Communications

#### Main-Group Hydrides

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## Stable Monomeric Germanium(II) and Tin(II) Compounds with Terminal Hydrides\*\*

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Metal hydrides and their complexes are considered valuable synthons in chemistry. It was demonstrated that main-group and transition-metal hydrides are important intermediates in some industrial processes and also function as catalysts.<sup>[1]</sup> Furthermore, in the quest for alternative energy sources, metal hydrides have been considered as potential feedstocks for hydrogen storage.<sup>[2]</sup> Group 14 hydrides such as R<sub>3</sub>SiH, R<sub>3</sub>GeH, and R<sub>3</sub>SnH are important reagents for some key reactions in organic synthesis. The preparation of these species is commonly carried out by reduction of the corresponding chloride compounds with lithium aluminum hydride.<sup>[3]</sup> However, the isolation and structural characterization of monomeric, terminal low-valent Group 14 hydrides seem to be difficult as a result of the potential reactivity and instability of these species. So far, only  $[{2,6-Trip_2C_6H_3Sn(\mu H_{2}$  (Trip = 2,4,6-*i*Pr<sub>3</sub>C<sub>6</sub>H<sub>2</sub>) has been structurally characterized and exhibits a dimeric structure with the tin(II) atoms connected by bridging hydride ligands,<sup>[4]</sup> although the existence of  $MH_2$  (M = Si to Pb) has been anticipated by theoretical calculations.<sup>[5]</sup> Previously, we reported on the preparation of the germanium(II) and tin(II) precursors [{HC- $(CMeNAr)_2$ GeCl] (1; Ar = 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) and [{HC-(CMeNAr)<sub>2</sub>[SnCl] (2).<sup>[6,7]</sup> Treatment of 1 with LiAlH<sub>4</sub> or NaBH<sub>4</sub> did not afford the terminal germanium(II) hydride, rather, the four-coordinate adduct but [{HC-(CMeNAr)<sub>2</sub>{Ge(H)BH<sub>3</sub>] was formed. Moreover, attempts to prepare a terminal tin(II) hydride from 2 in reactions with reducing reagents such as NaBH<sub>4</sub>, KBH<sub>4</sub>, and KH were unsuccessful. In contrast, the reactions of 1 and 2 with AlH<sub>3</sub>·NMe<sub>3</sub><sup>[8-10]</sup> in toluene at -4 °C yield the first monomeric and terminal germanium(II) and tin(II) hydrides [{HC-

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 $(CMeNAr)_2$ [GeH] (3, Scheme 1)<sup>[11]</sup> and [{HC-(CMeNAr)\_2]SnH] (4). Elimination of trimethylamine as a volatile by-product was observed during the course of the reactions of 1 and 2 with AlH<sub>3</sub>·NMe<sub>3</sub>. The color of the reaction mixture changed from yellow to orange-red in the synthesis of 3, and from pale yellow to green in the synthesis of 4. No further color change was observed for either reaction mixture upon warming to ambient temperature.



