ORGANOMETALLICS

COMMUNICATION

pubs.acs.org/Organometallics

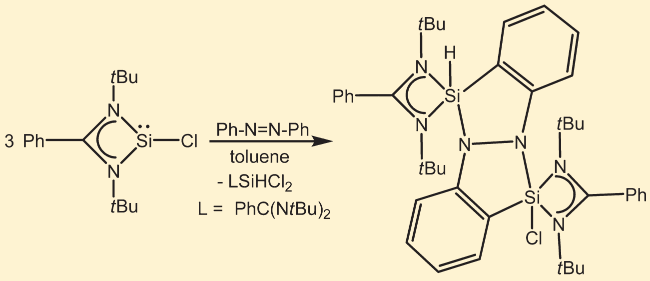
Formation of a Unsymmetrical Ring System via C–H Bond Activation of Diazobenzene by Stable N-Heterocyclic Chlorosilylene (PhC(N*t*Bu)$_2$SiCl)

Shabana Khan, Sakya S. Sen, Reent Michel, Daniel Kratzert, Herbert W. Roesky,* and Dietmar Stalke

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

Supporting Information

ABSTRACT: The reaction of N-heterocyclic chlorosilylene (**1**; LSiCl, L = PhC(N*t*Bu)$_2$) with diazobenzene is described, which afforded the unsymmetrical polycyclic product **2** via chlorosilylene mediated aromatic C–H bond activation. The reaction proceeds without the cleavage of the N–N bond of diazobenzene. Polycycle **2** was fully characterized by single-crystal X-ray diffraction analysis, multinuclear NMR spectroscopy, EI-MS spectrometry, and elemental analysis.



Since the isolation of stable silylenes,[1] it has been frequently experienced that addition of stable silylenes to homo- and heteronuclear multiple bonds is a convenient method for the synthesis of novel ring compounds containing silicon atoms.[2] Recently we have reported the synthesis of 1,2-disilacyclobutene[3] by treating benzamidinatochlorosilylene (**1**; LSiCl, L = PhC(N*t*Bu)$_2$) with diphenylalkyne. In sharp contrast to that, the reaction of **1** with adamantylphosphaalkyne leads to the formation of a Si_2CP four-membered ring system, which shows a zwitterionic configuration.[4] The structural and chemical aspects of these ring compounds are of interest because they contribute new insight into the bonding properties. In this respect diazobenzene is particularly interesting as a precursor, since it contains three reactive sites: a N=N π-bond and a lone pair of electrons on each nitrogen atom. The unique reactions of diazobenzene with lanthanide(II),[5a] Mg(I),[5b] Ge(I),[5c,d] and Sn(I)[5c] have already been described. Despite such evident interest, until now there have been very limited examples of silylene addition to diazobenzene[6,7] and the results show dissimilar behavior of diazobenzene toward different silylenes. Ando et al. reported on the photolysis of hexamesitylcyclotrisilane and tetramesityldisilene on exposure to light in the presence of diazobenzene, which afforded 1,2-disiladiazacyclobutane.[6a] Formation of a similar product was also observed by So et al. very recently from the reaction between silylsilylene [{PhC(N*t*Bu)$_2$}SiSi(Cl)-{N(*t*Bu)$_2$C(H)Ph}] and diazobenzene.[6b] In marked contrast, Weidenbruch and co-workers described the reactions of the sterically encumbered silylenes R_2Si: (R = 2,4,6-$Me_3C_6H_2$, 2,4,6-*i*$Pr_3C_6H_2$) generated in situ with diazobenzene, furnishing 1,3-diaza-2-silaindan or 1-aza-2-silaindan derivatives.[7] The most intriguing feature of this reaction is the activation of the *o*-C–H bond of diazobenzene and an entire cleavage of the N=N double bond. C–H bonds of the phenyl ring are considered to be unreactive, although we recently showed selective C–H bond activation with silylene.[8] Moreover, direct activation of the C–H bond to form a Si–C bond under mild conditions is rare, and in this respect the formation of C–H activation products obtained from the reactions between silylene and alkane or diethyl ether is particularly noteworthy.[9] Given the growing importance of silylene in synthetic chemistry, we presume that treatment of **1** with diazobenzene may also activate the C–H bond of the phenyl group and lead to a unusual addition and rearrangement product or furnish a siladiaziridine derivative.

