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Reactivity Studies of Heteroleptic Silylenes PhC(N*t*Bu)$_2$SiX (X = NPh$_2$, NMe$_2$) toward Selected Azides

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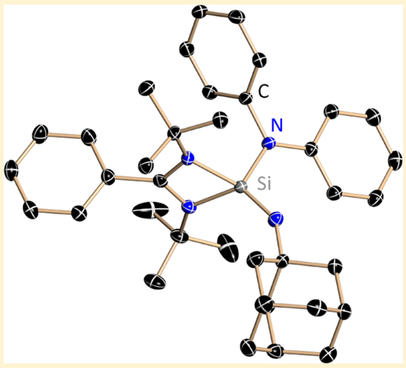
Supporting Information

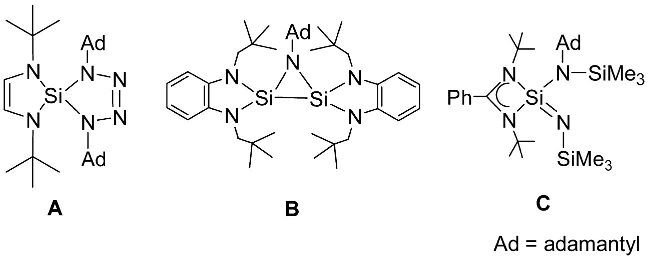
ABSTRACT: The reaction of LSiX (L = PhC(N*t*Bu)$_2$, X = NPh$_2$ (**1**), NMe$_2$ (**2**)) with trimethylsilyl azide (**3**) resulted in silaimines [LSi(=NSiMe$_3$)X] (X = NPh$_2$ (**5**), NMe$_2$ (**7**)). Similarly the reaction of **1** and **2** with adamantyl azide (**4**) yielded [LSi(=NAd)X] (X = NPh$_2$ (**6**), NMe$_2$ (**8**), Ad = adamantyl) compounds. Silaimines **5**−**8** contain tetracoordinate silicon atoms. Compounds **6** and **8** are the first tetracoordinate silicon compounds having the terminal Si=NAd unit. All compounds were characterized by spectroscopic and spectrometric techniques. The molecular structures of **5**, **6**, and **8** were unequivocally established by single-crystal X-ray structure analysis.



INTRODUCTION

During the last two decades considerable attention has been focused on the reactivity studies of stable singlet silylenes.[1] The presence of two nonbonding electrons in the HOMO and a vacant p-orbital as the LUMO shows that silylenes have the tendency to function both as Lewis acids and as Lewis bases.[2] Due to the presence of an ambiphilic character, many noteworthy reactivity studies such as insertion, addition, metal complexes, and Lewis acid adducts with stable silylenes have been reported.[3−11] We synthesized heteroleptic silylenes by the facile metathesis reaction of alkali metal amide, phosphide, alkoxide, or organoalkyl reagent with amidinato ligand stabilized monochlorosilylene LSiCl [L = PhC(N*t*Bu)$_2$] in toluene as a solvent.[12] The synthesis of stable compounds with double bonds to silicon is fascinating.[1,9i,13] Silaimines (R$^a_2$Si=NR^b, R^a and R^b are alkyl or aryl) are silicon analogues of imines.[13] In 1985, Wiberg et al. reported the first stable silaimine, (*t*Bu)$_2$Si=NSi(*t*Bu)$_3$.[14] Klingebiel et al. isolated the base-free silaimine (*i*Pr)$_2$Si=N(2,4,6-(*i*Pr)$_3$C$_6$H$_2$) in 1986.[15] A THF molecule coordinated silicon-containing silaimine was reported by West et al. by the reaction of a stable N-heterocyclic silylene (NHSi) with sterically hindered Ph$_3$CN$_3$.[16] Further, Kira et al. synthesized base-free silaimines with terminal Ph, CH$_2$Ph, SiMe$_3$, and Ad (Ad = adamantyl) groups.[17a] Cui et al. reported on NHC-stabilized silaimines.[17b,c] The reaction of stable silylenes toward azides shows a diverse reactivity pattern depending on the nature of the reactant and reaction conditions.[1,9i,16−18] A survey of the literature reveals that the reactivity of adamantyl azide with stable NHSis shows a different reactivity pattern.[1,9i,16,18] The reaction of stable NHSis (*t*BuNCH=CHN*t*Bu)Si and [(NCH$_2$*t*Bu)$_2$C$_6$H$_4$-1,2]Si with adamantyl azide yielded the silatetrazoline (**A**) and azadisilacyclopropane (**B**), respectively (Chart 1).[16,18] Recently we reported on the reaction of LSiN(SiMe$_3$)$_2$ with adamantyl azide, which resulted in the silaimine compound LSi(N(Ad)-SiMe$_3$)(=N(SiMe$_3$)) (**C**).[9i] In this reaction migration of one of the SiMe$_3$ groups was observed (Chart 1). Curious to know the products of the reactions of other NHSis with azides, we treated LSiX (X = NPh$_2$ (**1**), NMe$_2$ (**2**)) with trimethylsilyl azide (**3**) and adamantyl azide (**4**) and obtained tetracoordinate silicon containing silaimine products **5**−**8**. Compounds **6** and **8** are the first silaimine compounds (having a tetracoordinate silicon atom) possessing the terminal Si=NAd unit.