Compound 3 is thermally stable over a long period of time when stored in an inert atmosphere in a glove box, whereas 4 decomposes slowly under the same conditions to form an insoluble gray solid within four days. However, 4 is stable at -32 °C over a longer period of time. Both 3 and 4 are air- and moisture-sensitive and were characterized by IR spectroscopy, multinuclear NMR spectroscopy, single-crystal X-ray structural analysis, and DFT calculations. In the IR spectrum of **3**, a strong absorption was observed at  $1733 \text{ cm}^{-1}$ , which can be attributed to the Ge-H stretching mode and compares well with that reported for  $Ar'(H)GeGe(H)Ar'^{[13]}$  (1785 cm<sup>-1</sup>;  $Ar' = 2,6-Dipp_2C_6H_3$ ,  $Dipp = 2,6-iPr_2C_6H_3$ ), but is found at a lower frequency than that for [{HC(CMeNAr)<sub>2</sub>}Ge(H)BH<sub>3</sub>] (1928 cm<sup>-1</sup>).<sup>[7]</sup> Hydride complexes of germanium(IV) show Ge–H absorptions in the range from 1953 to 2175 cm $^{-1}$ .<sup>[3a, 14–16]</sup> The Sn-H stretching mode of 4 (1849  $\text{cm}^{-1}$ ) is comparable to those in the hydrogen-bridged tin compound [{2,6-Trip\_2C\_6H\_3Sn( $\mu$ -H)}\_2] (1828, 1771 cm<sup>-1</sup>).<sup>[4]</sup> In the <sup>1</sup>H NMR spectrum of 3, the Ge-H hydrogen atom resonates at lower field ( $\delta = 8.08$  ppm) than those in Ar'(H)GeGe(H)Ar' ( $\delta =$ 3.48 ppm) and Ar'(H)<sub>2</sub>GeGeAr'·PMe<sub>3</sub> ( $\delta = 3.81$  ppm).<sup>[13]</sup> Interestingly, the Ge-H proton resonance of 3 is in the range of germanium(IV) hydrides.<sup>[17]</sup> The Sn-H proton resonance of **4** is found at a surprisingly low-field shift ( $\delta =$ 13.83 ppm) relative to that in  $[\{2,6-\text{Trip}_2C_6H_3\text{Sn}(\mu-H)\}_2]$  ( $\delta =$ 7.87 ppm), and is flanked by Sn satellites  $({}^{1}J({}^{119}Sn, {}^{1}H) =$ 64 Hz).<sup>[4]</sup> The Sn-H resonance of 4 is the lowest-field chemical shift observed for a tin hydride.[3a, 18-20] The <sup>119</sup>Sn NMR resonance of **4** ( $\delta = -224.7$  ppm) is in accordance with a three-coordinate tin(II) environment ([{HC-(CMeNAr)<sub>2</sub>]SnCl]:  $\delta = -224 \text{ ppm};^{[7]}$  [{H<sub>2</sub>B(pz)<sub>2</sub>}SnCl]:  $\delta =$ -305 ppm; [{Ph<sub>2</sub>B(pz)<sub>2</sub>}SnCl]:  $\delta = -353 \text{ ppm};$  [{H<sub>2</sub>B- $(pz')_{2}$ SnCl]:  $\delta = -271$  ppm; pz = pyrazole, pz' = 3-methylpyrazole).<sup>[21]</sup>

Orange-red single crystals of **3** and green crystals of **4** suitable for X-ray structural analysis<sup>[22]</sup> were grown from saturated hexane solutions at -32 °C within two days (**3**) or

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after one week (4). Compound **3** crystallizes in the monoclinic space group  $P2_1/n$  with two independent isostructural monomers in the asymmetric unit. Although the Ge–H hydrogen atom in **3** could not be localized in the difference electrondensity map, the Ge–H linkage was unequivocally confirmed by IR and <sup>1</sup>H NMR spectroscopy (see above). In **3**, the germanium atom is tetrahedrally coordinated by the  $\beta$ diketiminato ligand, a hydrogen atom, and, we assume, a lone pair of electrons at the fourth coordination site (Figure 1). Compound **3** exhibits Ge–N bond lengths of 1.989(2) Å (molecule 1) as well as 1.994(2) and 1.988(2) Å (molecule 2), and these lengths are very similar to those of **1** (1.988(2), 1.997(2) Å).<sup>[6]</sup>



**Figure 1.** Thermal-ellipsoid plot of one molecule of **3** at the 50% probability level. Hydrogen atoms are omitted for clarity. The Ge-H hydrogen atom could not be localized. Only the numbering scheme of molecule 1 is depicted. Selected bond lengths [Å] and angles [°]: molecule 1: Ge(1)-N(1) 1.989(2), Ge(1)-N(2) 1.989(2), N(1)-Ge(1)-N(2) 90.3(1); molecule 2: Ge(2)-N(1A) 1.994(2), Ge(2)-N(2A) 1.988(2), N(1A)-Ge(2)-N(2A) 90.5(1).

Compound 4 crystallizes in the monoclinic space group C2/c with one monomer in the asymmetric unit. Weak intermolecular contacts between the lone pair of electrons on the tin atom and the Sn-H hydrogen atom from another molecule generate hydrogen bridges and formation of a dimer (d(Sn(1)···H(1A)): 4.01(3) Å; d(Sn···Sn): 3.71 Å). Compound 4 comprises a distorted tetrahedral geometry at the tin atom, which coordinates to a monoanionic β-diketiminato ligand, a hydrogen atom, and, we assume, a lone pair of electrons at the fourth coordination site (Figure 2). The Sn-H hydrogen atom was localized from the residual electron density. The most prominent structural feature of 4 is the Sn-H bond length of 1.74(3) Å, which is in good agreement with Sn-H bond lengths predicted by theoretical calculations (1.77 Å).<sup>[5,25]</sup> However, this length is shorter than those of [{2,6- $Trip_2C_6H_3Sn(\mu-H)$ ]2], which exhibits two different  $\mu$ -hydrogen bonds (d(Sn-H): 1.89(3), 1.95(3) Å).<sup>[4]</sup>

