Silicon

The Donor-Stabilized Silylene Bis[*N*,*N*'-diisopropylbenzamidinato(—)]silicon(II): Synthesis, Electronic Structure, and Reactivity

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Dedicated to Professor Helmut Werner on the occasion of his 80th birthday

Abstract: A convenient and robust synthesis of bis[*N*,*N*'-diisopropylbenzamidinato(–)]silicon(II) (1), a donor-stabilized silylene, has been developed (35 g scale). To get further information about the reactivity profile of 1, a series of oxidative addition reactions were studied. Treatment of 1 with PhSe–SePh (Se–Se bond activation), C_6F_6 (C–F activation), and CO₂ (C=O activation/cycloaddition) yielded the neutral six-coordinate silicon(IV) complexes 10, 11, and 13, respectively. Treatment of 1 with N₂O resulted in the formation of the dinuclear five-coordinate silicon(IV) complex 12 (oxidative addition/dimerization), which contains a four-membered Si₂O₂ ring. Compounds 10–13 were characterized by NMR spectroscopic studies in the solid state and in solution and

Introduction

In the past 2–3 decades, stable silylenes have proven to be versatile reagents in organosilicon chemistry, which has been demonstrated quite impressively by Jutzi et al., West et al., Heinicke et al., Kira et al., Roesky et al., Driess et al., Filippou et al., and others.^[1–4] In this context, higher-coordinate (donor-stabilized) silylenes with amidinato ligands are of particular interest because of their relatively easy accessibility and manifold reactivity.^[4] Recently, we have reported on the synthesis of bis[N,N'-diisopropylbenzamidinato(–)]silicon(II) (1), a new donor-stabilized silylene,^[5] and the first reactivity studies with

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201402483. by crystal structure analyses. Silylene 1 is three-coordinate in the solid state (from crystal structure analysis) and exists as the four-coordinate isomer 1' in benzene solution (from computational studies). Based on state-of-the-art relativistic DFT analyses, the four-coordinate species 1' was demonstrated to be the thermodynamically favored isomer in benzene solution (favored by $\Delta G = 6.6$ kcal mol⁻¹ over the three-coordinate species 1). The reason for this was studied by bonding analyses of 1 and 1'. Furthermore, the ²⁹Si NMR chemical shifts of 1 and 1' were computed, and in the case of 1' it was analyzed how this NMR spectroscopic parameter is affected by solvation. These studies further supported the assumption that the silylene is four-coordinate in solution.

this compound.^[5,6] According to the crystal structure analysis, compound **1** is a three-coordinate silylene; however, NMR spectroscopic studies indicated that in solution the four-coordinate species **1**' may also play a role. Furthermore, in all the reactions studied so far, compound **1** formally reacted as a four-coordinate species. For example, treatment of **1** with S₈, Se, Te, or I₂ led to the five- or six-coordinate silicon(IV) complexes **2–5** (oxidative additions),^[5,6a] and treatment of **1** with [Fe(CO)₅] or [M(CO)₆] (M=Cr, Mo, W) yielded the five-coordinate silicon(II) compounds **6–9** (nucleophilic substitutions).^[5,6b] In continuation of these studies, we have now improved the synthesis of **1** and have investigated a series of further oxidative addition reactions. In addition, we have performed computational studies on **1** and **1**'.

Herein, we report on 1) an improved synthesis of 1 (35 g scale), 2) the syntheses of compounds **10–13** (formed by treatment of **1** with PhSeSePh, C_6F_{6r} , N_2O , or CO_2), and 3) quantum-chemical studies to elucidate the structure of **1** in solution and to get information about the bonding situation of **1** and its four-coordinate isomer **1**'. These investigations were performed as part of our systematic studies on higher-coordinate silicon(II) and silicon(IV) compounds (for recent publications, see references [5–7]).

Chem. Eur. J. 2014, 20, 1–12 Wil

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Results and Discussion

Syntheses

Compounds **1** and **10–13** were synthesized according to Scheme 1.

The donor-stabilized silvlene 1 was prepared by treatment of chlorohydridobis[N,N'-diisopropylbenzamidinato(-)]silicon(IV) (14) with 1.05 molar equivalents of potassium bis(trimethylsilyl)amide in benzene at 20 °C and was isolated in 82 % yield as an orange-colored crystalline solid. The synthetic method used for the preparation of 1 was the same as described earlier;^[5] however, modifications concerning the solvent, the molar ratio of the reactants, and the reaction time were made. The modified method is very convenient and robust and allows the synthesis of 1 on the 35 g scale. Compound 1 shows a remarkable thermal stability; it melts at 127 °C and recrystallizes upon cooling without decomposition. It is soluble and stable in organic solvents such as benzene, toluene, n-hexane, THF, and diethyl ether, but decomposes rapidly in dichloromethane, DMSO, DMF, and acetonitrile.

The six-coordinate silicon(IV) complexes **10** and **11** were synthesized by treatment of **1** with one molar equivalent of diphenyl diselenide or hexafluorobenzene in toluene at 20 °C. The dinuclear five-coordinate silicon(IV) complex **12** was obtained by treatment of **1** with an excess of dinitrogen monoxide in toluene at -78 °C (\rightarrow 20 °C). The six-coordinate silicon(IV) complex **13** was synthesized by treatment of **1** with an excess of carbon dioxide in toluene at 20 °C. Compound **10** was isolated as a yellow crystalline solid, whereas **11**·0.5*n*·C₆H₁₄, **12**·C₆H₅CH₃, and **13** were obtained as colorless crystalline solids (yields: **10**, 92; **11**·0.5*n*·C₆H₁₄, 87; **12**·C₆H₅CH₃, 93; **13**, 78%). The identities of these compounds were established by

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elemental analyses (C, H, N), multinuclear NMR spectroscopic studies in the solid state (¹⁵N, ²⁹Si, ⁷⁷Se) and in solution (¹H, ¹³C, ²⁹Si, ⁷⁷Se), and crystal structure analyses (compound **10** was crystallographically characterized as the solvate **10**-CH₃CN).

The formation of 10–13 can be formally described in terms of oxidative addition reactions. In the case of 10 and 11, this reaction implies an activation of a Se-Se and C-F bond, respectively. The formation of 12 and 13 can be rationalized as two-step processes (Scheme 2): In the first step, the five-coordinate silicon(IV) complex 12' (an oxygen analogue of the stable sulfur, selenium, and tellurium compounds 2-4) is formed as an intermediate (not detected experimentally; generation of CO monitored as described in ref. [8]), which then dimerizes to give the dinuclear five-coordinate silicon(IV) complex 12 or reacts with a further equivalent of carbon dioxide to give the sixcoordinate silicon(IV) complex 13. Compound 13 represents the first structurally characterized silicon(IV) complex with a chelating carbonato(2-) ligand. The formation of 13 can be described as a [2+2] cycloaddition of 12' and carbon dioxide. In the reactions



Scheme 1. Syntheses of compounds 1 and 10-13.

2

Chem. Eur. J. 2014, 20, 1 – 12 ww

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Scheme 2. Proposed formation of 12 and 13 via the intermediate 12'.

1→**10**, **1**→**11**, and **1**→**13**, compound **1** formally behaves as a four-coordinate silylene to give six-coordinate silicon(IV) complexes. In contrast, in the reaction **1**→**12**, compound **1** formally reacts as a three-coordinate silylene to give a five-coordinate silicon(IV) complex (the formation of the proposed intermediate **12**' formally implies a reaction as a four-coordinate silylene).

