ORGANOMETALLICS
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Reactivity of Stable Heteroleptic Silylene $PhC(NtBu)_2SiNPh_2$ toward Diazobenzene and *N*-Benzylidineaniline

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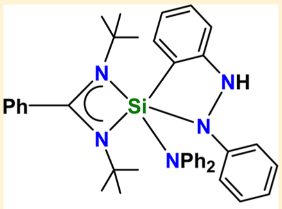
Supporting Information

ABSTRACT: The reaction of heteroleptic silylene $LSiNPh_2$ [L = $PhC(NtBu)_2$] with diazobenzene afforded product **6**. This involves one *o*-C−H bond activation at one of the phenyl groups of diazobenzene and migration of this hydrogen atom from the phenyl ring to one of the nitrogen atoms, which leads to the formation of the new C−Si and N−Si bonds. The reaction of benzylidineaniline with $LSiNPh_2$ results in the oxidative addition of the three-membered silaaziridine derivative **7**. Compounds **6** and **7** were fully characterized by elemental analysis, multinuclear NMR spectroscopy, and EI-MS spectrometry. The molecular structures of compounds **6** and **7** were established unequivocally by single-crystal X-ray structural analysis.



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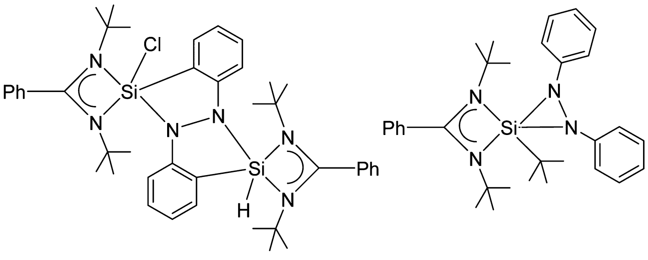
■ INTRODUCTION

Silylenes are compounds with divalent silicon atom and are the silicon congeners of carbenes.[1] For many decades, silylenes had been recognized as short-lived species either in the gas phase, in solution, or trapped in frozen matrixes.[2] They feature both nucleophilic as well as electrophilic reactive sites at the silicon atom, which have a lone pair orbital and a vacant pπ orbital.[3] In 1986, the remarkable divalent silicon ten-coordinate π complex, $(Me_5C_5)_2Si$, was synthesized by Jutzi and co-workers.[4] The first stable N-heterocyclic silylene (NHSi), the silicon analogue of N-heterocyclic carbene (NHC), was reported by West et al. in 1994.[5] The NHCs have been studied extensively and find a wide variety of applications, such as organocatalyst reagents and also as excellent σ-donor ligands to stabilize compounds with unusual oxidation states.[6,7] Many noteworthy reactivity studies of stable NHSi's toward a variety of substrates have been reported, such as insertion,[8−13] addition,[14] metal complexation,[15] and Lewis acidic behavior.[16] Recently, we reported on functionalized silylenes that were prepared by the facile metathesis reaction of alkali metal amide, phosphide, alkoxide, or organoalkyl reagent with LSiCl[17,18] in toluene as a solvent.[19] A brief literature survey reveals that the reactivity pattern of different silylenes with diazobenzene shows unlike behavior. This might be due to the presence of two reactive sites of diazobenzene, the N=N π bond and the two lone pairs of electrons where each resides on a nitrogen atom. In 1991, Ando et al. reported on the synthesis of 1,2-diaza-3,4-disilacyclobutane by the photochemical treatment of tetramesityldisilene with diazobenzene.[20] Recently, So et al. described the formation of 1,2-diaza-3,4-disilacyclobutane containing a five-coordinate silicon center by the reaction of $\{PhC(NtBu)_2\}$-$SiSi(Cl)\{(NtBu)_2C(H)Ph\}$ with diazobenzene.[21] Weidenbruch et al. observed the formation of a 1,3-diaza-2-silaindan or 1-aza-2-silaindan derivative by the reaction of sterically encumbered silylene R_2Si: (R = 2,4,6-$Me_3C_6H_2$, 2,4,6-$iPr_3C_6H_2$) with diazobenzene.[22] The reaction might proceed via the intermediate of siladiaziridine, followed by insertion of the N−N single bond into the *o*-C−H bond of one of the phenyl rings or into the C−*H*Me_2 bond of one of the *o*-isopropyl groups. We also reported on the diverse reactivity pattern of silylenes LSiCl (**1**) and LSi*t*Bu (**3**) with diazobenzene. In the reaction of **1**, the unsymmetrical polycycle **2** (Chart 1) was formed with *o*-C−H bond activation of the phenyl ring.[23] Treatment of **3** with diazobenzene resulted in the siladiaziridine derivative **4** (Chart 1).[24] We were curious to know the reactivity pattern of diazobenzene with the $LSiNPh_2$ (**5**). As expected, the reaction proceeds in a different manner and the product **6** was obtained. We surmise that the product of the reaction is dependent on the substituents at the silicon center. On the one hand, compound **6** was formed by the activation of one *o*-C−H bond atom of one of the phenyl groups of diazobenzene and migration of this hydrogen atom from the phenyl ring to one of the nitrogen atoms. This is connected with the formation of the new C−Si and N−Si bonds. On the other hand, the reaction of benzylidineaniline with $LSiNPh_2$ led to the formation of the three-membered silaaziridine derivative **7**, similar to the silaaziridine products obtained from the reaction of LSiCl and LSi*t*Bu with diazobenzene,[24,29] respectively.

