

Bis[*N,N'*-diisopropylbenzamidinato(–)]silicon(II): A Silicon(II) Compound with Both a Bidentate and a Monodentate Amidinato Ligand

Konstantin Junold, Johannes A. Baus, Christian Burschka, and Reinhold Tacke*

Dedicated to Professor Gerd Müller on the occasion of his 70th birthday

In the past two decades, stable silylenes have attracted much attention owing to their unique structural features and reactivity.^[1–4] Silylenes with two-coordinate silicon have been studied extensively,^[2] while higher-coordinate silicon(II) species are still relatively rare.^[3,4] In this context, three- and four-coordinate amidinato-substituted silicon(II) compounds should be mentioned.^[4]

In continuation of our systematic studies on higher-coordinate silicon(IV) complexes,^[5] we have succeeded in synthesizing the six-coordinate bis(amidinato)silicon(IV) complex **1** (Scheme 1).^[6] Inspired by a recent study by

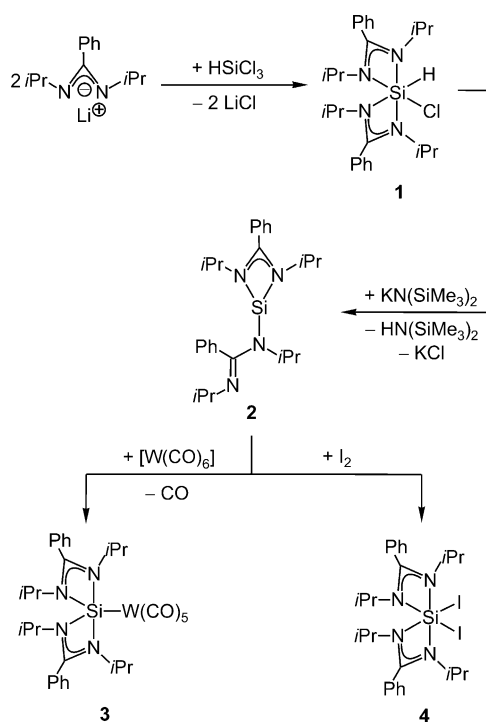
Roesky et al.,^[4d] we transformed **1** into the three-coordinate silicon(II) species **2** by using a reductive HCl elimination. Compound **2** can be described as a donor-stabilized silylene with both a bidentate and a monodentate amidinato ligand. With the imino group (a potential donor function) of its monodentate ligand, this silicon(II) species offers an interesting reactivity profile. Herein we present the syntheses of **1** and **2** and the results of preliminary reactivity studies of **2**.

Compound **1** was synthesized by treatment of trichlorosilane with two molar equivalents of lithium *N,N'*-diisopropylbenzamidinate in diethyl ether (–20°C to 20°C, 70% yield; Scheme 1). Reaction of **1** with one molar equivalent of potassium bis(trimethylsilyl)amide in toluene at 20°C afforded compound **2** (86% yield; Scheme 1).

To obtain some information about the reactivity of **2**, it was treated with tungsten hexacarbonyl and iodine, respectively (Scheme 1). Reaction of **2** with one molar equivalent of [W(CO)₆] in toluene at 20°C afforded **3** (89% yield). Treatment of **2** with one molar equivalent of I₂ in toluene at 20°C resulted in an oxidative addition to give **4** (89% yield). To the best of our knowledge, compound **3** with its SiN₄W skeleton is the first five-coordinate silicon(II) species reported, and compound **4** with its SiN₄I₂ skeleton is the first structurally characterized six-coordinate silicon(IV) complex with Si–I bonds.

The identities of the crystalline compounds **1–4** were established by elemental analyses (C, H, N), NMR spectroscopic studies in the solid state (¹⁵N, ²⁹Si) and in solution (¹H, ¹³C, ¹⁵N (**2** and **3** only), ²⁹Si),^[6] and crystal structure analyses.^[7] The molecular structures of **1–4** are depicted in Figures 1–4, respectively.