Crystal structure analyses

Compounds **10**·CH₃CN, **11**·0.5 *n*-C₆H₁₄, **12**·C₆H₅CH₃, and **13** were structurally characterized by single-crystal X-ray diffraction. The crystal data and the experimental parameters used for the crystal structure analyses are given in Table S1 (see the Supporting Information). The molecular structures of **10–13** are shown in Figures 1–4 (hydrogen atoms omitted for clarity); selected bond lengths and angles are given in the corresponding figure legends.

The silicon coordination polyhedra of the neutral six-coordinate silicon(IV) complexes **10**, **11**, and **13** are best described as strongly distorted octahedra, with maximum deviations from the ideal 90/180° angles of 21.57/21.57 (**10**), 22.58/19.07 (**11**), and 20.56/18.33° (**13**). The silicon coordination polyhedra of the neutral dinuclear five-coordinate silicon(IV) complex **12** are strongly distorted trigonal bipyramids, with axial O–Si–N angles of 159.16(6) and 158.28(6)°. The sum of the equatorial bond angles amounts to 356.97 and 356.84°, and the Berry distortions^[9] were calculated at 33.9 (Si1) and 37.4% (Si2).

The structural features of compounds **10**, **11**, and **13** are very similar to what has been found for other six-coordinate silicon(IV) complexes with two bidentate amidinato ligands and two monodentate ligands.^[5,7c] As observed for the silicon(II) complex **1**,^[5] one bidentate and one monodentate amidinato ligand are bound to each of the two silicon coordination centers of the five-coordinate silicon(IV) complex **12**. The different coordination modes of the amidinato ligands in **10–13** (bidentate and/or monodentate) are reflected by different degrees of electron delocalization in the NC(Ph)N moieties as

can be seen from the different N–C bond lengths in these units (Table 1).

As can be seen from Table 2, Si-N(amidinato) the bond lengths of 10-13 depend on the coordination mode of the two amidinato ligands. The Si-N distances of the six-coordinate silicon(IV) complexes 10, 11, and 13 (two bidentate amidinato ligands) are similar and range from 1.8711(14) to 1.9744(13) Å. In the case of the five-coordinate silicon(IV) complex 12 (one bidentate and one monodentate amidinato ligand at each of the two silicon atoms), a strong differentiation between the Si-N

bond lengths is observed. The axial Si–N distances (2.0966(17) and 2.0909(16) Å) are significantly longer than the equatorial ones (1.7569(16)–1.8001(16) Å), and the equatorial Si–N bond distances of the bidentate amidinato ligands (1.7967(15) and 1.8001(16) Å) are somewhat longer than those of the monodentate amidinato ligands (1.7569(16) and 1.7600(15) Å).



Figure 1. Molecular structure of 10 in the crystal of 10-CH₃CN (probability level of displacement ellipsoids 50%). Selected bond lengths [Å] and angles [°]: Si–Se1 2.4470(10), Si–Se2 2.4309(11), Si–N1 1.888(2), Si–N2 1.894(2), Si–N3 1.879(2), Si–N4 1.940(2), N1–C1 1.336(3), N2–C1 1.331(3), N3–C14 1.338(3), N4–C14 1.330(3); Se1-Si-Se2 90.07(3), Se1-Si-N1 97.69(8), Se1-Si-N2 165.74(7), Se1-Si-N3 96.08(8), Se1-Si-N4 83.14(7), Se2-Si-N1 97.20(7), Se2-Si-N2 95.49(7), Se2-Si-N3 99.31(7), Se2-Si-N4 165.11(7), N1-Si-N2 68.63(10), N1-Si-N3 158.43(9), N1-Si-N4 96.83(9), N2-Si-N3 95.96(10), N2-Si-N4 94.23(9), N3-Si-N4 68.43(9), N1-C1-N2 106.1(2), N3-C14-N4 107.3(2).

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Chem. Eur. J. 2014, 20, 1-12



Figure 2. Molecular structure of **11** in the crystal of **11**·0.5 *n*- C_6H_{14} (probability level of displacement ellipsoids 50%). Selected bond lengths [Å] and angles [°]: Si–F1 1.6484(9), Si–N1 1.8711(14), Si–N2 1.9354(12), Si–N3 1.8816(14), Si–N4 1.9744(13), Si–C27 2.0042(16), N1–C1 1.3396(18), N2–C1 1.320(2), N3–C14 1.341(2), N4–C14 1.311(2); F1-Si-N1 94.05(5), F1-Si-N2 160.93(6), F1-Si-N3 98.58(5), F1-Si-N4 89.54(5), F1-Si-C27 92.31(6), N1-Si-N2 68.12(5), N1-Si-N3 161.67(6), N1-Si-N4 99.60(6), N1-Si-C27 98.26(6), N2-Si-N3 97.37(6), N2-Si-N4 86.98(5), N2-Si-C27 96.80(6), N3-Si-N4 67.42(6), N3-Si-C27 94.47(6), N4-Si-C27 161.87(6), N1-C1-N2 106.59(12), N3-C14-N4 107.70(13).

Table 1. Comparison of the N–C bond lengths [Å] of the NC(Ph)N moieties in 10–13.				
Compound	N1-C1	N2-C1	N3-C14	N4-C14
10	1.336(3)	1.331(3)	1.338(3)	1.330(3)
11	1.3396(18)	1.320(2)	1.341(2)	1.311(2)
12	1.349(2)	1.309(2)	1.400(3)	1.284(2)
	1.351(2) ^[a]	1.311(2) ^[b]	1.396(2) ^[c]	1.279(2) ^[d]
13	1.331(3)	1.337(3)	1.326(3)	1.335(3)
[a] N5–C27. [b] N6–C27. [c] N7–C40. [d] N8–C40.				

The Si–Se bond lengths of **10** (2.4470(10) and 2.4309(11) Å) are similar to those observed for the related compound **15** (2.3989(8) and 2.4142(7) Å),^[7c] and the Si–F distance of **11** is almost identical with the Si–F bond lengths of **16**.^[7c] The Si–C distance of **11** is 2.0042(16) Å. The tricyclic compound **12** contains a central four-membered Si₂O₂ ring (Si–O–Si: 93.43(7) and 93.54(7)°; O–Si–O: 86.48(7) and 86.42(7)°). The axial Si–O bond distances (1.7205(13) and 1.7199(13) Å) are somewhat longer than the equatorial ones (1.6590(13) and 1.6565(13) Å). Similar structural features have been observed for a series of related five-coordinate silicon(IV) complexes that also contain a four-membered Si₂O₂ ring.^[4j,m] Compound **13** contains a four-membered SiO₂C ring formed by the bidentate carbonato ligand and the silicon coordination center, with Si–O bond