To investigate the electronic properties of **3** and **4**, ab initio calculations were carried out by using the Gaussian program package<sup>[26]</sup> with the well-established DFT-variant B3LYP.<sup>[27-29]</sup> Two different basis sets were employed to achieve a suitable description of the electronic structure. The LANL2DZ<sup>[30]</sup> basis set (for Ge and Sn) and the 6-



**Figure 2.** Thermal-ellipsoid plot of **4** at the 50% probability level. Carbon-bound H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Sn(1)-H(1) 1.74(3), Sn(1)-N(1) 2.195(2), Sn(1)-N(2) 2.198(2), Sn(1)-··H(1A) 4.01(3); H(1)-Sn(1)-N(1) 93.4(8), H(1)-Sn(1)-N(2) 92.6(8), N(1)-Sn(1)-N(2) 85.1(1).

31G<sup>[31,32]</sup> basis set (for the remaining atoms) with additional double-diffuse functions were used. The structures of both complexes were determined by full geometry optimization. The obtained equilibrium geometries were in good agreement with the X-ray data. Since the structural parameters are the result of the calculated molecular orbitals, an analysis of the electronic structure was perfomed with the natural bond order (NBO)<sup>[33]</sup> procedure, which makes it possible to describe and quantify the contribution of the atomic orbitals to the molecular orbitals. The calculations showed that the electron density of the lone pair on the central atom in each of 3 and 4 contributes to the bonding in the complex. The NBO analysis of the M-H bond shows that the contribution of the lone pair of electrons on germanium can best be described as an  $sp^{0.32}$  hybrid, while the hybrid for tin is of the type  $sp^{0.25}$  (see the Supporting Information). The larger p character at the Ge center in compound 3 (20% greater than that at the Sn center in 4) leads to an enhanced delocalization of  $\pi$  electrons over the neighboring p orbitals of the nitrogen atoms. Remarkably, in the case of 4, there is no participation of the hydrogen s orbital in the lone pair of electrons.

Analysis of the metal-hydrogen bond by using the natural localized molecular orbitals (NLMO) reveals significant differences between **3** and **4**. For the Ge-H bond in **3**, the hydrogen atom contributes 65%, and the corresponding hydrogen atom in the Sn-H bond contributes 70%. Analysis of the molecular orbitals of **4** also shows that there is no participation of the hydrogen s orbital in the wave function describing the lone pair of electrons. Another factor that influences the electron density at the hydrogen atom is the amount of donor-acceptor interaction with the nitrogen atoms of the ring system. This interaction occurs mainly through two-electron stabilization in a donor-acceptor situation<sup>[34]</sup> involving the bonding Ge-H orbital and nonbond-

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ing orbitals of the ring system, which transfers electron density from the nitrogen atoms into the Ge–H bond. This effect is 50% larger for **3** than for **4**. Taking these findings into account, the low-field chemical shift of the hydrogen atom in **4** might be deduced. The lack of further stabilization from delocalization causes the tin atom to pull out electron density strongly from the hydride ligand to compensate for its electron-deficient character. Hence, the "naked" nature of the hydrogen atom in the Sn–H bond is a reflection of extreme deshielding and leads to such a low-field chemical shift.

In summary, we were able to isolate and structurally characterize compounds of composition [{HC-(CMeNAr)<sub>2</sub>]GeH] and [{HC(CMeNAr)<sub>2</sub>}SnH] by the reactions of AlH<sub>3</sub>·NMe<sub>3</sub> with the appropriate chloride precursors. These compounds represent the first examples of terminal, monomeric hydrides of germanium(II) and tin(II).

### **Experimental Section**

All manipulations were performed in a dry and oxygen-free atmosphere ( $N_2$  or Ar) by using Schlenk-line and glove-box techniques. Solvents were purified prior to use by distillation over appropriate drying agents under nitrogen.