The silicon coordination polyhedra of the six-coordinate silicon(IV) complexes **1** (Figure 1) and **4** (Figure 4) are strongly distorted octahedra, with the two monodentate ligands in *cis* positions. The maximum deviations from the ideal 90 and 180° angles range from 20.38(11) to 22.19(9)° and from 15.14(8) to 17.24(9)°, respectively. These strong distortions mainly result from the two highly strained four-membered SiN₂C chelate rings formed by the silicon coordination center and the bidentate amidinato ligands, with N–Si–N angles ranging from 67.89(9) to 70.17(11)°. Generally, the structural features of **1** and **4** are very similar to those observed for a series of related compounds, which contain two identical (pseudo)halogeno ligands (F, Cl, Br, CN, N₃, NCO, NCS) instead of the two monodentate ligands of **1** and **4**. The Si–I bond lengths of **4** (the first structurally characterized six-



Scheme 1. Syntheses of compounds **1–4**.

[*] Dipl.-Chem. K. Junold, Dipl.-Chem. J. A. Baus, Dr. C. Burschka, Prof. Dr. R. Tacke
Universität Würzburg, Institut für Anorganische Chemie
Am Hubland, 97074 Würzburg (Germany)
E-mail: r.tacke@uni-wuerzburg.de

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201203109>.

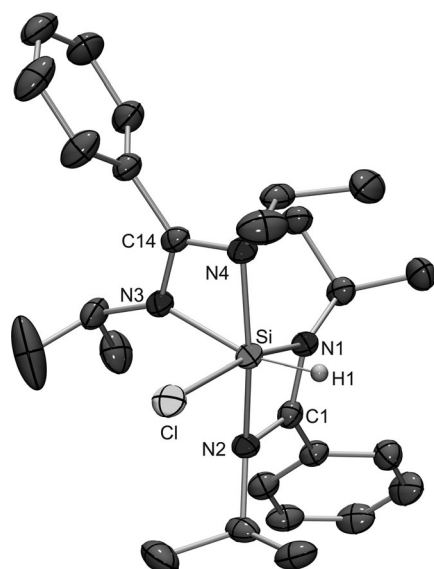


Figure 1. Molecular structure of **1** in the crystal (ellipsoids set at 50% probability; hydrogen atoms apart from H1 omitted for clarity). Selected bond lengths [Å] and angles [°]: Si–Cl 2.2518(11), Si–N1 1.969(2), Si–N2 1.887(2), Si–N3 1.962(2), Si–N4 1.876(2), Si–H1 1.42(2), N1–C1 1.315(3), N2–C1 1.352(3), N3–C14 1.320(3), N4–C14 1.333(3); Cl–Si–N1 164.53(7), Cl–Si–N2 96.36(7), Cl–Si–N3 89.16(7), Cl–Si–N4 93.80(7), Cl–Si–H1 92.1(8), N1–Si–N2 68.43(9), N1–Si–N3 90.29(9), N1–Si–N4 100.31(9), N1–Si–H1 92.9(8), N2–Si–N3 98.32(10), N2–Si–N4 162.76(9), N2–Si–H1 98.2(9), N3–Si–N4 67.89(9), N3–Si–H1 163.2(9), N4–Si–H1 95.3(9), N1–C1–N2 108.9(2), N3–C14–N4 107.9(2).

coordinate silicon(IV) species with Si–I bonds; 2.6441(8) and 2.6614(8) Å) are somewhat shorter than that reported for the only known five-coordinate silicon(IV) complex with an Si–I bond (2.7396(8) Å).^[8]

The silicon coordination polyhedron of **2** (Figure 2) is best described as a distorted pseudo-tetrahedron, with the lone pair as the fourth ligand. The two N–Si–N angles amount to 102.63(5) and 102.29(6)°, respectively. The Si–N bond length of the monodentate ligand (1.7885(12) Å) is significantly shorter than those of the bidentate ligand (1.9065(12) and 1.9026(12) Å), clearly reflecting the different coordination modes of the two amidinato ligands. Furthermore, the strong differences between the two N–C bond lengths in the monodentate ligand (1.2815(17) vs. 1.3978(16) Å) indicate the higher degree of localization of the N=C double bond compared to the bidentate ligand (1.3319(17) vs. 1.3314(17) Å).