Figure 3. Molecular structure of 12 in the crystal of $12 \cdot C_6H_5CH_3$ (probability level of displacement ellipsoids 50%). Selected bond lengths [Å] and angles [°]: Si1–O1 1.7205(13), Si1–O2 1.6565(13), Si2–O1 1.6590(13), Si2–O2 1.7199(13), Si1–N1 1.7967(15), Si1–N2 2.0966(17), Si1–N3 1.7569(16), Si2–N5 1.8001(16), Si2–N6 2.0909(16), Si2–N7 1.7600(15), N1–C1 1.349(2), N2–C1 1.309(2), N3–C14 1.400(3), N4–C14 1.284(2), N5–C27 1.351(2), N6–C27 1.311(2), N7–C40 1.396(2), N8–C40 1.279(2); Si1-O1-Si2 93.43(7), Si1-O2-Si2 93.54(7), O1-Si1-O2 86.48(7), O1-Si2-O2 86.42(7), O1-Si1-N1 97.20(7), O1-Si-N2 159.16(6), O1-Si1-N3 104.19(7), O1-Si2-N5 124.82(7), O1-Si2-N6 90.91(6), O1-Si2-N7 116.46(7), O2-Si1-N1 123.72(7), O2-Si1-N2 91.67(7), O2-Si1-N3 116.71(7), O2-Si2-N5 97.22(7), O2-Si2-N6 158.28(6), O2-Si2-N7 104.79(7), N1-Si1-N2 66.74(7), N1-Si1-N3 116.54(7), N2-Si1-N3 95.19(7), N5-Si2-N6 66.87(7), N5-Si2-N7 115.56(7), N6-Si2-N7 95.70(7), N1-C1-N2 108.41(16), N3-C14-N4 121.54(17), N5-C27-N6 108.29(15), N7-C40-N8 120.38(18).

lengths of 1.7794(17) and 1.7793(19) Å and an O–Si–O angle of 73.54(8) °. The O–C–O angles (105.7(2), 126.9(2), and 127.4(2) °) reflect the trigonal-planar coordination of the carbonato carbon atom (sum of O–C–O bond angles is 360 °). The C–O bond lengths of the silicon-bound oxygen atoms amount to 1.338(3) and 1.334(3) Å, whereas the C=O double bond of the carbonato ligand is significantly shorter (1.219(3) Å).



NMR spectroscopic studies

4

Compounds **10–13** were studied by using NMR spectroscopy in the solid state (¹⁵N, ²⁹Si, ⁷⁷Se; **10**, **11**·0.5 *n*-C₆H₁₄, **12**·CH₃CN, **13**) and in solution (¹H, ¹³C, ²⁹Si, ⁷⁷Se; solvent, CD₂Cl₂ (**10**, **13**) or C₆D₆ (**11**, **12**)). The data obtained (see the Experimental Section) confirm the identities of the compounds studied.

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Figure 4. Molecular structure of 13 in the crystal (probability level of displacement ellipsoids 50%). Selected bond lengths [Å] and angles [°]: Si–O1 1.7794(17), Si–O2 1.7793(19), Si–N1 1.887(2), Si–N2 1.873(2), Si–N3 1.875(2), Si–N4 1.8839(19), O1–C27 1.338(3), O2–C27 1.334(3), O3–C27 1.219(3), N1–C1 1.331(3), N2–C1 1.337(3), N3–C14 1.326(3), N4–C14 1.335(3); O1-Si-O2 73.54(8), O1-Si-N1 96.54(8), O1-Si-N2 96.66(8), O1-Si-N3 96.74(8), O2-Si-N4 95.83(9), N1-Si-N2 69.45(9), N1-Si-N3 162.07(10), N1-Si-N4 99.69(7), N2-Si-N3 97.04(9), N2-Si-N4 96.96(9), N3-Si-N4 69.44(8), O1-C27-O2 105.7(2), O1-C27-O3 126.9(2), O2-C27-O3 127.4(2), N1-C1-N2 106.82(19), N3-C14-N4 107.17(19).

As can be seen from Table 3, the respective isotropic ²⁹Si chemical shifts of 10-13 in the solid state and in solution are similar, indicating that these six- and five-coordinate silicon(IV) complexes also exist in solution. The shift differences observed for **10** ($\Delta \delta^{29}$ Si = 7.3 ppm) and **12** ($\Delta \delta^{29}$ Si = 10.1/9.0 ppm) are larger than those for 11 ($\Delta \delta^{29}$ Si = 0.5 ppm) and 13 ($\Delta \delta^{29}$ Si = 1.5 ppm) and may reflect somewhat different structures in the solid state and in solution, however, without changes in the silicon coordination number. For compound 10, also differences in the isotropic ⁷⁷Se chemical shifts were observed (solid state: δ^{77} Se = 205.2/280.9 ppm; solution: solvent, CD₂Cl₂; δ^{77} Se = 436.6 ppm). These differences could be explained by different steric arrangements of the two SePh groups in the solid state and in solution. Generally, the ⁷⁷Se chemical shift is very sensitive to the surroundings of the ⁷⁷Se nucleus, and this is also reflected by the two different isotropic ⁷⁷Se chemical shifts of **10** in the solid state, in which a chemical shift difference of

Table 2. Comparison of selected Si–X (X = C, N, O, F, Se) bond lengths [A] of 10–13 .					
Bond	10	11	12	13	
Si–N1	1.888(2)	1.8711(14)	1.7967(15) ^[a]	1.887(2)	
Si2–N5			1.8001(16)		
Si–N2	1.894(2)	1.9354(12)	2.0966(17) ^[b]	1.873(2)	
Si2–N6			2.0909(16)		
Si–N3	1.879(2)	1.8816(14)	1.7569(16) ^[c]	1.875(2)	
Si2–N7			1.7600(15)		
Si–N4	1.940(2)	1.9744(13)		1.8839(19)	
Si–C27		2.0042(16)			
Si01			1.7205(13) ^[d]	1.7794(17)	
Si201			1.6590(13)		
Si–O2			1.6565(13) ^[e]	1.7793(19)	
Si202			1.7199(13)		
Si—F		1.6484(9)			
Si–Se1	2.4470(10)				
Si–Se2	2.4309(11)				

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Table 3. Comparison of the isotropic ²⁹Si chemical shifts (ppm) of **10–13** in the solid state (T=22 °C) and in solution (T=23 °C).

Compound	$\delta^{ m 29}$ Si (solid state) $^{ m [a]}$	$\delta^{\rm 29}{\rm Si}$ (solution) ^[b]		
10	-177.3	-170.0		
11	-160.0 ^[c]	-160.5 ^[d]		
12	-93.0, -91.9	-82.9		
13	-164.4	-165.9		
[a] Compounds 11 and 12 were studied as the solvates $11 \cdot 0.5 n - C_6 H_{14}$ and 12 $\cdot C_6 H_5 CH_3$. [b] Solvent, $CD_2 CI_2$ (10 , 13) or $C_6 D_6$ (11 , 12). [c] Doublet, ${}^{1}J({}^{29}Si, {}^{19}F) = 245.5 Hz$. [d] Doublet, ${}^{1}J({}^{29}Si, {}^{19}F) = 250.0 Hz$.				

75 ppm for the two crystallographically independent selenium sites was observed.