3: A solution of AlH<sub>3</sub>·NMe<sub>3</sub> (1.18 mL, 1.0 m in toluene) was slowly added to a solution of 1 (0.62 g, 1.18 mmol) in toluene (25 mL) at -4 °C, and the yellow solution immediately turned to orange-red. The cooling bath was removed after 20 min, and stirring of the solution was continued until the elimination of NMe3 had ceased. All volatiles were removed in vacuum, and the remaining orange-red residue was extracted with n-hexane (15 mL). The solvent was removed in vacuo to yield 3 as an orange-red powder. Yield: 0.32 g (60%); m.p. 170°C (decomp); IR (KBr pellet):  $\tilde{\nu} = 1733 \text{ cm}^{-1}$  (s, GeH); <sup>1</sup>H NMR (300 MHz,  $C_6D_6$ , 25 °C, TMS):  $\delta = 8.08$  (s, 1 H, GeH), 7.15–7.07 (m, 6H, ArH), 4.92 (s, 1H,  $\gamma$ -CH), 3.58 (sept,  ${}^{3}J(H,H) =$ 6.8 Hz, 2H,  $CH(CH_3)_2$ ), 3.41 (sept,  ${}^{3}J(H,H) = 6.8$  Hz, 2H,  $CH(CH_3)_2$ ), 1.55 (s, 6H, CH<sub>3</sub>), 1.37 (d,  ${}^{3}J(H,H) = 6.8$  Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.29 (d,  ${}^{3}J(H,H) = 6.8 \text{ Hz}, 6 \text{ H}, CH(CH_{3})_{2}, 1.19 \text{ (d, } {}^{3}J(H,H) = 6.8 \text{ Hz}, 6 \text{ H},$  $CH(CH_3)_2)$ , 1.17 ppm (d,  ${}^{3}J(H,H) = 6.8 Hz$ , 6H,  $CH(CH_3)_2)$ ; <sup>13</sup>C NMR (125.8 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C, TMS):  $\delta = 167.5$  (CN), 146.5, 143.5, 141.6, 127.3, 124.6, 124.3 (Ar), 97.8 (y-CH), 29.0 (CH<sub>3</sub>), 28.2 (CH(CH<sub>3</sub>)<sub>2</sub>), 27.0 (CH(CH<sub>3</sub>)<sub>2</sub>), 24.8 (CH(CH<sub>3</sub>)<sub>2</sub>), 24.4 (CH(CH<sub>3</sub>)<sub>2</sub>), 23.7 (CH(CH<sub>3</sub>)<sub>2</sub>), 22.8 ppm (CH(CH<sub>3</sub>)<sub>2</sub>); EI-MS (70 eV): *m*/*z* (%): 491 (100) [M-H]<sup>+</sup>, 449 (40) [M-iPr]<sup>+</sup>. Elemental analysis (%) calcd for  $C_{29}H_{42}GeN_2$  (491.26): C 70.69, H 8.60, N 5.70; found: C 70.20, H 8.53, N 5.36.

4: A solution of 2 (1.85 g, 3.24 mmol) in toluene (30 mL) was cooled to -4°C and added slowly to a solution of AlH<sub>3</sub>·NMe<sub>3</sub> (3.24 mL, 1.0 m in toluene). The cooling bath was removed after 15 min, and the solution was stirred further until NMe<sub>3</sub> elimination had ceased. The color of the solution changed from pale yellow to green. The solvent was removed in vacuo, and the green residue was extracted with *n*-hexane. The solvent was removed to afford 4 as a green powder. Yield: 1.58 g (91%); m.p. 125°C (decomp); IR (KBr pellet):  $\tilde{\nu} = 1849 \text{ cm}^{-1}$  (m, SnH); <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C, TMS):  $\delta = 13.83$  (s,  ${}^{1}J({}^{119}\text{Sn},{}^{1}\text{H}) = 64$  Hz, 1 H, SnH), 7.15–7.06 (m, 6H, ArH), 4.89 (s, 1H,  $\gamma$ -CH), 3.52 (sept,  ${}^{3}J(H,H) = 6.8$  Hz, 2H, CH- $(CH_3)_2$ ), 3.46 (sept,  ${}^{3}J(H,H) = 6.8$  Hz, 2H,  $CH(CH_3)_2$ ), 1.62 (s, 6H, CH<sub>3</sub>), 1.34 (d,  ${}^{3}J(H,H) = 6.8$  Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.27 (d,  ${}^{3}J(H,H) =$ 6.8 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.19 (d,  ${}^{3}J(H,H) = 6.8$  Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.17 ppm (d,  ${}^{3}J(H,H) = 6.8$  Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>);  ${}^{13}C$  NMR (125.8 MHz,  $C_6D_6$ , 25°C, TMS):  $\delta = 167.7$  (CN), 145.5, 143.0, 142.8, 126.8, 124.7, 124.3 (Ar), 98.3 (γ-CH), 29.0 (CH<sub>3</sub>), 27.8 (CH(CH<sub>3</sub>)<sub>2</sub>), 26.8 (CH(CH<sub>3</sub>)<sub>2</sub>), 24.8 (CH(CH<sub>3</sub>)<sub>2</sub>), 24.4 (CH(CH<sub>3</sub>)<sub>2</sub>), 24.0 (CH-  $(CH_3)_2$ ), 23.4 ppm (CH( $CH_3$ )<sub>2</sub>); <sup>119</sup>Sn NMR (186.5 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C, Me<sub>4</sub>Sn):  $\delta = -224.7$  ppm; EI-MS (70 eV): m/z (%): 537 (5)  $[M-H]^+$ . Elemental analysis (%) calcd for C<sub>29</sub>H<sub>42</sub>N<sub>2</sub>Sn (537.36): C 64.82, H 7.88, N 5.21; found: C 64.20, H 7.45, N 5.33.