Chart 1



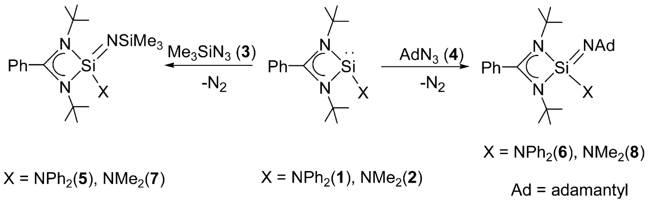
RESULTS AND DISCUSSION

Compounds [LSi(=NSiMe$_3$)X] (X = NPh$_2$ (**5**), NMe$_2$ (**7**)) were obtained by the reaction of LSiX (X = NPh$_2$ (**1**), NMe$_2$ (**2**)) with trimethylsilyl azide (**3**). Similarly, compounds [LSi(=NAd)X] (X = NPh$_2$ (**6**), NMe$_2$ (**8**)) were prepared by treating **1** and **2** with adamantyl azide (**4**). All the reactions proceed with the elimination of nitrogen gas. Compounds **5**−**8**

Received: November 27, 2012
Published: January 3, 2013

are stable both in the solid state and in solution for a long time without any decomposition under an inert gas atmosphere.

Scheme 1. Synthesis of Compounds 5−8



The ^{29}Si NMR spectrum of **5** exhibits two resonances, at δ −71.65 (L*Si*) and −20.80 (Si═N*Si*Me$_3$) ppm. The *t*Bu protons for compound **5** in its ^{1}H NMR spectrum appear as a singlet (δ 1.03 ppm). The SiMe$_3$ protons resonate at δ 0.57 ppm. Like **5**, compound **7** displays two resonances in its ^{29}Si NMR spectrum (δ −59.15 (L*Si*), −21.18 (Si═N*Si*Me$_3$) ppm). The SiMe$_3$ protons of compound **7** exhibit a single resonance at δ 0.62, and those of the *t*Bu group resonate at δ 1.05 ppm in its ^{1}H NMR spectrum. The mass spectra of compounds **5** and **7** show the molecular ion at *m*/*z* 514 and 390, respectively. The molecular structure of **5** was established by single-crystal X-ray diffraction studies. It is depicted in Figure 1. Compound **5** crystallized in the monoclinic space group $P2_1/n$. The central silicon atom is tetracoordinate. It is in a tetrahedral geometry. The coordination environment is made up of four nitrogen atoms (two from the amidinato ligand, one from the previous azide moiety, and one from amide moiety). The bond length between the silicon and nitrogen atom of the amide group is 1.7435(15) Å. The Si1−N3 bond length for **5** is 1.5828(15) Å, which is comparable to the Si═N value reported in the literature.[17b] The bite angle (N−Si−N) at the silicon atom with the backbone ligand is 71.88(5)°.

