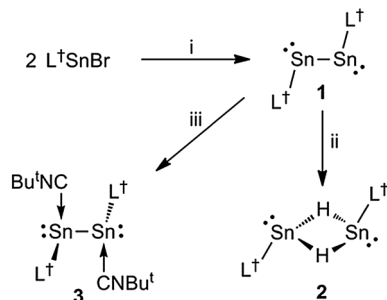
To date, efforts to prepare the distannyne analogues of  $L^*GeGeL^*$  and  $L^{\dagger}GeGeL^{\dagger}$  have not been successful, though this would be of interest as amido-distannynes are unknown. Moreover, a recent theoretical study has suggested that they should possess Sn–Sn single bonds, and should activate H<sub>2</sub> *via* a similar mechanism to that calculated for amido-digermynes, albeit in a less thermodynamically and kinetically favourable fashion.<sup>13</sup> Here, we report the synthesis of the first amido-distannyne,  $L^{\dagger}SnSnL^{\dagger}$ ,<sup>14</sup> and reveal that it does, indeed, activate H<sub>2</sub> slowly under ambient conditions to give the known tin(II) hydride,  $L^{\dagger}Sn(\mu-H)_2SnL^{\dagger}$ .<sup>12</sup> In addition, the irreversible formation of an adduct of  $L^{\dagger}SnSnL^{\dagger}$  with the isocyanide,  $Bu^iNC$ , is described.

Previous attempts to prepare amido-distannynes *via* the reduction of  $LSnCl$  ( $L = L^*$  or  $L^{\dagger}$ ) with the magnesium(II) dimer,  $\{^{Mes}Nacnac\}Mg_2$  ( $^{Mes}Nacnac = [(MesNCMe)_2CH]^-$ , Mes = mesityl) led only to tin deposition and formation of LH.<sup>11,12</sup> It was postulated that related reductions with  $LSnBr$  would proceed at lower temperatures, which might allow for the isolation of distannyne products. This proved to be the case for the reduction of  $L^{\dagger}SnBr$  (see ESI† for full synthetic and structural details) with  $\{^{Mes}Nacnac\}Mg_2$ ,<sup>15</sup> which afforded the amido-distannyne,  $L^{\dagger}SnSnL^{\dagger}$  **1**, in a moderate isolated

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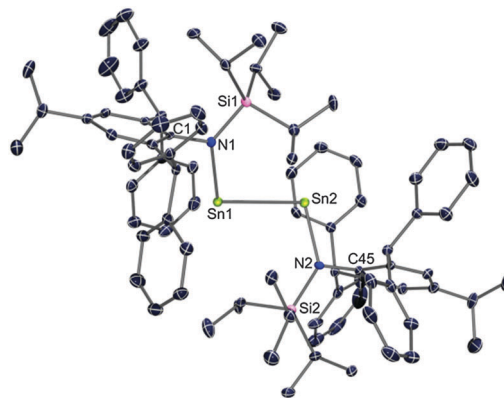


**Scheme 1** Reagents and conditions: (i)  $\{(\text{MesNacnac})\text{Mg}\}_2$ ,  $-\{(\text{MesNacnac})\text{Mg}(\mu\text{-Br})_2\}$ ; (ii)  $\text{H}_2$ ; (iii)  $\text{Bu}^t\text{NC}$ .

yield as dark green/orange dichroic crystals (Scheme 1). The compound is thermally stable in the solid state, though it decomposes in solution at ambient temperature over the course of two days, depositing tin metal and yielding  $\text{L}^+\text{H}$ . The  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of **1** both display one set of amide signals, which implies the compound has a symmetrical structure in solution. No signal was observed in the  $^{119}\text{Sn}\{^1\text{H}\}$  NMR spectrum, presumably as a result of large chemical shift anisotropies arising from the two-coordinate tin environments.<sup>7</sup> Only one distinguishable absorption band ( $\lambda_{\text{max}}$  409 nm,  $\epsilon = 6500 \text{ L mol}^{-1} \text{ cm}^{-1}$ ) was observed in the UV/visible spectrum of **1**, which contrasts with organo-distannynes, all of which display moderately intense  $\pi \rightarrow \pi^*$  absorption bands at *ca.*  $\lambda_{\text{max}}$  600 nm, and are, therefore, thought to possess  $\text{Sn-Sn}$  multiple bonds in solution.<sup>7</sup> This difference may indicate that **1** does not exhibit  $\text{Sn-Sn}$  multiple bond character in solution or the solid state, a situation which is consistent with the results of DFT calculations on the model compound,  $\text{L}'\text{SnSnL}'$  ( $\text{L}' = -\text{NMe}_2$ ), the electronic ground state structure of which has a  $\text{Sn-Sn}$  single bond.<sup>13</sup>