Addition of a toluene solution of diazobenzene to a colorless toluene solution of **1** in a 1:3 molar ratio at ambient temperature resulted in a greenish yellow solution after stirring for 12 h (Scheme 1).[10] Single block-shaped yellow crystals of **2** suitable for X-ray diffraction analysis were grown from a saturated toluene solution (Figure 1).[11] Selected bond lengths and bond angles of **2** are given in the legend of Figure 1. Compound **2** crystallizes in the triclinic space group $P\bar{1}$ and has a crystallographic inversion center in the middle of the N–N bond.[11] The molecular structure of **2** displays a unsymmetrical polycycle of six (four-, five-, and six-membered) rings. The silicon atom Si1 is 5-fold coordinated and exhibits a distorted-trigonal-bipyramidal geometry. It is coordinated by two nitrogen atoms (N1 and N2) from the backbone of the chelating ligand, one carbon atom (C16) of the diazobenzene phenyl ring, and one bridging nitrogen atom (N3). The fifth position in the coordination sphere of Si1 shows Cl/H disorder. Hydrogen (H1) and chlorine (Cl1) atoms were found on similar positions, each with 50% occupancy. There are two possible reasons for this disorder: (i) alternating orientation of the Si–H

Received: March 7, 2011
Published: April 18, 2011

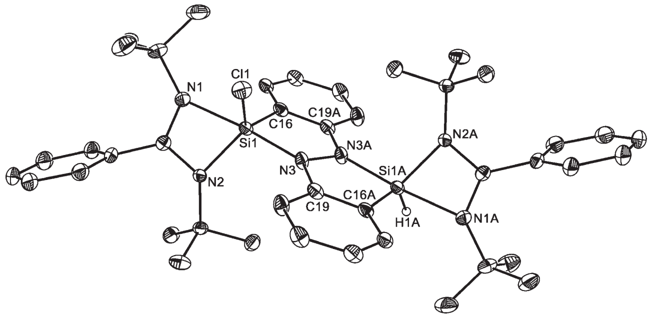
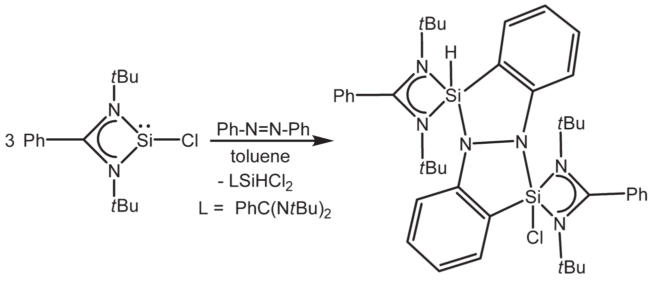


Figure 1. Crystal structure of **2**·(toluene). Hydrogen atoms, except those freely refined at Si1, and disordered toluene are not shown for clarity. Atoms labeled with the letter A are symmetry-generated by inversion. Cl1 and H1 are disordered in a 1:1 ratio, but Cl1A and H1 are omitted for clarity. Anisotropic displacement parameters are depicted at the 50% probability level. Selected bond distances (Å) and bond angles (deg): N1−Si1 = 1.980(2), N2−Si1 = 1.822(2), Si1−N3 = 1.811(2), C16−Si1 = 1.855(3), Cl1−Si1 = 2.1507(15), H1A−Si1A = 1.44(7), N3−N3A = 1.426(4), C19−N3 = 1.372(3); N1−Si1−N2 = 69.06(9), N1−Si1−N3 = 174.55(10), N2−Si1−N3 = 105.96(10), N3−Si1−C16 = 86.10(10), N2−Si1−C16 = 117.48(11), N2−Si1−Cl1 = 114.27(8), N3−Si1−Cl1 = 90.17(8), N3A−N3−Si1 = 115.5(2), C19A−C16−Si1 = 111.38(17).

Scheme 1. Preparation of 2



and Si−Cl fragments in the crystal packing and (ii) a 1:1 ratio of the dihydro and dichloro derivatives of **2** in the crystal. However, a detailed spectrochemical analysis of the data gives strong evidence for compound **2** (Figure 1).

The Si1−N3 bond length is 1.811(2) Å, in accordance with the Si−N single bonds reported in the literature.[12a,b] The N−N bond length is 1.426(4) Å, which is consistent with a single bond.[5d,12c,12d] The coordination of the nitrogen atoms is almost planar in **2**, with an angular sum of 349.5°. The N3−N3A bond is arranged in such a manner that it provides the bridging platform for the formation of a unsymmetrical polycycle via fusion of two different units so that it ultimately forms the fused ring system in Figure 1. The most noticeable feature is the formation of a new Si−C bond via *o*-C−H bond activation of the phenyl group of diazobenzene. The new Si−C bond length is 1.855(3) Å, which is consistent with a Si−C single-bond distance.[13] Another interesting feature is the C19−N3 bond distance (1.372(3) Å), which is shorter compared to that of diazobenzene (1.43 Å).