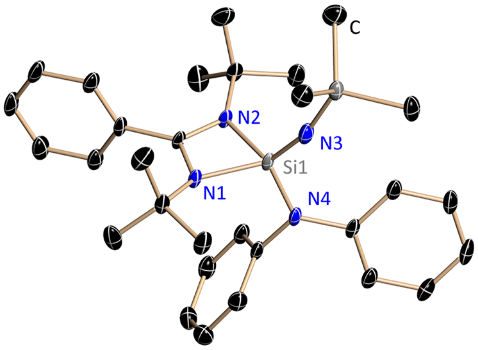


Figure 1. Molecular structure of **5**. The anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): N1−Si1 1.8217(13), N2−Si2 1.8336(12), N3−Si1 1.5828(15), N4−Si1 1.7435(15), N3−Si2 1.6553(16); N1−Si1−N2 71.88(5), N2−Si1−N3 120.88(7), N3−Si1−N4 118.88(7), N2−Si1−N4 107.22(6), Si1−N3−Si2 165.72(10).

Compounds **6** and **8** resonate at δ −66.60 and −67.19 ppm in their respective ^{29}Si NMR spectrum. In the ^{1}H NMR spectra, the *t*Bu groups of **6** and **8** display their resonances at δ 1.20 ppm. Further, **6** and **8** show the molecular ions in their respective EI-MS at *m*/*z* 576 and 452. The molecular structures of compounds **6** and **8** are given in Figures 2 and 3. Compounds **6** and **8** crystallize in the triclinic and monoclinic space groups $P\bar{1}$ and $P2_1/c$. Like **5**, the central silicon atom is four-coordinate. It consists of four nitrogen atoms and is in a tetrahedral geometry. The Si1−N4 bond lengths for **6** and **8** are 1.5728(12) and 1.584(5) Å. The bond length between the silicon and nitrogen atom of the amide group in **8** is 1.701(5) Å.[19] This is comparable to the reported one (1.724(2) Å) for LSiNMe$_2$ (**2**).[20] The bite angles for **6** and **8** are 71.10(5)° and 70.3(2)°.

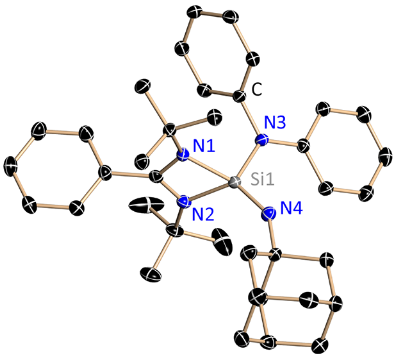


Figure 2. Molecular structure of **6**. The anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): N1−Si1 1.8340(12), N2−Si1 1.8563(12), N3−Si1 1.7613(12), N4−Si1 1.5728(12), N1−Si1−N2 71.10(5), N2−Si1−N3 106.09(6), N1−Si1−N3 105.34(5), N1−Si1−N4 126.24(6), N2−Si1−N4 125.89(6), N3−Si1−N4 114.21(6).

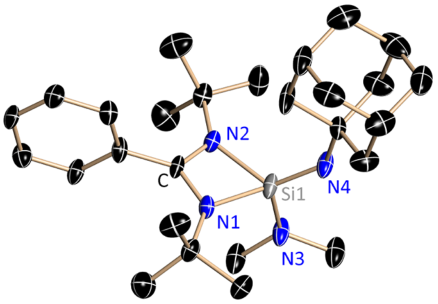


Figure 3. Molecular structure of **8**. The anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): N1−Si1 1.854(5), N2−Si1 1.845(5), N3−Si1 1.701(5), N4−Si1 1.584(5), N1−Si1−N2 70.3(2), N2−Si1−N3 107.3(2), N1−Si1−N3 107.9(2), N1−Si1−N4 125.0(2), N3−Si1−N2 107.3(2), N2−Si1−N4 124.6(3), N3−Si1−N4 114.1(2).