In order to shed light on the nature of the  $\text{Sn-Sn}$  bonding in **1** in the solid state, its X-ray crystal structure was determined (Fig. 1). The compound displays a *trans*-bent structure with a  $\text{Sn-Sn}$  bond (3.1429(7) Å, *cf.* 3.038 Å calculated for  $\text{L}'\text{SnSnL}'$ <sup>13</sup>) that is longer than in any previously reported distannyne. This, combined with the rather narrow  $\text{N-Sn-Sn}$  angles (104.00° mean, *cf.* 94.4° calculated for  $\text{L}'\text{SnSnL}'$ <sup>13</sup>), clearly signifies that **1** possesses a  $\text{Sn-Sn}$  single bond.<sup>16</sup> It is likely that  $\text{Sn-Sn}$  multiple bonding in the distannyne is frustrated by its essentially planar  $\text{Sn}_2\text{NSiC}$  fragments, which presumably allows for a degree of  $\text{N} \rightarrow \text{Sn}$   $\pi$ -donation (*cf.* singly bonded  $\text{L}^+\text{GeGeL}^+$ <sup>11</sup>). A similar planarization of the  $\text{Ge}_2\text{NSiC}$  fragments in the multiply bonded digermine analogue of **1**, *viz.*  $\text{L}^+\text{GeGeL}^+$ , is doubtless prevented by greater steric buttressing between the amide ligands, which occurs because of the smaller covalent radius of Ge (1.20 Å) *vs.* Sn (1.39 Å).<sup>17</sup> Despite this, there is still significant steric crowding in **1**, as evidenced by the marked twisting of its  $\text{N}_2\text{Sn}_2$  fragment away from planarity (torsion angle: 148.6°).

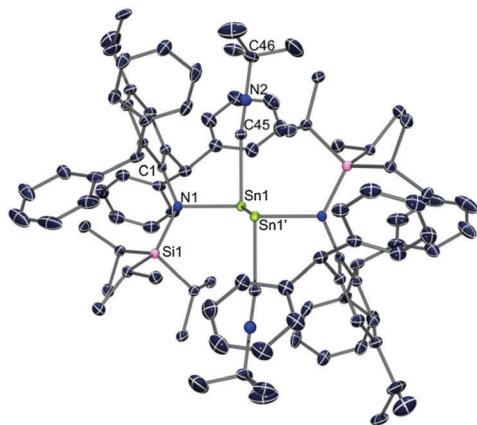
With the amido-distannyne, **1**, in hand, its reactivity towards  $\text{H}_2$  was investigated by placing a solution of the compound in  $\text{C}_6\text{D}_6$  under an atmosphere of dihydrogen at ambient temperature and pressure. Monitoring the reaction by NMR spectroscopy showed that *ca.* 30% of **1** had converted to the previously reported tin(II) hydride complex, **2**,<sup>12</sup> after 3 h. After 24 h the reaction was



**Fig. 1** Molecular structure of **1** (25% thermal ellipsoids; hydrogen atoms omitted). Selected bond lengths (Å) and angles (°):  $\text{Sn}(1)-\text{N}(1)$  2.128(4),  $\text{Sn}(1)-\text{Sn}(2)$  3.1434(5),  $\text{Sn}(2)-\text{N}(2)$  2.118(4),  $\text{N}(1)-\text{Sn}(1)-\text{Sn}(2)$  104.53(10),  $\text{N}(2)-\text{Sn}(2)-\text{Sn}(1)$  103.48(11).

*ca.* 70% complete, though because of the low thermal stability of both **1** and **2**, small amounts of  $\text{L}^+\text{H}$  and tin metal were also present in the reaction mixture at that time. Points to note about this experiment are, firstly, that the hydrogenation of **1** is considerably slower than that of the corresponding digermine,  $\text{L}^+\text{GeGeL}^+$  (which is complete after 20 min), and that the product of the digermine reaction exists in a different isomeric form in the solid state, *viz.*  $\text{L}^+(\text{H})\text{Ge}=\text{Ge}(\text{H})\text{L}^+$ , than does **2**. Both of these facts were predicted by the prior theoretical study of the hydrogenation of  $\text{L}'\text{EEL}'$  ( $\text{E} = \text{Ge}$  or  $\text{Sn}$ ).<sup>13</sup> That study also suggested that unlike hydrogenations of aryl-distannynes (which likely all occur *via* their multiply bonded forms), the mechanism of hydrogenation of  $\text{L}'\text{SnSnL}'$  (and by implication, **1**) involves an initial donation of  $\text{H}_2$   $\sigma$ -bond electron density into the  $\text{Sn-Sn}$   $\pi$ -bonded LUMO of  $\text{L}'\text{SnSnL}'$ , with concomitant back-donation of high *p*-character  $\text{Sn-Sn}$   $\sigma$ -bond HOMO density into the  $\sigma^*$  orbital of  $\text{H}_2$ . Moreover, as the hydrogenation of  $\text{L}'\text{SnSnL}'$  to give  $\text{L}'\text{Sn}(\mu\text{-H})_2\text{SnL}'$  is essentially thermo-neutral ( $\Delta G = 0.7 \text{ kcal mol}^{-1}$ ),<sup>13</sup> the possibility exists that the hydrogenation of **1** might be reversible under mild conditions. We have, however, seen no experimental evidence for such reversibility.