Chart 1



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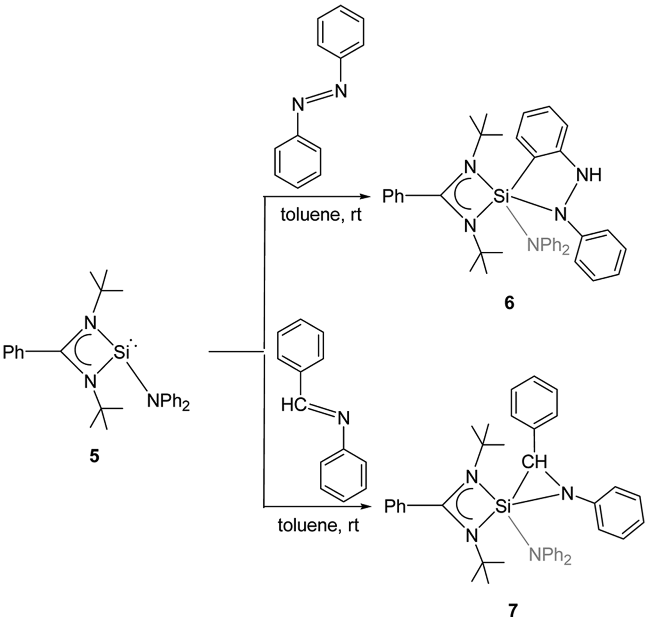
Received: October 24, 2012
Published: December 7, 2012

dx.doi.org/10.1021/om300999e | *Organometallics* 2012, 31, 8608−8612

■ RESULTS AND DISSCUSSION

Compounds **6** and **7** were obtained by one-pot reactions of $LSiNPh_2$ (**5**) with PhN═NPh (for **6**) and PhN═CHPh (for **7**) in the molar ratio of 1:1 (Scheme 1). Compounds **6** and **7** are soluble in common organic solvents, and they are stable, both in the solid state as well as in solution without any decomposition under an inert gas atmosphere. Compounds **6** and **7** were fully characterized by spectroscopic methods. The molecular structures of compounds **6** and **7** were established unambiguously by single-crystal X-ray structural analysis.

Scheme 1. Synthesis of Compounds 6 and 7



Compound **6** shows a single resonance at δ −88.2 ppm in its ^{29}Si NMR spectrum, which is upfield shifted when compared with that of $LSiNPh_2$ (δ −20.5 ppm).[19b] The *t*Bu protons of compound **6** in the ^1H NMR spectrum exhibit a double resonance of equal intensity for the *t*Bu groups that reside over the nitrogen atoms (δ 0.91 and 1.00 ppm). The N−H proton shows a singlet at 5.35 ppm. Further, compound **6** displays its molecular ion in the mass spectrum at m/z 609.