As already observed for other silicon(IV) complexes with two amidinato ligands,^[5,6a,7d] compounds **11** and **12** show a dynamic behavior in solution at 23 °C. Whereas the ¹H NMR spectra of 10 and 13 (solvent, CD₂Cl₂) show four doublets and two septets for the four isopropyl groups, one doublet and one septet are found in the ¹H NMR spectrum of **12** (C₆D₆) and two doublets and one septet in the ¹H NMR spectrum of **11** (C_6D_6). Accordingly, one CH₃CHCH₃ and one CH₃CHCH₃ resonance signal are found in the $^{13}\text{C}\{^1\text{H}\}\,\text{NMR}$ spectrum of 12, whereas two CH₃CHCH₃ signals and one CH₃CHCH₃ signal are observed for 11. The ${}^{13}C{}^{1}H$ NMR spectrum of 10 shows three CH₃CHCH₃ signals (relative intensities: 1:2:1) and two CH₃CHCH₃ signals, and the spectrum of 13 shows four CH₃CHCH₃ signals and two CH₃CHCH₃ signals. These findings can be explained by a rapid exchange of the amidinato-nitrogen binding sites of 11 and 12 at 23 °C, whereas such kind of dynamic behavior was not observed for 10 and 13.

As already stated earlier,^[5] the ²⁹Si NMR spectra of the silylene **1** suggest that this species is four-coordinate (1') in solution ([D₈]toluene). This holds true for a wide temperature range (-80 to 70 °C), in which no significant changes in the ²⁹Si chemical shift were observed. This can be interpreted by the presence of **1**' as a single species rather than an equilibri-

Chem. Eur. J. 2014 , 20, 1–12		www.chemeurj.org		
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um between 1 and 1' in solution. This is in excellent agreement with the results of the computational studies.

Computational studies

To elucidate the structure of **1** in solution, we have conducted theoretical analyses based on relativistic density functional theory. These calculations include an exploration of the geometry and relative energy of various isomers and aggregates as well as analyses of the Si–N bonding mechanism between [N,N'-diisopropylbenzamidinato(-)]silicon(II) (DIBA-Si⁺) and a second N,N'-diisopropylbenzamidinato(-) (DIBA-⁻) ligand to understand how the preferred structure arises (**1** vs. **1**'). Furthermore, we have compared the ²⁹Si chemical shifts for the isomers **1** and **1**' and have studied how this NMR spectroscopic parameter is affected by solvation.

All calculations were performed with the Amsterdam Density Functional (ADF) program^[10] using relativistic density functional theory at the ZORA-BLYP-D3(BJ)/TZ2P level of theory for geometry optimization and energies.^[11-13] The calculations of the ²⁹Si NMR chemical shifts (relative to SiMe₄) were performed at the ZORA-SAOP/ET-pVQZ//ZORA-BLYP-D3(BJ)/TZ2P level of theory.^[14,15] Solvation in benzene was simulated using the conductor-like screening model (COSMO).^[16] All stationary points were verified to be minima on the potential energy surface through vibrational analysis. The bonding mechanism was analyzed within the framework of quantitative Kohn-Sham molecular orbital theory in combination with a quantitative energy decomposition analysis of the interaction energy ΔE_{int} of selected bonds into classical electrostatic attraction $\Delta V_{elstatr}$ Pauli repulsion ΔE_{Pauli} between occupied orbitals, stabilizing orbital interactions ΔE_{oir} such as the highest occupied molecular orbital/lowest unoccupied molecular orbital (HOMO/LUMO) interactions, and dispersion interactions ΔE_{disp} (for details, see ref. [17]).

The computed relative energies, Si-N bond lengths, and ²⁹Si NMR chemical shifts for the three- (1) and four-coordinate silvlene (1') in the gas phase and in solution (benzene) are given in Table 4. The calculated molecular structures of 1 and 1' in solution are shown in Figure 5 and Figure 6. Structure 1'is characterized by a rather shallow potential energy surface as a function of Si-N distances (e.g., variation in the Si-N1 bond length of 0.1 Å is associated with a change in energy of less than 0.1 kcalmol⁻¹). As also found experimentally (crystal structure analysis), the silicon coordination polyhedron of 1 is a distorted Ψ -tetrahedron, whereas a Ψ -trigonal-bipyramidal structure is obtained for 1', with the lone pair in an equatorial position. As can be seen from Table 4, the four-coordinate structure 1' is clearly more stable than the three-coordinate structure (1), both in the gas phase $(7.4 \text{ kcal mol}^{-1})$ and in solution (6.9 kcalmol⁻¹); the same holds true in terms of Gibbs free energy at 298.15 K and 1 atm (ΔG^{298}). This is in line with the experimental NMR spectroscopic studies, which suggest the presence of a four-coordinate species in solution (in this context, see ref. [5]). Table 4 also shows that the respective Si-N distances of 1 and 1' in the gas phase and in solution are very similar. Although four-coordinate 1' is the thermodynamically **Table 4.** Computed relative energies,^[a] Si–N distances,^[a] and ²⁹Si NMR chemical shifts^[b] for 1 and 1' in the gas phase and in solution (benzene).

Full Paper

Gas phase		Solution (benzene)	
, 	1	I	_
0.0	-7.4	0.0	-6.9
0.0	-7.1	0.0	-6.6
_[c]	2.38	_[c]	2.31
1.82	1.88	1.82	1.88
1.96	2.03	1.94	2.03
1.93	1.90	1.92	1.89
-22.3	-61.1	-19.7	-62.7
	-53.0		-49.5
	-45.9		-43.0
	Gas phase 1 0.0 0.0 ^[c] 1.82 1.96 1.93 22.3	Gas phase 1' 1 1' 0.0 -7.4 0.0 -7.1 -[c] 2.38 1.82 1.88 1.96 2.03 1.93 1.90 -22.3 -61.1 -53.0 -45.9	Gas phase Solution (b) 1 1' 1 0.0 -7.4 0.0 0.0 -7.1 0.0 _[c] 2.38 _[c] 1.82 1.88 1.82 1.96 2.03 1.94 1.93 1.90 1.92 -22.3 -61.1 -19.7 -53.0 -45.9

[a] Computed at ZORA-BLYP-D3(BJ)/TZ2P by using COSMO to estimate the effect of solvation. [b] Computed at ZORA-SAOP/ET-pVQZ//ZORA-BLYP-D3(BJ)/TZ2P relative to SiMe₄. [c] Dissociated bond.



Figure 5. Molecular structure of 1 computed at ZORA-BLYP-D3(BJ)/TZ2P in benzene (COSMO). Selected bond lengths [Å] and angles [°]: Si–N2 1.822, Si–N3 1.943, Si–N4 1.917, N1–C1 1.288, N2–C1 1.404, N3–C2 1.353, N4–C2 1.342; N2-Si-N3 100.60, N2-Si-N4 99.52, N1-C1-N2 120.70, N3-C2-N4 105.60.

favored species, three-coordinate **1** is found in the crystal. The reason for this is not yet fully understood.

Chem. Eur. J. 2014, 20, 1 – 12

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Figure 6. Molecular structure of 1' computed at ZORA-BLYP-D3(BJ)/TZ2P in benzene (COSMO). Selected bond lengths [Å] and angles [°]: Si–N1 2.313, Si–N2 1.881, Si–N3 2.028, Si–N4 1.893, N1–C1 1.318, N2–C1 1.361, N3–C2 1.344, N4–C2 1.346; N1-Si-N2 62.72, N1-Si-N3 146.29, N1-Si-N4 90.35, N2-Si-N3 97.82, N2-Si-N4 104.11, N3-Si-N4 66.82, N1-C1-N2 111.42, N3-C2-N4 106.95.