The silicon coordination polyhedron of **3** (Figure 3) is a strongly distorted trigonal bipyramid, with one nitrogen atom of each of the two amidinato ligands in the axial positions (N_{ax}–Si–N_{ax}, 145.97(11)°; sum of the equatorial angles, 360.0°). The axial Si–N bond lengths (2.081(3) and 2.129(3) Å) are significantly longer than the equatorial bond lengths (1.806(3) and 1.808(2) Å). The Si–W bond length (2.5803(9) Å) is very similar to that found for comparable Si^{II}–W^[4] and Si^{IV}–W^[9] bonds. The tungsten coordination polyhedron is best described as a slightly distorted octahedron.

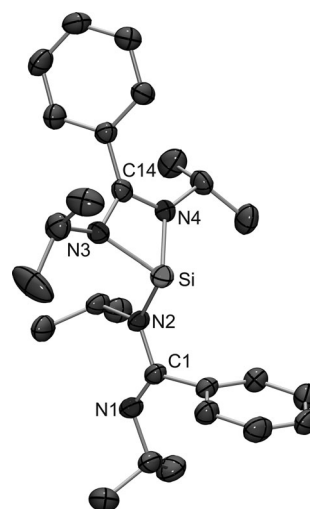


Figure 2. Molecular structure of **2** in the crystal (ellipsoids set at 50% probability; hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Si–N2 1.7885(12), Si–N3 1.9065(12), Si–N4 1.9026(12), N1–C1 1.2815(17), N2–C1 1.3978(16), N3–C14 1.3319(17), N4–C14 1.3314(17); N2–Si–N3 102.63(5), N2–Si–N4 102.29(6), N3–Si–N4 68.37(5), N1–C1–N2 121.22(12), N3–C14–N4 106.94(11), Si–N2–C1 119.85(9).

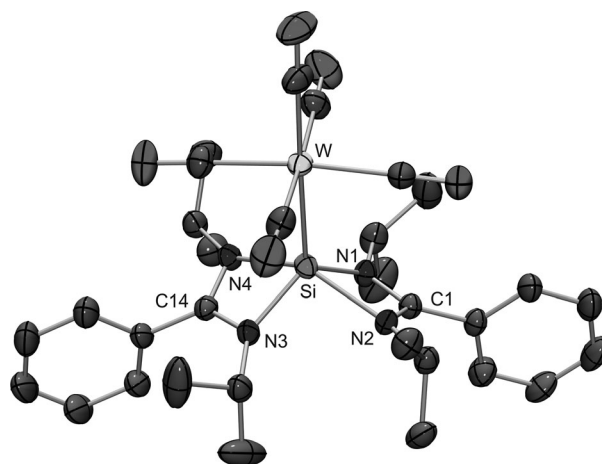


Figure 3. Molecular structure of **3** in the crystal (ellipsoids set at 50% probability; hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Si–W 2.5803(9), Si–N1 1.806(3), Si–N2 2.081(3), Si–N3 1.808(2), Si–N4 2.129(3), N1–C1 1.357(4), N2–C1 1.315(4), N3–C14 1.355(4), N4–C14 1.304(4); W–Si–N1 122.23(9), W–Si–N2 107.17(8), W–Si–N3 122.85(9), W–Si–N4 106.86(8), N1–Si–N2 67.42(11), N1–Si–N3 114.90(12), N1–Si–N4 93.68(11), N2–Si–N3 95.05(11), N2–Si–N4 145.97(11), N3–Si–N4 66.57(11), N1–C1–N2 108.6(2), N3–C14–N4 109.9(2).

