Supporting Information

For

Oxidative Addition of Ammonia at a Silicon(II) Center and a Unprecedented Hydrogenation Reaction of Compounds with Low Valent Group 14 Elements Using Ammonia Borane

Anukul Jana, Carola Schulzke, and Herbert W. Roesky*

Institut für Anorganische Chemie der Universität Göttingen, Tammannstrasse 4, 37077 Göttingen, Germany

* To whom correspondence should be addressed. Fax: +49-551-393373.

Email: hroesky@gwdg.de

Contents:

(1) Experimental Section

All manipulations were carried out under anaerobic and anhydrous conditions with Schlenk techniques.

(a) L′Si(H)NH_2 (**2**): Dry ammonia gas was added to a yellow solution of **1** (0.45 g, 1 mmol) in toluene (20 mL) at room temperature. The reaction mixture became colorless. Then the ammonia gas was bubbled through the solution for additional 15 min. After that the solvent was removed in vacuum and the residue was extracted with *n*-hexane (30 mL). The solution was reduced to half of the volume. Storage of the solution at –32 °C in a freezer for two days yielded colorless crystals suitable for single crystal X-ray diffraction studies. Yield: 0.41 g (90%); mp 223 °C. ^{1}H NMR (500 MHz, C_6D_6): δ = 7.02-7.22 (m, 6H, Ar-*H*), 5.31 (s, 1H, γ-C*H*), 4.97 (t, 1H, Si-*H*), 3.93 (s, 1H, CH_2), 3.62 (sept, 2H, C*H*$(CH_3)_2$), 3.59 (sept, 2H, C*H*$(CH_3)_2$), 3.35 (s, 1H, CH_2), 1.49 (s, 3H, CH_3), 1.40 (d, 6H, CH(CH_3)$_2$), 1.22-1.18 (m, 18H, CH(CH_3)$_2$), 0.35 (br, 2H, NH_2) ppm. IR (Nujol, KBr): $\tilde{\nu}$ = 3477, and 3382 (N-H), and 2633 (Si-H) cm $^{-1}$. EI-MS (70 eV): *m*/*z* (%): 446 (100) $[M\text{-}CH_3]^+$. Anal. calcd for $C_{29}H_{43}N_3Si$ (461.76): C, 75.43; H, 9.39; N, 9.10. Found: C, 75.10; H, 9.41; N, 9.14.

(b) **5**: 1,3-Di-*tert*-butylimidazol-2-ylidene (0.360 g, 2.0 mmol) and NH_3BH_3 (0.060 g, 2.0 mmol) were dissolved in toluene (30 mL) at room temperature. The reaction mixture was stirred overnight, then the solvent was removed in vacuum and the residue was extracted with *n*-hexane (30 mL). Yield: 0.630 g (95%). ^{1}H NMR (200 MHz, C_6D_6): δ = 5.48 (s, 2H, C-*H*), 4.24 (s, 2H, CH_2), 1.01 (s, 18H, C(CH_3)$_3$) ppm.[S1]

(c) LGeH (**6**): L′Ge (0.490 g, 1 mmol) and NH_3BH_3 (0.030 g, 1.0 mmol) were dissolved in toluene (20 mL) at room temperature. The color of the reaction mixture changed from brown red to red. The reaction mixture was stirred further for one hour. Then the solvent was removed in vacuum and the residue was extracted with *n*-hexane (30 mL). Yield: 0.42 g (85 %); mp 170 °C. ^{1}H NMR (200 MHz, C_6D_6): δ = 7.10-7.15 (m, 6H, Ar-*H*), 4.86 (s, 1H, γ-C*H*), 3.59 (sept, 2H, C*H*$(CH_3)_2$), 3.37 (sept, 2H, C*H*$(CH_3)_2$), 1.60 (s, 6H, CH_3), 1.35 (d, 6H, CH(CH_3)$_2$), 1.22 (d, 6H, CH(CH_3)$_2$), 1.19 (d, 12H, CH(CH_3)$_2$), ppm. [S2]

(2) X-ray crystallography

A suitable crystal of **2** was mounted on a glass fiber and data was collected on an IPDS II Stoe image-plate diffractometer (graphite monochromated Mo Kα radiation, λ = 0.71073 Å) at 133(2) K. The data was integrated with X-area. The structures were solved by Direct Methods (SHELXS-97)[S3] and refined by full-matrix least square methods against F^2 (SHELXL-97).[S3] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model, except H1 at silicon Si1 and H1N and H2N at nitrogen N1 we found. $C_{29}H_{43}N_3Si$, M = 461.75 g mol^{-1}, crystal size 0.28 x 0.19 x0.14 mm, orthorhombic, *Pbca*, a = 1552.9(5) pm, b = 1729.6(4) pm, c = 2089.7(4) pm, V = 5613(2) Å^3; Z = 8, $\rho_{calc.}$ = 1.093 Mg/m^3, μ = 0.104 mm^{-1}, T = 133(2) K, $2\theta_{max}$ = 53.96°, 51543 reflections measured, of which 6091 were independent, R_{int} = 0.0782, $R1$ = 0.0625 [$I > 2\sigma(I)$], $wR2$ = 0.1523 (all data), 1.007 / –0.452 e Å^{-3} residual densities. Complete crystallographic data are deposited at the Cambridge Crystallographic Data Centre, where it can be downloaded free of charge from www.ccdc.cam.ac.uk/ data_request/cif: at CCDC-717497.

[S1] Denk, M. K.; Rodezno, J. M.; Gupta, S.; Lough, A. J. *J. Organomet. Chem.* **2001**, *617-618*, 242-253.

[S2] (a) Pineda, L. W.; Jancik, V.; Starke, K.; Oswald, R. B.; Roesky, H. W. *Angew. Chem.* **2006**, *118*, 2664-2667; *Angew. Chem., Int. Ed.* **2006**, *45*, 2602-2605; (b) Jana, A.; Ghoshal, D.; Roesky, H. W.; Objartel, I.; Schwab, G.; Stalke, D. *J. Am. Chem. Soc*. **2009***, 131*, 1288-1293.

[S3] Sheldrick, G. M. *Acta Crystallogr. Sect. A* **2008**, *64*, 112-120.