Table 5. Bonding analyses for 1 and 1' in the gas phase. ^[a]			
	1	1′	
Energy-decomposition analysis [kcal mol ⁻¹]			
$\Delta E_{\rm int}$	-168.9	-176.2	
ΔE_{Pauli}	244.0	247.1	
$\Delta V_{\rm elstat}$	-237.0	-237.5	
ΔE_{oi}	-159.9	-168.2	
ΔE_{disp}	-16.0	-17.6	
Gross Mulliken populations [e]			
P(HOMO-2 of DIBA ⁻)	1.89	1.79	
P(LUMO+1 of DIBA-Si ⁺)	0.12	0.16	
$<$ DIBA $^-$ DIBA-Si $^+$ $>$ orbital overlap			
<homo-1 lumo-1="" =""></homo-1>	0.03	0.14	
[a] Computed at ZORA-BLYP-D3(BJ)/TZ2P. Energy decomposition analysis: $\Delta E_{int} = \Delta V_{elstat} + \Delta E_{Pauli} + \Delta E_{oi} + \Delta E_{disp} \text{ (see ref. [17])}.$			

The results of the bonding analyses are collected in Table 5. They show that the four-coordinate isomer 1' is more stable than the three-coordinate species 1 because of more stabilizing orbital interaction ΔE_{oi} between [*N*,*N*'-diisopropylbenzamidinato(–)]silicon(II) (DIBA-Si⁺) and the second *N*,*N*'-diisopropylbenzamidinato(–) (DIBA⁻) ligand. A more detailed Kohn–Sham molecular orbital (MO) analysis reveals that ΔE_{oi} mainly arises from donor–acceptor interactions, such as those between the HOMO–1 of DIBA⁻ and the LUMO+1 of DIBA-Si⁺. There are also other donor–acceptor interactions but this pair is particularly discriminating in favor of the four-coordinate isomer 1'. The 3D representations of these fragment MOs show that that in three-coordinate 1, the DIBA⁻ HOMO–1 can overlap with



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Figure 7. Key fragment orbitals of the donor-acceptor interaction between $DIBA^-$ and $DIBA-Si^+$ fragments in the three- (1, left) and four-coordinate sily-lene (1', right) as was revealed by Kohn–Sham MO analyses at ZORA-BLYP-D3(BJ)/TZ2P.

the DIBA-Si⁺ LUMO + 1 only through one lobe on either side, for example, lobe a + lobe a along one Si–N bond (Figure 7). At variance, in four-coordinate 1', two lobes on either side can build up overlap through two lobes on either side, that is, lobe a + lobe a and lobe b + lobe b along two Si–N bonds. Thus, the net overlap increases from 0.03 in 1 to 0.14 in 1', and the orbital interactions ΔE_{oi} are reinforced as reflected by the stronger depopulation and population of the DIBA⁻ HOMO-1 and DIBA-Si⁺ LUMO + 1, respectively (see Table 5). Fragment orbital energies of DIBA⁻ and DIBA-Si⁺ are not very different for 1 and 1', with differences of only 0.2 eV or less. We conclude that it is the enhanced donor–acceptor orbital overlap through two instead of only one Si–N bond, which makes the four-coordinate 1' the more stable and thus preferred isomer.

Finally, we have examined how the computed ²⁹Si NMR chemical shifts of 1 and 1' compare with the values determined in the solid state ($\delta = -15.4$ ppm; three-coordinate species 1 as demonstrated by crystal structure analysis) and in solution (C₆D₆, $\delta = -31.4$ ppm). The ²⁹Si NMR chemical shifts computed at the sophisticated ZORA-SAOP/ET-pVQZ//ZORA-BLYP-D3(BJ)/TZ2P level of theory using COSMO to simulate solvation in benzene do not match the experimental value of $\delta =$ -31.4 ppm, neither for the three- nor the four-coordinate species for which we computed $\delta = -19.7$ (1) and $\delta = -62.7$ ppm (1') (Table 4). This seems to be in contradiction with the abovementioned finding that 1' is thermodynamically clearly the favored isomer. We have carried out extensive and costly explorations to find more stable dimer aggregates of 1 or 1' in which the electronic environment of the silicon nucleus gives rise to the experimentally observed chemical shift. However, all attempts to find either covalently (Si=Si) or van der Waalsbound dimers resulted in species that are at significantly, that is, 10 to 23 kcalmol⁻¹, higher in Gibbs free energy than the monomers. This can be ascribed to the fact that the silicon atoms in these species are sterically highly congested by their

Chem. Eur. J. 2014, 20, 1 – 12 www.chemeurj.org

7



bulky substituents that prevent the formation of stable siliconsilicon bonding.

Next, we focused on the fact that the silicon center in the thermodynamically favored species 1' is directly exposed to the solvent and carries a large, outward-oriented lobe of the HOMO of the system (see Figure 8). In addition, the latter orbi-



Figure 8. HOMO of the four-coordinate silylene 1' computed at ZORA-BLYP-D3(BJ)/TZ2P.

tal is at relatively high energy (-3.7 eV; not shown in Table 5)as compared with the HOMO of, for example, SiMe₄, which is much lower in energy (-6.7 eV). This suggests that the local electronic environment of the silicon nucleus of 1' and, thus, its ²⁹Si NMR chemical shift may be affected more strongly than usually happens in situations in which the average effect of a continuum model (such as COSMO) suffices. Indeed, the introduction of discrete solvent molecules into the quantum chemical description of our model systems moves the ²⁹Si NMR chemical shift of 1' strongly into the direction of the experimental value (see Table 4). Thus, coordinating one and two benzene molecules through one of their C-H bonds to 1' leads to a weak donor-acceptor interaction between the HOMO of the silylene and the C–H antibonding LUMO+2 of benzene at 0.2 eV (charge transfer of 0.02 electrons), which pushes the ²⁹Si NMR chemical shift from $\delta = -62.7$ (1') through -49.5 ppm (1'·C₆H₆) to $\delta = -43.0$ ppm (1'·2C₆H₆) if we use COSMO to simulate the remaining bulk solvation in benzene. The same trend is found in the absence of COSMO as well as when we use other solvent molecules, such as tetrahydrofuran (C-H antibonding LUMO at 0.0 eV). In the case of SiMe₄, the introduction of discrete benzene solvent molecules has no noticeable effect on the ²⁹Si NMR chemical shift, in line with the notion that strong, local solvent effects as we find for 1' require a covalent component in the solute-solvent interaction. Our analyses show that including discrete solvent molecules in the quantum chemical treatment brings the computed 29 Si NMR chemical shift of 1' into better agreement with the experimental value. Full convergence of the computed value would require both more solvent molecules as well as a sampling of significantly more spatial configurations of the solvent using statistical methods, such as molecular dynamics (MD) or Monte Carlo simulations (MC); however, this is beyond the scope of the present work.

Conclusion

We have succeeded in developing a very convenient and robust method for the synthesis of the donor-stabilized silylene 1 on the 35 g scale. This allows a systematic investigation of the chemistry of this compound on a broad basis. As shown for a series of oxidative addition reactions, silylene 1 can formally react as a three- or four-coordinate silicon(II) species. In the reaction with diphenyl diselenide, hexafluorobenzene, and carbon dioxide, compound 1 formally behaves as a four-coordinate silylene to give the six-coordinate silicon(IV) complexes 10 (Se–Se activation), 11 (C–F activation), and 13 (CO₂ activation), respectively. In the reaction with dinitrogen monoxide, however, compound 1 formally reacts as a three-coordinate silylene to yield the dinuclear five-coordinate silicon(IV) complex 12 (N₂O activation). Thus, the unique reactivity profile of 1 is controlled by the different possible coordination modes of the two amidinato ligands, which can bind in a mono- and/or bidentate fashion and thereby affect the stability of the silicon(IV) compounds formed.