The different coordination modes observed for the two amidinato ligands in the silicon(II) species **2** (bidentate and monodentate) and **3** (both bidentate) can be explained by the increased Lewis acidity of the silicon atom in **3** owing to the transfer of electron density from the silicon to the tungsten atom. NMR spectroscopy studies (see below) suggest that **2** contains an SiN₄ skeleton in solution (at least in terms of a transient species).

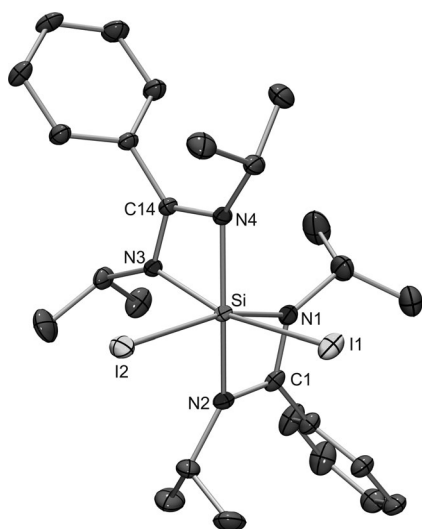


Figure 4. Molecular structure of **4** in the crystal (ellipsoids set at 50% probability; hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Si–I1 2.6614(8), Si–I2 2.6441(8), Si–N1 1.862(3), Si–N2 1.858(3), Si–N3 1.901(2), Si–N4 1.864(2), N1–C1 1.332(4), N2–C1 1.340(4), N3–C14 1.325(3), N4–C14 1.341(3); I1–Si–I2 90.84(3), I1–Si–N1 88.53(8), I1–Si–N2 94.21(8), I1–Si–N3 164.86(8), I1–Si–N4 95.32(8), I2–Si–N1 165.47(9), I2–Si–N2 95.41(8), I2–Si–N3 88.95(8), I2–Si–N4 94.55(8), N1–Si–N2 70.17(11), N1–Si–N3 95.41(11), N1–Si–N4 99.96(12), N2–Si–N3 100.88(11), N2–Si–N4 166.09(12), N3–Si–N4 69.62(10), N1–C1–N2 106.3(2), N3–C14–N4 107.5(2).

The isotropic ^{29}Si chemical shifts of **1**, **3**, and **4** in the solid state and in solution are very similar ($\Delta\delta^{29}\text{Si} = 0.8\text{--}5.9$ ppm), indicating that these compounds exist also in solution. In the case of **2**, this shift difference is significantly larger ($\Delta\delta^{29}\text{Si} = 16.0$ ppm), which could be explained by a rapid exchange of the four nitrogen sites, possibly involving a four-coordinate silicon(II) species with two bidentate amidinato ligands. This hypothesis is supported by the solution ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{15}\text{N}\{^1\text{H}\}$ NMR spectra of **2** measured in the temperature range -80 to 23°C (^1H : one doublet and one septet for $\text{CH}(\text{CH}_3)_2$; $^{13}\text{C}\{^1\text{H}\}$: two signals for $\text{CH}(\text{CH}_3)_2$; $^{15}\text{N}\{^1\text{H}\}$: one signal). The solution NMR spectra of **1**, **3**, and **4** show also a dynamic behavior in the temperature range -80 to 23°C ,^[5c] but there is no such a strong impact on the ^{29}Si chemical shifts as observed for **2**.