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- [1] a) H. D. Kaesz, R. B. Saillant, Chem. Rev. 1972, 72, 231–281;
  b) G. S. McGrady, G. Guilera, Chem. Soc. Rev. 2003, 32, 383–392;
  c) S. Aldridge, A. J. Downs, Chem. Rev. 2001, 101, 3305–3365;
  d) H.-J. Himmel, Dalton. Trans. 2003, 3639–3649;
  e) H.-J. Himmel, Z. Anorg. Allg. Chem. 2005, 631, 1551–1564;
  f) N. W. Mitzel, Angew. Chem. 2003, 115, 3984–3986; Angew. Chem. Int. Ed. 2003, 42, 3856–3858;
  g) W. M. Mueller, J. P. Blackledge, G. G. Libowitz, Metal Hydrides, Academic Press, London, 1968, pp. 1–21;
  h) F. Lefebvre, J.-M. Basset, Main Group Met. Chem. 2002, 25, 15–32;
  i) J. Zhao, A. S. Goldman, J. F. Hartwig, Science 2005, 307, 1080–1082.
- [2] a) R. F. Service, *Science* 2004, 305, 958–961; b) J. A. Turner, *Science* 2004, 305, 972–974; c) W. Grochala, P. P. Edwards, *Chem. Rev.* 2004, 104, 1283–1315; d) F. Schüth, B. Bogdanović, M. Felderhoff, *Chem. Commun.* 2004, 2249–2258.
- [3] a) E. J. Kupchik in Organotin Compounds, Vol. 1 (Ed.: A. K. Sawyer), Marcel Dekker, New York, 1971, pp. 7-72; b) A. G. Davies, P. J. Smith in Comprehensive Organometallic Chemistry, Vol. 2 (Eds.: G. Wilkinson, F. G. A. Stone, E. W. Abel), Pergamon, Oxford, 1982, pp. 584-585; c) M. Lesbre, P. Mazerolles, J. Satgé, The Organic Compounds of Germanium, Wiley, London, 1971, pp. 259-265; d) P. Rivière, M. Rivière-Baudet, J. Satgé, in Comprehensive Organometallic Chemistry, Vol. 2 (Eds.: G. Wilkinson, F. G. A. Stone, E. W. Abel), Pergamon, Oxford, 1982, pp. 424-425; for some selected applications of Group 14 hydrides in organic synthesis, see: e) V. I. Dodero, M. B. Faraoni, D. C. Gerbino, L. C. Koll, A. E. Zuñiga, T. N. Mitchell, J. Podestá, Organometallics 2005, 24, 1992-1995; f) D. S. Hays, G. C. Fu, J. Org. Chem. 1997, 62, 7070-7071; g) V. I. Dodero, L. C. Koll, M. B. Faraoni, T. N. Mitchell, J. Podestá, J. Org. Chem. 2003, 68, 10087-10091; h) V. I. Dodero, T. N. Mitchell, J. Podestá, Organometallics 2003, 22, 856-860; i) K. Sasaki, Y. Kondo, K. Maruoka, Angew. Chem. 2001, 113, 425-428; Angew. Chem. Int. Ed. 2001, 40, 411-414.
- [4] B. E. Eichler, P. P. Power, J. Am. Chem. Soc. 2000, 122, 8785– 8786.
- [5] G. Trinquier, J. Am. Chem. Soc. 1990, 112, 2130-2137.
- [6] Y. Ding, H. Hao, H. W. Roesky, M. Noltemeyer, H.-G. Schmidt, Organometallics 2001, 20, 4806–4811.
- [7] Y. Ding, H. W. Roesky, M. Noltemeyer, H.-G. Schmidt, Organometallics 2001, 20, 1190–1194.
- [8] R. A. Kovar, J. O. Callaway, Inorg. Synth. 1976, 22, 37-47.
- [9] H. W. Roesky, Aldrichimica Acta 2004, 37, 103–108.
- [10] S. S. Kumar, H. W. Roesky, Dalton Trans. 2004, 3927-3937.
- [11] Alternatively, compound 3 could also be prepared in good yield by the reaction of [{HC(CMeNAr)<sub>2</sub>}GeOH]<sup>[12]</sup> and AlH<sub>3</sub>·NMe<sub>3</sub>.
- [12] L. W. Pineda, V. Jancik, H. W. Roesky, D. Neculai, A. M. Neculai, Angew. Chem. 2004, 116, 1443–1445; Angew. Chem. Int. Ed. 2004, 43, 1419–1421.
- [13] A. F. Richards, A. D. Phillips, M. M. Olmstead, P. P. Power, J. Am. Chem. Soc. 2003, 125, 3204–3205.
- [14] A. Castel, P. Rivière, J. Satgé, H. Y. Ko, Organometallics 1990, 9, 205-210.