Silylene 1 is three-coordinate in the solid state (crystal structure analysis) and four-coordinate in solution (isomer 1'; computational studies). Based on state-of-the-art relativistic DFT analyses, we have shown that the four-coordinate species 1' is the thermodynamically favored isomer in benzene solution. This isomer is favored by $\Delta G = 6.6 \text{ kcal mol}^{-1}$ over the three-coordinate species 1. The reason is an increased Si–N donor-acceptor overlap in the four-coordinate isomer 1'.

Interestingly, the computed ²⁹Si NMR chemical shift of 1' depends extremely sensitively on local solute-solvent interactions between the exposed silicon center and discrete benzene or tetrahydrofuran solvent molecules. Therefore, to bring the computed and experimentally determined chemical shift of 1' into agreement, explicit solvent molecules must be included in the quantum chemical model system. This is at variance with the total energy in the present model systems, which is not much affected by simulating the presence of a solvent environment by a continuum approach, such as COSMO. Also, ²⁹Si NMR chemical shifts of solute systems with stable, lowenergy closed shells, such as SiMe₄, are not so sensitive to discrete solute-solvent interactions and can well be described with the COSMO approach. The explanation for this is a weak donor-acceptor interaction between the HOMO of 1' and the C-H antibonding LUMO+2 of benzene. These findings highlight once more that continuum approaches for simulating solvent effects should always be used with precaution. Nevertheless, these calculations also support the assumption that isomer $\mathbf{1}'$ is the more stable species in solution.

Experimental Section

General procedures

All syntheses were carried out under dry argon. The organic solvents used were dried, purified, and deoxygenated according to standard procedures and stored under argon. Solution ¹H, ¹³C{¹H}, ¹⁵N{¹H}, ²⁹Si{¹H}, and ⁷⁷Se{¹H} MMR spectra were recorded at 23 °C

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8



on a Bruker DRX-300 (¹H, 300.1 MHz; ¹³C, 75.5 MHz; ²⁹Si, 59.6 MHz) or Bruker Avance 500 NMR spectrometer (1H, 500.1 MHz; 13C, 125.8 MHz; ¹⁵N, 50.7 MHz; ²⁹Si, 99.4 MHz; ⁷⁷Se, 95.4 MHz) using CD_2CI_2 or C_6D_6 as the solvent. Chemical shifts (δ , ppm) were determined relative to internal CHDCl₂ (¹H, $\delta = 5.32$ ppm; CD₂Cl₂), internal C₆HD₅ (¹H, δ = 7.28 ppm; C₆D₆), internal CD₂Cl₂ (¹³C, δ = 53.8 ppm; CD₂Cl₂), internal C₆D₆ (13 C, δ = 128.0 ppm; C₆D₆), external TMS (²⁹Si, $\delta = 0$ ppm; CD₂Cl₂, C₆D₆), external formamide (90% w/w in DMSO) (¹⁵N, $\delta = -268.0$ ppm; C₆D₆), or external Me₂Se (5% w/w in C₆D₆) (⁷⁷Se, $\delta = 0$ ppm; CD₂Cl₂). Assignment of the ¹³C NMR data was supported by DEPT 135 and ¹H,¹H and ¹H,¹³C correlation experiments. Solid-state ¹⁵N, ²⁹Si, and ⁷⁷Se VACP/MAS NMR spectra were recorded at 22 °C on a Bruker DSX-400 NMR spectrometer with bottom layer rotors of ZrO₂ (diameter, 4 (10) or 7 mm (11.0.5 $n\text{-}C_6\text{H}_{14},\ 12\text{-}C_6\text{H}_5\text{CH}_3,\ 13)$ containing about 80 (4 mm) or 200 mg (7 mm) of sample (15N, 40.6 MHz; 29Si, 79.5 MHz; 77Se, 76.3 MHz; external standard, TMS (13 C, 29 Si, $\delta = 0$ ppm), glycine (15 N, $\delta = -342.0$ ppm), or Me₂Se (⁷⁷Se, $\delta = 0$ ppm); spinning rate, 10 (4 mm) or 7 kHz (7 mm); contact time, 3 (¹⁵N) or 5 ms (²⁹Si, ⁷⁷Se); 90° ¹H transmitter pulse length, 2.6 (4 mm) or 3.6 μ s (7 mm); repetition time, 4–7 s).

Syntheses

Compound 1: Benzene (350 mL) was added at 20°C in a single portion to a mixture of chlorohydrido[N,N'-diisopropylbenzamidinato(-)]silicon(IV)^[5] (47.1 g, 100 mmol) and potassium bis(trimethylsilyl)amide (21.0 g, 105 mmol), and the reaction mixture was then stirred at this temperature for 2 h. The resulting precipitate was filtered off, washed with benzene (2×50 mL), and discarded. The solvent of the filtrate (including the wash solutions) was removed in vacuo, followed by the addition of *n*-hexane (50 mL). The resulting suspension was heated until a clear solution was obtained, which was then cooled slowly to $-20\,^\circ\text{C}$ and kept undisturbed at this temperature for 1 d. The resulting orange-colored crystalline solid was isolated by filtration and dried in vacuo (20 °C, 6 h, 0.01 mbar). Yield: 35.6 g (81.9 mmol, 82%). ¹H NMR (C_6D_6 , 500.1 MHz): $\delta = 1.51$ $(d, {}^{3}J({}^{1}H, {}^{1}H) = 6.8 \text{ Hz}, 24 \text{ H}; CH_{3}), 3.63 \text{ (sept, } {}^{3}J({}^{1}H, {}^{1}H) = 6.8 \text{ Hz}, 4 \text{ H};$ $CH_{3}CHCH_{3}), \ \ 7.15-7.25 \ ppm \ \ (m, \ \ 10\,H; \ \ C_{6}H_{5}); \ \ ^{13}C\{^{1}H\} \ NMR \ \ (C_{6}D_{6'}), \ \ C_{6}H_{6'})$ 125.8 MHz): $\delta = 24.9$ (8 C; CH₃), 47.7 (4 C; CH₃CHCH₃), 128.3 (br, 4 C; o-C₆H₅), 128.5 (4 C; m-C₆H₅), 128.7 (2 C; p-C₆H₅), 134.4 (2 C; *i*-C₆H₅), 161.1 ppm (2 C; NCN); ¹⁵N{¹H} NMR (C₆D₆, 50.7 MHz): $\delta =$ -193.4 ppm; ²⁹Si{¹H} NMR (C₆D₆, 99.4 MHz): $\delta = -$ 31.4 ppm; ¹⁵N VACP/MAS NMR: $\delta = -230.4$, -204.4, -198.9, -103.0 ppm (NCN); ^{29}Si VACP/MAS NMR: $\delta\!=\!-15.4$ ppm; elemental analysis calcd (%) for C₂₆H₃₈N₄Si (*M*_r=434.70): C 71.84, H 8.81, N 12.89; found: C 70.6, H 9.1, N 12.5.