In conclusion, starting from the easily accessible six-coordinate silicon(IV) complex **1** (SiN₄ClH skeleton), we have succeeded in synthesizing the three-coordinate silicon(II) compound **2** (SiN₃, solid state), a donor-stabilized silylene, which could be easily obtained in high yield on a multigram scale. Treatment of **2** with [W(CO)₆] afforded the five-coordinate silicon(II) compound **3** (SiN₄W; reaction of **2** as a nucleophile), and treatment of **2** with I₂ resulted in an oxidative addition to give the six-coordinate silicon(IV) complex **4** (SiN₄I₂). With the transformations $\lambda^3\text{Si}^{\text{II}} \rightarrow \lambda^5\text{Si}^{\text{II}}$ (**2**→**3**) and $\lambda^3\text{Si}^{\text{II}} \rightarrow \lambda^6\text{Si}^{\text{IV}}$, it could be demonstrated that **2** may have a high potential for the synthesis of novel higher-coordinate silicon(II) and silicon(IV) compounds. Compared with other three-coordinate silicon(II) species, compound **2** with its additional imino functionality in the monodentate amidinato ligand formally reacts as a four-coordinate sili-

con(II) species and thereby offers quite new perspectives for both silicon(II) and silicon(IV) chemistry. We have started to investigate the synthetic potential of **2** and related bis(amidinato)silicon(II) and bis(guanidinato)silicon(II) compounds systematically.

Received: April 23, 2012

Published online: ■■ ■■, ■■■■

Keywords: coordination chemistry · N ligands · silicon compounds · silylenes · tungsten

- [1] For selected reviews dealing with stable silicon(II) compounds, see: a) S. Nagendran, H. W. Roesky, *Organometallics* **2008**, *27*, 457–492; b) Y. Mizuhata, T. Sasamori, N. Tokitoh, *Chem. Rev.* **2009**, *109*, 3479–3511; c) M. Asay, C. Jones, M. Driess, *Chem. Rev.* **2011**, *111*, 354–396; d) S. Yao, Y. Xiong, M. Driess, *Organometallics* **2011**, *30*, 1748–1767; e) S. S. Sen, S. Khan, P. P. Samuel, H. W. Roesky, *Chem. Sci.* **2012**, *3*, 659–682.
- [2] For selected publications dealing with stable two-coordinate silicon(II) compounds, see: a) M. Denk, R. Lennon, R. Hayash, R. West, A. V. Beljakov, H. P. Verne, A. Haaland, M. Wagner, N. Metzler, *J. Am. Chem. Soc.* **1994**, *116*, 2691–2692; b) B. Gehrhuss, M. F. Lappert, J. Heinicke, R. Boese, D. Bläser, *J. Chem. Soc. Chem. Commun.* **1995**, 1931–1932; c) B. Gehrhuss, P. B. Hitchcock, M. F. Lappert, J. Heinicke, R. Boese, D. Bläser, *J. Organomet. Chem.* **1996**, *521*, 211–220; d) R. West, M. Denk, *Pure Appl. Chem.