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- [15] F. Riedmiller, G. L. Wegner, A. Jockisch, H. Schmidbaur, Organometallics 1999, 18, 4217–4324.
- [16] P. Rivière, J. Satgé, Bull. Soc. Chim. Fran. 1967, 11, 4039-4046.
- [17] G. H. Spikes, J. C. Fettinger, P. P. Power, J. Am. Chem. Soc. 2005, 127, 12232–12233.
- [18] M. L. Maddox, N. Flitcroft, H. D. Kaesz, J. Organomet. Chem. 1965, 4, 50–56.
- [19] G. Yamamoto, S. Ohta, M. M. Kaneko, K. Mouri, M. Ohkuma, R. Mikami, Y. Uchiyama, M. Minoura, *Bull. Chem. Soc. Jpn.* 2005, 78, 487–497.
- [20] F. Schager, R. Goddard, K. Seevogel, K.-R. Pörschke, Organometallics 1998, 17, 1546–1551.
- [21] M. N. Hansen, K. Niedenzu, J. Serwatowska, J. Serwatowski, K. R. Woodrum, *Inorg. Chem.* 1991, 30, 866–868.
- [22] a) Crystal data for 3:  $C_{29}H_{42}GeN_2$ ,  $M_r = 491.24$ , crystal dimensions  $0.10 \times 0.05 \times 0.02 \text{ mm}^3$ , monoclinic, space group  $P2_1/n$ , a =15.238(3), b = 18.201(4), c = 20.485(4) Å,  $\beta = 99.11(3)^{\circ}$ , V =5610(2) Å<sup>3</sup>, Z = 8,  $\rho_{calcd} = 1.163 \text{ g cm}^{-3}$ , F(000) = 2096,  $\lambda =$ 1.54178 Å, T = 100(2) K,  $\mu(Cu_{K\alpha}) = 1.593$  mm<sup>-1</sup>. Of the 35990 measured reflections, 7983 were independent (R(int) = 0.0418). The final refinements converged to R1 = 0.0388 for  $I > 2\sigma(I)$ , wR2 = 0.1035 for all data. The final difference Fourier synthesis gave a min/max residual electron density of -0.476/ + 1.47 e Å<sup>-3</sup>; b) crystal data for **4**:  $C_{29}H_{42}SnN_2$ ,  $M_r = 537.34$ , crystal dimensions  $0.10 \times 0.05 \times 0.05$  mm<sup>3</sup>, monoclinic, space group C2/c, a =25.209(5), b = 15.139(3), c = 14.682(3) Å,  $\beta = 94.92(3)^{\circ}$ , V =5583(2) Å<sup>3</sup>, Z = 8,  $\rho_{\text{calcd}} = 1.279 \text{ g cm}^{-3}$ , F(000) = 2240,  $\lambda =$ 1.54178 Å, T = 100(2) K,  $\mu(Cu_{K\alpha}) = 7.392$  mm<sup>-1</sup>. Of the 22645 measured reflections, 4000 were independent (R(int) = 0.0315). The final refinements converged to R1 = 0.0216 for  $I > 2\sigma(I)$ , wR2 = 0.0548 for all data. The final difference Fourier synthesis gave a min/max residual electron density of -0.745/  $+0.749 \text{ e} \text{Å}^{-3}$ ; c) data for the structures were collected on a Bruker three-circle diffractometer, which was equipped with a SMART 6000 CCD detector. Intensity measurements were performed on a rapidly cooled crystal in the ranges  $6.54 \le 2\theta \le$  $117.94^{\circ}$  (3) and  $6.82 \le 2\theta \le 117.80^{\circ}$  (4). The structures were solved by direct methods with SHELXS-97<sup>[23]</sup> and refined for all data by full-matrix least squares on  $F^{2, [24]}$  All non-H atoms for **3** and 4 were refined anisotropically, and all H atoms for 3 and 4, except for the  $\gamma$ -C-H hydrogen atoms H(3A) and H(3AA) in 3 (the packing diagram shows chain formation through weak intermolecular interactions between the lone pair of electrons at the Ge atom and the y-C-H hydrogen atom of another molecule), were included in geometrically idealized positions and refined with the riding model. Localization of the H(3A) and H(3AA) atoms from the electron-density maps in 3 proved to be more accurate than fixing the atoms in the idealized positions and led to lower R1 and wR2 values. The Sn-H hydrogen atom in 4 was localized from the difference electrondensity map and refined isotropically with  $U_{ii}$  tied to the parent atom. CCDC-291156 and CCDC-291157 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.
- [23] SHELXS-97, Program for Structure Solution: G. M. Sheldrick, Acta Crystallogr. Sect. A 1990, 46, 467–473.
- [24] G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, Göttingen (Germany), 1997.
- [25] K. Balasubramanian, J. Chem. Phys. 1988, 89, 5731-5738.
- [26] Gaussian 03 (Revision C.02): M. J. Frisch et al., see the Supporting Information.
- [27] C. Lee, W. Yang, R. G. Parr, Phys. Rev. B 1988, 37, 785-789.
- [28] B. Miehlich, A. Savin, H. Stoll, H. Preuss, Chem. Phys. Lett. 1989, 157, 200–206.
- [29] A. D. Becke, J. Chem. Phys. 1993, 98, 5648-5652.