Compound **6** crystallizes in the monoclinic space group $P2_1/n$, and the molecular structure is shown in Figure 1. The tentative mechanism for the formation of **6** has been proposed in Scheme 2. The silicon atom is five-coordinate, and the coordination environment is made up from four nitrogen atoms and a carbon atom from the phenyl group. The structural index τ, which defines the extent of deviation from trigonal-bipyramidal to square-pyramidal geometry ($\tau = 1$ for perfect trigonal-bipyramidal; $\tau = 0$ for perfect square-based pyramid[25]), is 0.78, indicating a closer arrangement to the regular trigonal-bipyramidal geometry. The N1−Si1−N2 bite angle between the silicon atom with the backbone ligand is 68.08(8)°. The bond length between the Si and nitrogen atom of the NPh_2 moiety is 1.777(2) Å. Here, the azo compound is converted into the hydrazine derivative. The position of the hydrogen atom at N5 was taken from the difference Fourier map and refined freely. The bond length between N4−N5 is 1.422(2) Å and indicates a N−N bond length that is quite comparable to the N−N bond lengths of other hydrazine or hydrazone derivatives that are reported in the literature.[26,27] The bond lengths of the phenyl ring, which is attached to the silicon atom (between adjacent carbon atoms C34−C39), is in the range of 1.37−1.4 Å, indicating complete delocalization of π-electron density within the ring, retaining its aromatic character. The Si1−N4 bond length is 1.8306(18) Å and indicates a Si−N single-bond character.[28]

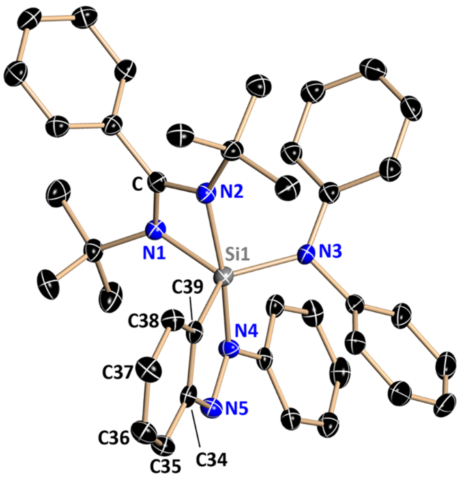


Figure 1. Molecular structure of **6**. The anisotropic displacement parameters are depicted at the 50% probability level. Selected bond lengths (Å) and bond angles (deg): N2−Si1 2.0239(18), N1−Si1 1.847(2), N3−Si1 1.777(2), N4−Si1 1.8306(18), N4−N5 1.422(2); N1−Si1−N2 68.08(8), N3−Si1−N4 93.44(9), Si1−N4−N5 114.79(13).

The silaaziridine compound **7** formed by [1 + 2]-cycloaddition reaction exhibits a single resonance at δ −133.1 ppm in its ^{29}Si NMR spectrum. Like **6**, the *t*Bu protons reside over the nitrogen atoms of compound **7** and display a double resonance of equal intensity in the ^1H NMR spectrum (δ 0.67, 1.34 ppm). The imino proton shows a singlet at δ 4.27 ppm. Further, compound **7** shows its molecular ion in the mass spectrum at m/z 608.