* **1996**, *68*, 785–788; e) J. Heinicke, A. Oprea, M. K. Kindermann, T. Karpati, L. Nyulászi, T. Veszprémi, *Chem. Eur. J.* **1998**, *4*, 541–545; f) M. Haaf, A. Schmiedl, T. A. Schmedake, D. R. Powell, A. J. Millevolte, M. Denk, R. West, *J. Am. Chem. Soc.* **1998**, *120*, 12714–12719; g) M. Kira, S. Ishida, T. Iwamoto, C. Kabuto, *J. Am. Chem. Soc.* **1999**, *121*, 9722–9723; h) M. Driess, S. Yao, M. Brym, C. van Wüllen, D. Lentz, *J. Am. Chem. Soc.* **2006**, *128*, 9628–9629; i) P. Zark, A. Schäfer, A. Mitra, D. Haase, W. Saak, R. West, T. Müller, *J. Organomet. Chem.* **2010**, *695*, 398–408.
- [3] For selected publications dealing with higher-coordinate silicon(II) compounds, see: a) P. Jutzi, D. Kanne, C. Krüger, *Angew. Chem.* **1986**, *98*, 163–164; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 164; b) H. H. Karsch, U. Keller, S. Gamper, G. Müller, *Angew. Chem.* **1990**, *102*, 297–298; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 295–296; c) P. Jutzi, A. Mix, B. Rummel, W. W. Schoeller, N. Neumann, H. G. Stammer, *Science* **2004**, *305*, 849–851; d) S. Yao, M. Brym, C. van Wüllen, M. Driess, *Angew. Chem.* **2007**, *119*, 4237–4240; *Angew. Chem. Int. Ed.* **2007**, *46*, 4159–4162; e) P. Jutzi, K. Leszczyńska, B. Neumann, W. W. Schoeller, H.-G. Stammer, *Angew. Chem.* **2009**, *121*, 2634–2637; *Angew. Chem. Int. Ed.* **2009**, *48*, 2596–2599; f) R. S. Ghadwal, H. W. Roesky, S. Merkel, J. Henn, D. Stalke, *Angew. Chem.* **2009**, *121*, 5793–5796; *Angew. Chem. Int. Ed.* **2009**, *48*, 5683–5686; g) A. C. Filippou, O. Chernov, G. Schnakenburg, *Angew. Chem.* **2009**, *121*, 5797–5800; *Angew. Chem. Int. Ed.* **2009**, *48*, 5687–5690; h) Y. Xiong, S. Yao, M. Driess, *J. Am. Chem. Soc.* **2009**, *131*, 7562–7563; i) R. S. Ghadwal, H. W. Roesky, S. Merkel, D. Stalke, *Chem. Eur. J.* **2010**, *16*, 85–88; j) Y. Gao, J. Zhang, H. Hu, C. Cui, *Organometallics* **2010**, *29*, 3063–3065; k) J. Li, S. Merkel, J. Henn, K. Meindl, A. Döring, H. W. Roesky, R. S. Ghadwal, D. Stalke, *Inorg. Chem.* **2010**, *49*, 775–777; l) A. Meltzer, S. Inoue, C. Präsang, M. Driess, *J. Am. Chem. Soc.* **2010**, *132*, 3038–3046; m) A. C. Filippou, O. Chernov, B. Blom, K. W. Stumpf, G. Schnakenburg, *Chem. Eur. J.* **2010**, *16*, 2866–2872; n) R. Rodriguez, D. Gau, Y. Contie, T. Kato, N. Saffon-Merceron, A. Baceiredo, *Angew. Chem.* **2011**, *123*, 11694–11697; *Angew. Chem. Int. Ed.* **2011**, *50*, 11492–11495.