Angew. Chem. Int. Ed. 2006, 45, 2602-2605

- [30] a) P. J. Hay, W. R. Wadt, J. Chem. Phys. 1985, 82, 270–283;
  b) W. R. Wadt, P. J. Hay, J. Chem. Phys. 1985, 82, 270–298;
  c) P. J. Hay, W. R. Wadt, J. Chem. Phys. 1985, 82, 299–310.
- [31] G. A. Petersson, M. A. Al-Laham, J. Chem. Phys. 1991, 94, 6081-6090.
- [32] G. A. Petersson, A. Bennett, T. G. Tensfeldt, M. A. Al-Laham, W. A. Shirley, J. Mantzaris, *J. Chem. Phys.* **1988**, *89*, 2193–2218.
- [33] a) J. E. Carpenter, F. Weinhold, J. Mol. Struct. 1988, 169, 41-62;
  b) J. P. Foster, F. Weinhold, J. Am. Chem. Soc. 1980, 102, 7211-7218;
  c) A. E. Reed, F. Weinhold, J. Chem. Phys. 1985, 83, 1736-1740;
  d) A. E. Reed, L. A. Curtiss, F. Weinhold, Chem. Rev. 1988, 88, 899-926.
- [34] F. Weinhold, C. Landis, Valency and Bonding, University Press, Cambridge, 2005, pp. 19–20; F. Weinhold, C. Landis, Valency and Bonding, University Press, Cambridge, 2005, pp. 94–96; F. Weinhold, C. Landis, Valency and Bonding, University Press, Cambridge, 2005, pp. 125–128; F. Weinhold, C. Landis, Valency and Bonding, University Press, Cambridge, 2005, pp. 184–188.