■ CONCLUSION

In summary we report on the reactivity of heteroleptic silylene, LSiX (X = NPh$_2$ (**1**), NMe$_2$ (**2**)), with trimethylsilyl azide (**3**) and adamantyl azide (**4**), which afforded the silaimine products [LSi(═NSiMe$_3$)X] (X = NPh$_2$ (**5**), NMe$_2$ (**7**)) and [LSi(═NAd)X] (X = NPh$_2$ (**6**), NMe$_2$ (**8**)). Compounds **6** and **8** are the first tetracoordinate silicon compounds having the terminal Si═NAd unit.

■ EXPERIMENTAL SECTION

Syntheses were carried out under an inert atmosphere of dinitrogen in oven-dried glassware using standard Schlenk techniques. All other manipulations were accomplished in a dinitrogen filled glovebox. Solvents were purified by a MBraun MB SPS-800 solvent purification system. Compounds **1** and **2** were prepared as reported in the literature.[12b] ^{1}H and ^{29}Si NMR spectra were recorded with a Bruker

Avance DPX 300 or a Bruker Avance DRX 500 spectrometer, using C_6D_6 as solvent. Chemical shifts δ are given relative to $SiMe_4$. EI-MS spectra were obtained using a Finnigan MAT 8230 spectrometer. Elemental analyses were performed at the Institut für Anorganische Chemie, Universität Göttingen. For elemental analysis compounds were dried under vacuum for 6 h to remove the solvent molecules.

Synthesis of 5. To a toluene (30 mL) solution of **1** (0.42 g, 0.98 mmol) in a Schlenk flask (100 mL) was added trimethylsilyl azide (**3**) (0.12 g, 1.04 mmol) in toluene (20 mL) drop by drop at −78 °C. The solution was warmed to room temperature and stirred for 6 h. The solvent was reduced *in vacuo* (10 mL) and stored at −26 °C in a freezer to obtain single crystals of **5** in 4 days. Yield: 0.40 g, 78%. Anal. Calcd for $C_{30}H_{42}N_4Si_2$ (514.85): C, 69.99; H, 8.22; N, 10.88. Found: C, 69.86; H, 8.16; N, 10.81. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ 0.57 (s, 9H, Si(CH_3)$_3$), 1.03 (s, 18H, *t*Bu), 6.76−7.21 (m, Ar*H*), 7.58−7.63 (m, Ar*H*) ppm. $^{29}Si\{^1H\}$ NMR (99.36 MHz, C_6D_6, 25 °C): δ −71.65 (L*Si*), −20.80 (Si=N*Si*Me$_3$) ppm. EI-MS: *m/z* 514 [M$^+$].

Synthesis of 6. Toluene (40 mL) was added to a Schlenk flask (100 mL) containing **1** (0.32 g, 0.75 mmol) and adamantyl azide (**4**) (0.14 g, 0.79 mmol). The reaction mixture was stirred at room temperature for 6 h. The solvent was reduced *in vacuo* (10 mL) and stored at −26 °C to obtain single crystals of **6** in a week. Yield: 0.32 g, 74%. Anal. Calcd for $C_{37}H_{48}N_4Si$ (576.89): C, 77.03; H, 8.39; N, 9.71. Found: C, 77.01; H, 8.33; N, 9.63. ^1H NMR (500 MHz, C_6D_6, 25 °C): δ 1.20 (s, 18H, *t*Bu), 1.42−2.32 (m, Ad*H*), 6.83−7.19 (m, Ar*H*), 7.73−7.78 (m, Ar*H*) ppm. $^{29}Si\{^1H\}$ NMR (99.36 MHz, C_6D_6, 25 °C): δ −66.60 (L*Si*) ppm. EI-MS: *m/z* 576 [M$^+$].