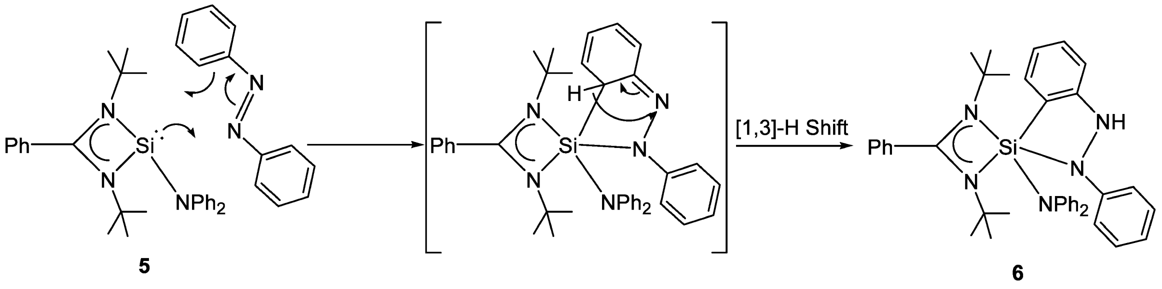
The molecular structure of compound **7** is shown in Figure 2. It crystallizes in the monoclinic space group $P2_1/c$. Like **6**, the silicon atom in **7** is also five-coordinate (four nitrogen atoms and one carbon atom) with $\tau = 0.45$. The N1−Si1−N2 bite angle is 69.61(6)°. Again, the position of the hydrogen atom at C16 was taken from the difference Fourier map and refined freely. The angles of the newly formed NSiC three-membered ring are N3−Si1−C16 (48.95(7)°), Si1−N3−C16 (69.91(9)°), and N3−C16−Si1 (61.13(9)°). Likewise, the bond lengths within the ring are Si1−N3 (1.7410(16) Å), C16−N3 (1.499(2) Å), and Si1−C16 (1.8672(19) Å). These values are quite comparable to those of Si−N,[24,29] C−N,[24,29] and Si−C[24,29] distances reported in the literature. The Si1−N4 bond length is 1.7356(16) Å.

Moreover, it is worth mentioning that Woerpel et al.[30] reported on the three-membered ring expansion of silaaziridines with organic substrates. The presence of an aromatic group either at the carbon or at the nitrogen atom of the silaaziridine moiety undergoes dearomatization upon treatment with benzaldehyde with the relief of strain in the three-membered ring.

■ CONCLUSION

In conclusion, we have shown a unique reactivity pattern of diazobenzene with heteroleptic silylene $LSiNPh_2$, leading to

Scheme 2. Proposed Mechanism for the Formation of 6



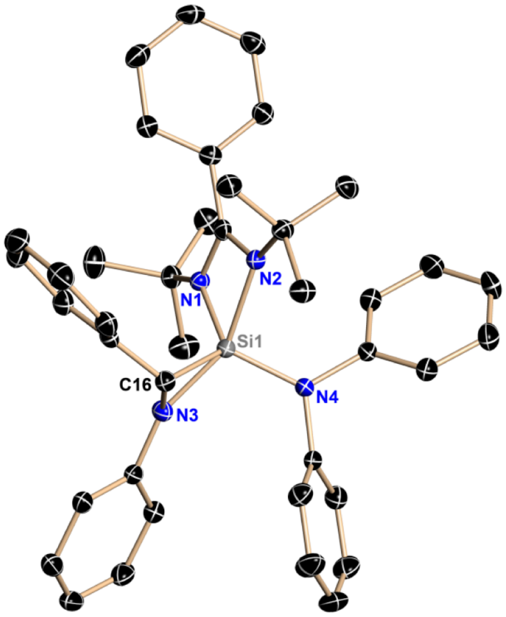


Figure 2. Molecular structure of **7**. The anisotropic displacement parameters are depicted at the 50% probability level. Selected bond lengths (Å) and bond angles (deg): N1−Si1 1.8241(16), N2−Si1 1.9299(16), N3−Si1 1.7410(16), N4−Si1 1.7356(16), C16−N3 1.499(2), Si1−C16 1.8672(19); N1−Si1−N2 69.61(6), N1−Si1−N3 105.84(7), N2−Si1−N3 149.08(7), N3−Si1−N4 108.13(7), C16−Si1−N3 48.95(7), Si1−N3−C16 69.91(9), N3−C16−Si1 61.13(9).

product **6**. This was formed by the activation of the *o*-C−H bond of one of the phenyl groups and migration of this hydrogen atom to one of the nitrogen atoms of diazobenzene. The reaction of benzylidineaniline with $LSiNPh_2$ led to the formation of the three-membered silaaziridine ring **7**.