Compound 10: Toluene (5 mL) was added at 20 °C in a single portion to a mixture of 1 (300 mg, 690 µmol) and diphenyl diselenide (215 mg, 689 µmol), and the reaction mixture was then stirred at this temperature for 16 h. The solvent was removed in vacuo, and *n*-pentane (5 mL) was added to the residue. The resulting solid was isolated by filtration and dried in vacuo (20 °C, 4 h, 0.01 mbar), followed by the addition of acetonitrile (2 mL). The resulting suspension was heated until a clear solution was obtained, which was then cooled slowly to -20 °C and kept undisturbed at this temperature for 2 d. The resulting yellow crystalline solid was isolated by filtration, washed with *n*-pentane (2×5 mL), and dried in vacuo (20 °C, 4 h, 0.01 mbar). Yield: 471 mg (631 µmol, 92%). ¹H NMR $(CD_2CI_2, 500.1 \text{ MHz}): \delta = 1.17 \text{ (d, } {}^3J({}^1H, {}^1H) = 6.8 \text{ Hz}, 6\text{ H}; CH_3), 1.22 \text{ (d,}$ ${}^{3}J({}^{1}H,{}^{1}H) = 6.8$ Hz, 6H; CH₃), 1.26 (d, ${}^{3}J({}^{1}H,{}^{1}H) = 6.8$ Hz, 6H; CH₃), 1.33 $(d, {}^{3}J({}^{1}H, {}^{1}H) = 6.8 \text{ Hz}, 6 \text{ H}; CH_{3}), 3.48 \text{ (sept, } {}^{3}J({}^{1}H, {}^{1}H) = 6.8 \text{ Hz}, 2 \text{ H};$ CH₃CHCH₃), 3.93 (sept, ³J(¹H, ¹H) = 6.8 Hz, 2H; CH₃CHCH₃), 7.27–7.33 (m, 2H; o-C₆H₅), 7.33–7.38 (m, 6H; m- and p-SeC₆H₅), 7.38–7.44 (m, 2H; $o-C_6H_5$), 7.46–7.56 (m, 6H, *m*- and $p-C_6H_5$), 7.60–7.67 ppm (m, 4H; $o-SeC_6H_5$); ¹³C{¹H} NMR (CD₂Cl₂, 125.8 MH2): $\delta = 23.0$ (2 C; CH₃), 23.6 (4 C; CH₃), 23.9 (2 C; CH₃), 46.9 (2 C; CH₃CHCH₃), 47.3 (2 C; CH₃CHCH₃), 127.1 (br, 2 C; $o-C_6H_5$), 127.9 (br, 2 C; $o-C_6H_5$), 128.6 (2 C; $p-SeC_6H_5$), 128.9 (br, 2 C; $m-C_6H_5$), 129.0 (br, 2 C; $m-C_6H_5$), 128.6 (2 C; $m-SeC_6H_5$), 130.3 (2 C; $i-SeC_6H_5$; ⁷⁷Se satellites could not be observed), 130.8 (2 C; $p-C_6H_5$), 133.1 (2 C; $i-C_6H_5$), 133.7 (4 C, ⁷⁷Se satellites (²J(¹³C,⁷⁷Se) = 10.6 Hz); $o-SeC_6H_5$), 168.7 ppm (2 C; NCN); ²⁹Si{¹H} NMR (CD₂Cl₂, 99.4 MHz): $\delta = -170.0$ ppm; ⁷⁷Se[¹H} NMR (CD₂Cl₂, 99.4 MH2): $\delta = -170.0$ ppm; ⁷⁷Se[¹H} NMR (CD₂Cl₂, 99.4 MH2): $\delta = -177.3$ ppm (br); ⁷⁷Se VACP/MAS NMR: $\delta = -200.7$, -198.0, -194.9, -190.6 ppm; ²⁹Si VACP/MAS NMR: $\delta = -177.3$ ppm (br); ⁷⁷Se VACP/MAS NMR: $\delta = 205.2$, 280.9 ppm; elemental analysis calcd (%) for $C_{38}H_{48}N_4Se_2Si$ ($M_r = 746.83$): C 61.11, H 6.48, N 7.50; found: C 60.7, H 6.5, N 7.6.

Compound 11.0.5 n-C₆H₁₄: Hexafluorobenzene (214 ma, 1.15 mmol) was added at 20 °C in a single portion to a stirred solution of 1 (500 mg, 1.15 mmol) in toluene (20 mL), and the reaction mixture was then stirred at this temperature for 1 h. The volatile components were removed in vacuo, and *n*-hexane (2 mL) was added to the residue. The resulting suspension was heated until a clear solution was obtained, which was then cooled slowly to -20°C and kept undisturbed at this temperature for 1 d. The resulting colorless crystalline solid was isolated by filtration and dried in vacuo (20°C, 5 h, 0.01 mbar). Yield: 667 mg (1.00 mmol, 87%). ¹H NMR (C₆D₆, 500.1 MHz): $\delta = 1.00$ (t, ³J(¹H, ¹H) = 7.0 Hz, 3 H; $CH_3(CH_2)_4CH_3$, 1.24 (d, ${}^{3}J({}^{1}H,{}^{1}H) = 6.8$ Hz, 12H; CH_3CHCH_3), 1.26 (d, ${}^{3}J({}^{1}H,{}^{1}H) = 6.8 \text{ Hz}, 12 \text{ H}; CH_{3}CHCH_{3}), 1.31-1.42 \text{ (m, 4H; CH}_{3}-1.42 \text{ (m, 4H; CH}_{3}-1.42$ $(CH_2)_4CH_3$, 3.63 (br sept, ${}^{3}J({}^{1}H,{}^{1}H) = 6.8$ Hz, 4H; CH₃CHCH₃), 7.17– 7.21 and 7.44–7.49 ppm (m, 10H; C_6H_5); ${}^{13}C{}^{1}H$ NMR (C_6D_6 , 125.8 MHz): $\delta = 14.3$ (1 C; CH₃(CH₂)₄CH₃), 23.0 (1 C; CH₃CH₂-(CH₂)₂CH₂CH₃), 23.7 (4 C; CH₃CHCH₃), 24.2 (4 C; CH₃CHCH₃), 31.9 (1 C; CH₃CH₂(CH₂)₂CH₂CH₃), 46.4 (4 C; CH₃CHCH₃), 122.6-123.8 (m, 2 C; C₆F₅), 128.1 (4 C; o-C₆H₅), 128.5 (4 C; m-C₆H₅), 129.7 (2 C; p-C₆H₅), 132.4 (2 C; *i*-C₆H₅), 136.2–136.9 (m, 1 C; C₆F₅), 138.1–139.3 (m, 2 C; C₆F₅), 140.7–141.2 (m, 1 C; C₆F₅), 169.4 ppm (2 C; NCN); ²⁹Si{¹H} NMR (C₆D₆, 99.4 MHz): $\delta = -160.5$ ppm (d, ¹J(¹⁹F,²⁹Si) = 250.0 Hz); ¹⁵N VACP/MAS NMR: $\delta = -222.5$, -211.4, -199.3, -188.8 ppm; ²⁹Si VACP/MAS NMR: $\delta = -160.0$ ppm (d, ¹J(¹⁹F,²⁹Si) = 245.4 Hz); elemental analysis calcd (%) for $C_{35}H_{45}F_6N_4Si$ ($M_r =$ 663.85): C 63.33, H 6.83, N 8.44; found: C 63.1, H 7.2, N 8.6.