Synthesis of 7. To a toluene (30 mL) solution of **2** (0.30 g, 0.99 mmol) in a Schlenk flask (100 mL) was added trimethylsilyl azide (**3**) (0.12 g, 1.04 mmol) in toluene (20 mL) drop by drop at −78 °C. The solution was warmed to room temperature and stirred for 6 h. The solvent was reduced *in vacuo* (15 mL) and stored at −26 °C in a freezer to obtain crystals of **7** in 2 days. Yield: 0.31 g, 79%. Anal. Calcd for $C_{20}H_{38}N_4Si_2$ (390.71): C, 61.48; H, 9.80; N, 14.34. Found: C, 61.42; H, 9.71; N, 14.26. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ 0.62 (s, 9H, Si(CH_3)$_3$), 1.05 (s, 18H, *t*Bu), 2.75 (s, 6H, N(CH_3)$_2$), 6.72−7.03 (m, Ar*H*) ppm. $^{29}Si\{^1H\}$ NMR (59.63 MHz, C_6D_6, 25 °C): δ −59.15 (L*Si*), −21.18 (Si=N*Si*Me$_3$) ppm. EI-MS: *m/z* 390 [M$^+$].

Synthesis of 8. Toluene (40 mL) was added to a Schlenk flask (100 mL) containing **2** (0.38 g, 1.25 mmol) and adamantyl azide (**4**) (0.23 g, 1.29 mmol). The reaction mixture was stirred at room temperature for 6 h. The solvent was reduced *in vacuo* (10 mL) and stored at −26 °C to obtain single crystals of **8** in 4 days. Yield: 0.49 g, 86%. Anal. Calcd for $C_{27}H_{44}N_4Si$ (452.75): C, 71.63; H, 9.80; N, 12.37. Found: C, 71.54; H, 9.76; N, 12.36. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ 1.20 (s, 18H, *t*Bu), 1.38−2.23 (m, Ad*H*), 2.87 (s, 6H, N(CH_3)$_2$), 6.99−7.14 (m, Ar*H*) ppm. $^{29}Si\{^1H\}$ NMR (99.36 MHz, C_6D_6, 25 °C): δ −67.19 (L*Si*) ppm. EI-MS: *m/z* 452 [M$^+$].

Crystal Structure Determination. Crystals were taken out of the mother liquor under argon atmosphere using NVH oil. Diffraction data were collected at 100 K on a Bruker three-circle diffractometer equipped with a SMART 6000 CCD area detector and a Cu Kα rotating anode. The data sets of **5**, **6**, and **8** were collected to the edge of the Ewald sphere with high completeness and high multiplicity. Raw data were integrated with SAINT,[21] and an empirical absorption correction with SADABS[22] was applied. The structures were solved by direct methods (SHELXS-97) and refined against F^2 by full-matrix least-squares methods using all data SHELXL.[23] SHELXLE[24] was used as refinement GUI. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were constrained to ride on their parent atom with displacement parameters constrained to 1.2 or 1.5 of the U_{iso} of their parent atom. Anisotropic displacement parameters of carbon and nitrogen atoms were restrained in the refinement of **8** using SIMU, ISOR, and RIGU[25] commands.

■ ASSOCIATED CONTENT

Supporting Information

Crystal and structure refinement parameters for compounds **5**, **6**, and **8** (Table S1). CIF files for **5** (CCDC-911153), **6** (CCDC-911154), and **8** (CCDC-911155). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the Deutsche Forschungsgemeinschaft (DFG) for supporting this work. R.A. is grateful to the Alexander von Humboldt Stiftung for a research fellowship.

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