To further explore analogies between the reactivity of **1** and aryl-distannynes, the former was generated *in situ* and treated with two equiv. of the isocyanide,  $\text{Bu}^t\text{NC}$ . Upon work-up, the adduct complex, **3**, was obtained in moderate isolated yield as dichroic orange/green crystals (Scheme 1). Unlike the corresponding aryl-distannyne complex,  $\text{Ar}'(\text{Bu}^t\text{NC})\text{SnSn}(\text{CNBu}^t)\text{Ar}'$ , which fully dissociates to  $\text{Ar}'\text{SnSnAr}'$  and  $\text{Bu}^t\text{NC}$  in solution at 25 °C,<sup>18</sup> compound **3** is stable in  $\text{C}_6\text{D}_6$  solutions at room temperature ( $^{119}\text{Sn}\{^1\text{H}\}$  NMR:  $\delta$  241 ppm; *cf.*  $\delta$  181 ppm for  $\text{Ar}'(\text{Bu}^t\text{NC})\text{SnSn}(\text{CNBu}^t)\text{Ar}'$ ), and is returned when volatiles are removed from those solutions *in vacuo*. This is perhaps surprising, as it might be thought that the isocyanide-Sn interactions in **3** would be weak, given the crowding around the tin centres of **1**, and the fact that the infrared spectrum of crystals of **3** exhibit a  $\text{C}\equiv\text{N}$  stretching mode at  $2138 \text{ cm}^{-1}$  (*cf.*  $2162/2175 \text{ cm}^{-1}$  for  $\text{Ar}'(\text{Bu}^t\text{NC})\text{SnSn}(\text{CNBu}^t)\text{Ar}'$ ) which is only slightly shifted relative to that for free  $\text{Bu}^t\text{NC}$  ( $2134 \text{ cm}^{-1}$ ).<sup>18,19</sup> It is also noteworthy that



**Fig. 2** Molecular structure of **3** (25% thermal ellipsoids; hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Sn(1)–N(1) 2.202(3), Sn(1)–C(45) 2.325(4), Sn(1)–Sn(1') 3.0759(6), N(2)–C(45) 1.149(6), N(1)–Sn(1)–Sn(1') 105.76(10), C(45)–Sn(1)–Sn(1') 92.23(12), N(1)–Sn(1)–C(45) 89.39(14). Symmetry operation: '  $-x + 1, -y, -z + 2$ .

reaction of the related singly bonded digermynes,  $\text{L}^*\text{GeGeL}^*$ , with  $\text{Bu}^t\text{NC}$  did not give a stable adduct complex, but instead led to facile reductive coupling of two  $\text{Bu}^t\text{NC}$  molecules.<sup>20</sup> This indicates that  $\text{L}^*\text{GeGeL}^*$  is more reducing than  $\text{L}^+\text{SnSnL}^+$ .

The apparent weakness of the isocyanide–Sn interactions in **3** is borne out by its X-ray crystal structure (Fig. 2), which reveals NC→Sn distances (2.325(4) Å) that are longer than those in Ar'(Bu'NC)SnSn(CNBu')Ar' (2.301 Å mean).<sup>18</sup> Moreover, the purely dative nature of those interactions is evidenced by the isocyanide CN bond lengths, 1.149(6) Å (*cf.* 1.159 Å mean in Ar'(Bu'NC)SnSn(CNBu')Ar'), which are typical for triple bonds.<sup>21</sup> It is interesting to note that the Sn–Sn bond in **3** (3.0759(6) Å) is significantly shorter than that in **1**, presumably because the bond takes on more s-character ( $\Sigma$  angles at Sn(1) = 287.4°) upon isocyanide coordination. This differs to coordination of Ar'SnSnAr' by Bu'CN, which leads to a lengthening of its Sn–Sn bond by 0.374 Å, due to loss of multiple bond character for that bond.<sup>18</sup> Somewhat related is the likelihood that any N–Sn  $\pi$ -character in **1** must be lost upon isocyanide coordination, as the planar NSiC fragments of **3** are essentially orthogonal to the Sn<sub>2</sub>N<sub>2</sub> plane in that compound. Although the increased Sn–N bond lengths in **3** (Sn–N 2.202(3) Å), relative to those in **1** (Sn–N 2.123 Å mean), might support this proposal, this difference could also be due to the increased coordination number in the former. Indeed, the observed values are close to the mean Sn–N distances for all crystallographically characterised 2- and 3-coordinate tin(II) amides, *viz.* 2.10 Å and 2.20 Å respectively.<sup>22</sup>

In summary, the first example of an amido-distannyne,  $\text{L}^\dagger\text{SnSnL}^\dagger$  **1**, has been prepared and shown to possess a very long Sn–Sn single bond. The compound activates dihydrogen under ambient conditions to give the known tin(II) hydride complex,  $\text{L}^\dagger\text{Sn}(\mu\text{-H})_2\text{SnL}^\dagger$  **2**, and reacts with  $\text{Bu}^t\text{NC}$  to give the

stable adduct,  $\text{L}^\dagger(\text{Bu}^t\text{NC})\text{SnSn}(\text{CNBu}^t)\text{L}^\dagger$  **3**. We are currently exploring the further chemistry of **1**.

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