■ 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 the MBRAUN solvent purification system MB SPS-800. All chemicals were purchased from Aldrich and used without further purification. $LSiNPh_2$[19b] (**5**) was prepared as reported in the literature. ^1H 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 a 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 6. Toluene (60 mL) was added to a 100 mL Schlenk flask containing $LSiNPh_2$ (**5**) (0.48 g, 1.12 mmol) and PhN═NPh (0.21 g, 1.15 mmol) at room temperature. The reaction mixture was stirred for 14 h. Then the reaction mixture was filtered, and the solvent of the filtrate was reduced *in vacuo* to 20 mL. The concentrate was stored at −27 °C in a freezer for a week, and finally, maroon-colored crystals of **6** were obtained (0.52 g, 76%). Elemental analysis (%) calcd for $C_{39}H_{43}N_5Si$ (609.88): C, 76.81; H, 7.11; N, 11.48. Found: C, 76.76; H, 7.02; N, 11.37. ^1H NMR (500 MHz, C_6D_6, 25 °C): δ 0.91 (s, 9H, $C(CH_3)_3$), 1.00 (s, 9H, $C(CH_3)_3$), 5.35 (s, 1H, N*H*), 6.70−8.39 (m, Ar*H*) ppm. $^{29}Si\{^1H\}$ NMR (99.36 MHz, C_6D_6, 25 °C): δ −88.2 ppm. EI−MS: *m*/*z* 609 [M^+].

Synthesis of 7. Toluene (60 mL) was added to a 100 mL Schlenk flask containing $LSiNPh_2$ (**5**) (0.45 g, 1.05 mmol) and PhN═CHPh (0.20 g, 1.10 mmol) at room temperature. The reaction mixture was stirred for 14 h. The reaction mixture was then filtered, and the solvent of the filtrate was reduced *in vacuo* to 20 mL. The concentrate was stored at −27 °C in a freezer for 3 days to obtain the colorless crystals of **7** (0.55 g, 86%). Elemental analysis (%) calcd for $C_{40}H_{44}N_4Si$ (608.89): C, 78.90; H, 7.28; N, 9.20. Found: C, 78.77; H, 7.16; N, 9.12. ^1H NMR (500 MHz, C_6D_6, 25 °C): δ 0.67 (s, 9H, $C(CH_3)_3$), 1.34 (s, 9H, $C(CH_3)_3$), 4.27 (s, 1H, C*H*Ph), 6.53−8.13 (m, Ar*H*) ppm. $^{29}Si\{^1H\}$ NMR (59.63 MHz, C_6D_6, 25 °C): δ −133.1 ppm. EI−MS: *m*/*z* 608 [M^+].

Crystal Structure Determination. Suitable single crystals for X-ray structural analysis of **6** and **7** were mounted at low temperature in inert oil under an argon atmosphere by applying the X-Temp 2 device.[31] The diffraction data were collected at 100 K on a Bruker D8 three circle diffractometer equipped with a SMART APEX II CCD detector and a microfocus source with INCOATEC Quazar mirror optics ($\lambda = 0.71073$ Å).[32] The data were integrated with SAINT,[33] and an empirical absorption correction with SADABS[34] was applied. The structures were solved by direct methods (SHELXS-97) and refined against all data by full-matrix least-squares methods on F^2 (SHELXL-97).[35] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their U_{iso} values constrained to $1.5U_{eq}$ of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms. In **6**, H1 (attached to N5) and, in **7**, H16 (attached to C16) were refined freely from the $F_o - F_c$ density map.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystal and structure refinement parameters for compounds **6** and **7** (Table S1). CIF files for **6** and **7**. 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 are thankful to the Deutsche Forschungsgemeinschaft (DFG RO 224/60-1) and Prohama, Ludwigshafen, for supporting this work. R.A. is thankful to the Alexander von Humboldt Stiftung for a research fellowship. D.S. and H.W. are grateful to the DNRF funded Center for Materials Crystallography (CMC) for support, and the Land Niedersachsen for providing a fellowship in the Catalysis of Sustainable Synthesis (CaSuS) Ph.D. program.

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