Compound 12 \cdot C_6 H_5 CH_3: Dinitrogen monoxide (ca. 500 mg) was passed at -78°C within 3 min through a stirred solution of 1 (500 mg, 1.15 mmol) in toluene (20 mL), and the reaction mixture was then stirred at this temperature for 10 min and then at 20 $^\circ\text{C}$ for a further 1 h. The resulting solution was concentrated in vacuo to a volume of 2 mL, cooled slowly to -20 °C, and then kept undisturbed at this temperature for 2 d. The resulting colorless crystalline solid was isolated by filtration, washed with *n*-pentane ($2 \times$ 5 mL), and dried in vacuo (20 °C, 6 h, 0.01 mbar). Yield: 532 mg (535 μ mol, 93%). ¹H NMR (CD₂Cl₂, 500.1 MHz): δ = 1.48 (brd, ${}^{3}J({}^{1}H,{}^{1}H) = 6.4 \text{ Hz}, 48 \text{ H}; CH_{3}CHCH_{3}), 2.24 \text{ (s, } 3 \text{ H}; C_{6}H_{5}CH_{3}), 3.44 \text{ (br s)}$ (FWHH = 30.4 Hz), 8H; CH₃CHCH₃), 7.10-7.32 and 7.41-7.58 ppm (m, 25 H; C_6H_5 and $C_6H_5CH_3$); ¹³C{¹H} NMR (CD₂Cl₂, 125.8 MHz): $\delta =$ 21.4 (1 C; C₆H₅CH₃), 24.7 (br, 16 C; CH₃CHCH₃), 48.4 (br, 8 C; CH₃CHCH₃), 125.6, 128.0, 128.2, 128.5, 128.9, 129.3, and 136.1 (C₆H₅ and $C_6H_5CH_3$; assignment of the aromatic ¹³C resonance signals was not possible), 163.6 ppm (br, 4 C; NCN); $^{29}Si\{^{1}H\}$ NMR (CD₂Cl₂, 99.4 MHz): $\delta = -82.9$ ppm; ¹⁵N VACP/MAS NMR: $\delta = -262.2$ (1 N), -261.2 (1 N), -253.2 (1 N), -234.3 (1 N), -172.9 (1 N), -171.1 (1 N), -98.9 ppm (2 N); ²⁹Si VACP/MAS NMR: $\delta = -91.9$, -93.0 ppm; elemental analysis calcd (%) for C₅₉H₈₄N₈O₂Si₂ (*M*_r=993.54): C 71.33, H 8.52, N 11.28; found: C 70.0, H 8.7, N 11.3.

Chem. Eur. J. **2014**, 20, 1–12

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9

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Compound 13: Carbon dioxide (ca. 500 mg) was passed at 20 °C within 5 min through a stirred solution of 1 (500 mg, 1.15 mmol) in toluene (20 mL), and the reaction mixture was then stirred at this temperature for 15 min. The resulting suspension was heated until a clear solution was obtained, which was then cooled slowly to -20°C and kept undisturbed at this temperature for 1 d. The resulting colorless crystalline solid was isolated by filtration, washed with *n*-pentane (2×5 mL), and dried in vacuo (20 °C, 4 h, 0.01 mbar). Yield: 444 mg (897 μmol, 78%); ¹H NMR (CD₂Cl₂, 500.1 MHz): $\delta = 1.08$ (d, ${}^{3}J({}^{1}H,{}^{1}H) = 6.8$ Hz, 6H; CH₃), 1.13 (d, ${}^{3}J({}^{1}H,{}^{1}H) = 6.8$ Hz, 6H; CH₃), 1.24 (d, ${}^{3}J({}^{1}H,{}^{1}H) = 6.8$ Hz, 6H; CH₃), 1.30 $(d, {}^{3}J({}^{1}H, {}^{1}H) = 6.8 \text{ Hz}, 6 \text{ H}; CH_{3}), 3.50 \text{ (sept, } {}^{3}J({}^{1}H, {}^{1}H) = 6.8 \text{ Hz}, 2 \text{ H};$ CH₃CHCH₃), 3.53 (sept, ³J(¹H, ¹H) = 6.8 Hz, 2 H; CH₃CHCH₃), 7.23–7.29 (m, 2H; o-C₆H₅), 7.42–7.47 (m, 2H; o-C₆H₅), 7.49–7.58 ppm (m, 6H; *m*- and *p*-C₆*H*₅); ¹³C{¹H} NMR (CD₂Cl₂, 125.8 MHz): $\delta = 22.8$ (2 C; CH₃), 23.3 (2 C; CH₃), 23.9 (2 C; CH₃), 24.0 (2 C; CH₃), 46.6 (2 C; CH₃CHCH₃), 46.9 (2 C; CH₃CHCH₃), 127.1 (br, 2 C; o-C₆H₅), 128.1 (br, 2 C; o-C₆H₅), 129.15 (br, 2 C; m-C₆H₅), 129.22 (br, 2 C; m-C₆H₅), 129.7 (2 C; *i*-C₆H₅), 130.7 (2 C; *p*-C₆H₅), 159.5 (CO₃), 173.6 ppm (2 C; NCN); ²⁹Si{¹H} NMR (CD₂Cl₂ 99.4 MHz): $\delta = -165.9$; ¹⁵N VACP/MAS NMR: $\delta\!=\!-217.6,\,-213.1,\,-212.1,\,-205.0$ ppm; $^{\rm 29}{\rm Si}$ VACP/MAS NMR: $\delta\!=$ -164.4; elemental analysis calcd (%) for $C_{\rm 27}H_{\rm 38}N_4O_3Si$ (494.71): C 65.55, H 7.74, N 11.33; found: C 65.2, H 7.9, N 11.3.

Crystal structure analyses

Suitable single crystals of 10·CH₃CN were obtained by slow cooling of a saturated solution of 10 in CH₃CN from 70 to -20 °C. Suitable single crystals of $11.0.5 n - C_6 H_{14}$, $12.C_6 H_5 C H_3$, and 13 were obtained as described in the Experimental Section dealing with the syntheses. The crystals were mounted in inert oil (perfluoropolyalkyl ether, ABCR) on a glass fiber and then transferred to the cold nitrogen gas stream of the diffractometer (Stoe IPDS, graphite-monochromated Mo_{K\!\alpha} radiation, $\lambda \!=\! 0.71073$ Å). The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares methods on F^2 for all unique reflections (SHELXL-97).^[18] SHELXLE was used as refinement GUI.^[19] For the CH hydrogen atoms, a riding model was employed. CCDC-983211 CCDC-983212 (10·CH₃CN), $(11.0.5 n-C_6 H_{14}),$ CCDC-983213 (12·C₆H₅CH₃), and CCDC-983214 (13) 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.

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10

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FULL PAPER

Silicon

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The Donor-Stabilized Silylene Bis[N,N'-diisopropylbenzamidinato(–)]silicon(II): Synthesis, Electronic Structure, and Reactivity



Silicon(II)/silicon(IV): The donor-stabilized silylene 1 (three-coordinate in the solid state) was synthesized on the 35 g scale. In benzene solution, the four-coordinate isomer 1' is the thermodynamically favored species. Treatment of the silylene with PhSeSePh, C_6F_{6r} , N_2O , and CO_2 yields the respective silicon(IV) complexes **2–5**.

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12