- [4] For selected publications dealing with stable higher-coordinate silicon(II) compounds containing amidinato ligands, see: a) C.-W. So, H. W. Roesky, J. Magull, R. B. Oswald, *Angew. Chem.* **2006**, *118*, 4052–4054; *Angew. Chem. Int. Ed.* **2006**, *45*, 3948–3950; b) C.-W. So, H. W. Roesky, P. M. Gurubasavaraj, R. B. Oswald, M. T. Gamer, P. G. Jones, S. Blaurock, *J. Am. Chem. Soc.* **2007**, *129*, 12049–12054; c) W. Yang, H. Fu, H. Wang, M. Chen, Y. Ding, H. W. Roesky, A. Jana, *Inorg. Chem.* **2009**, *48*, 5058–5060; d) S. S. Sen, H. W. Roesky, D. Stern, J. Henn, D. Stalke, *J. Am. Chem. Soc.* **2010**, *132*, 1123–1126; e) G. Tavčar, S. S. Sen, R. Azhakar, A. Thorn, H. W. Roesky, *Inorg. Chem.* **2010**, *49*, 10199–10202; f) S. S. Sen, J. Hey, R. Herbst-Irmer, H. W. Roesky, D. Stalke, *J. Am. Chem. Soc.* **2011**, *133*, 12311–12316; g) A. Jana, D. Leusser, I. Objartel, H. W. Roesky, D. Stalke, *Dalton Trans.* **2011**, *40*, 5458–5463; h) R. Azhakar, S. P. Sarish, H. W. Roesky, J. Hey, D. Stalke, *Inorg. Chem.* **2011**, *50*, 5039–5043; i) R. Azhakar, R. S. Ghadwal, H. W. Roesky, H. Wolf, D. Stalke, *J. Am. Chem. Soc.* **2012**, *134*, 2423–2428; j) R. Azhakar, R. S. Ghadwal, H. W. Roesky, H. Wolf, D. Stalke, *Chem. Commun.* **2012**, *48*, 4561–4563.
- [5] For recent publications, see: a) S. Cota, M. Beyer, R. Bertermann, C. Burschka, K. Götz, M. Kaupp, R. Tacke, *Chem. Eur. J.* **2010**, *16*, 6582–6589; b) S. Metz, B. Theis, C. Burschka, R. Tacke, *Chem. Eur. J.* **2010**, *16*, 6844–6856; c) K. Junold, C. Burschka, R. Bertermann, R. Tacke, *Dalton Trans.* **2010**, *39*, 9401–9413; d) K. Junold, C. Burschka, R. Bertermann, R. Tacke, *Dalton Trans.* **2011**, *40*, 9844–9857; e) C. Kobelt, C. Burschka, R. Bertermann, C. Fonseca Guerra, F. M. Bickelhaupt, R. Tacke, *Dalton Trans.* **2012**, *41*, 2148–2162; f) K. Junold, C. Burschka, R. Tacke, *Eur. J. Inorg. Chem.* **2012**, 189–193; g) B. Theis, J. Weiß, W. P. Lippert, R. Bertermann, C. Burschka, R. Tacke, *Chem. Eur. J.* **2012**, *18*, 2202–2206; h) J. Weiß, B. Theis, S. Metz, C. Burschka, C. Fonseca Guerra, F. M. Bickelhaupt, R. Tacke, *Eur. J. Inorg. Chem.* **2012**, DOI: 10.1002/ejic.2012200308.
- [6] The Supporting Information contains details of the syntheses of **1–4** and the analytical and NMR spectroscopic data of these compounds.
- [7] CCDC 876288 (**1**), 876289 (**2**), 876290 (**3**), and 876291 (**4**) 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. For selected crystallographic data, see the Supporting Information.
- [8] S. Metz, C. Burschka, D. Platte, R. Tacke, *Angew. Chem.* **2007**, *119*, 7136–7139; *Angew. Chem. Int. Ed.* **2007**, *46*, 7006–7009.
- [9] a) T. S. Koloski, D. C. Pestana, P. J. Carroll, D. H. Berry, *Organometallics* **1994**, *13*, 489–499; b) H. Wagner, J. Baumgartner, C. Marschner, *Organometallics* **2005**, *24*, 4649–4653.



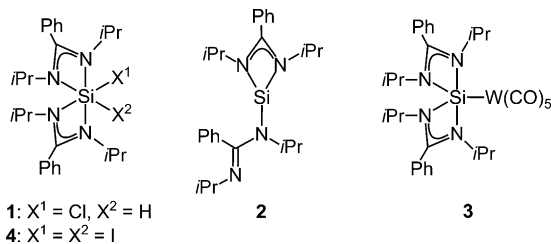
Communications



Silicon Chemistry

K. Junold, J. A. Baus, C. Burschka,
R. Tacke* ————— ■■■■-■■■■

Bis[*N,N'*-
diisopropylbenzamidinato(−)]silicon(II):
A Silicon(II) Compound with Both
a Bidentate and a Monodentate
Amidinato Ligand



Well looked-after: Reductive HCl elimi-
nation of the λ^6 -silicon(IV) complex
1 leads to the λ^3 -silicon(II) species **2**,
a novel type of donor-stabilized silylene.

Reaction of **2** with $[\text{W}(\text{CO})_6]$ and with I_2
yields the λ^5 -silicon(II) complex **3** and the
 λ^6 -silicon(IV) complex **4**, respectively.