The crystal structure was further supported by the spectroscopic data. The ^{1}H NMR spectrum exhibits resonances for two sets of *t*Bu protons (δ 0.94 and 1.46 ppm) and each set corresponds to 18 protons. The resonance for one Si−H proton appears at δ 6.34 ppm as a doublet, and the integration confirms the presence of only one Si−H proton in the polycycle **2**. The ^{29}Si NMR spectrum exhibits a doublet resonance (δ −94.28 ppm) with a coupling constant of ^1J(Si−H) = 280.42 Hz.[14] Another silicon center attached to a chlorine atom shows a resonance at δ −86.7 ppm. In the ^{13}C NMR spectrum two sets of resonances were observed; they confirm the presence of two chemically different silicon atoms in **2**. The IR spectrum displays a characteristic absorption band at 2086 cm^{-1} for the Si−H bond.[14] The molecular ion was observed in the EI-MS spectrum as the most abundant peak with the highest relative intensity at m/z 734 [M$^+$]. A molecular ion with a high relative intensity is an additional proof for the presence of Si−H and Si−Cl units in **2**. The formation of LSiHCl$_2$ as a byproduct was observed during the reaction, and it was confirmed by a ^{29}Si NMR investigation (δ −96.8 ppm).[3]

The C−H bond activation, a phenomenon known mainly for s- and d-block elements, is not common for silicon compounds.[7−9] In 1998 Weidenbruch et al. reported the formation of a bicyclic system by the reaction of dimesitylsilylene with diazobenzene, and they explained the formation of the final product as the result of the cleavage of the N−N bond and C−H bond activation altogether.[7] It is noteworthy to mention that in our case we isolated the final product without cleavage of the N−N bond. Although the mechanism of this reaction is still unknown, it can be proposed that the first step of the reaction is the formation of the five-membered ring intermediate via a [1 + 4] cycloaddition reaction between the silicon(II) center and the PhN− moiety of diazobenzene, followed by rearomatization, which in situ gives rise to the formation of the unsymmetrical polycycle **2** (see the Supporting Information for the tentative mechanism). This is the first example, to the best of our knowledge, where stable silylene reacts with diazobenzene to form the dimeric unsymmetrical polycycle **2** via C−H bond activation as well as Si−C bond formation without cleavage of the N−N bond. Here it is noteworthy that there was no reaction observed between *t*Bu−N═N−*t*Bu and **1**. Therefore, it is obvious that the activation of the aromatic *o*-C−H bond of diazobenzene is the key step for the reaction along with rearomatization.

In summary we have shown a unique reactivity of chlorosilylene **1** with diazobenzene featuring aromatic *o*-C−H bond activation without the cleavage of the N−N bond to form the unsymmetrical polycycle **2**. This is the first example of six rings (four-, five-, and six-membered) being arranged together by [1 + 4] cycloaddition of diazobenzene with LSiCl.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. A figure giving the tentative mechanism for the formation of **2** and a CIF file giving crystallographic data for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Tel: +49551393001. Fax: +49551393373. E-mail: hroesky@gwdg.de.

■ ACKNOWLEDGMENT

We are thankful to the Deutsche Forschungsgemeinschaft for supporting this work. S.K. is grateful to the Deutscher Akademischer Austausch Dienst for a research fellowship. D. S. thanks 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.

■ REFERENCES

(1) For recent reviews see: (a) Gehrhus, B.; Lappert, M. *Polyhedron* **1998**, *17*, 999–1000. (b) Haaf, M.; Schmedake, T. A.; West, R. *Acc. Chem. Res.* **2000**, *33*, 704–714. (c) Weidenbruch, M. *Organometallics* **2003**, *22*, 4348–4360. (d) Kira, M. *J. Organomet. Chem.* **2004**, *689*, 4475–4488. (e) Ottosson, H.; Steel, P. G. *Chem. Eur. J.* **2006**, *12*, 1576–1585. (f) Nagendran, S.; Roesky, H. W. *Organometallics* **2008**, *27*, 457–492. (g) Mizuhata, Y.; Sasamori, T.; Tokitoh, N. *Chem. Rev.* **2009**, *109*, 3479–3511. (h) Wang, Y.; Robinson, G. H. *Chem. Commun.* **2009**, 5201–5213. (i) Kira, M. *Chem. Commun.* **2010**, *46*, 2893–2903. (j) Mandal, S. K.; Roesky, H. W. *Chem. Commun.* **2010**, *46*, 6016–6041. (k) Asay, M.; Jones, C.; Driess, M. *Chem. Rev.* **2011**, *111*, 354–396.

(2) For recent papers see: (a) Yao, S.; van Wüllen, C.; Sun, X.-Y.; Driess, M. *Angew. Chem.* **2008**, *120*, 3294–3297; *Angew. Chem., Int. Ed.* **2008**, *47*, 3250–3253. (b) Sen, S. S.; Roesky, H. W.; Stern, D.; Meindl, K.; Henn, J.; Stückl, A. C.; Stalke, D. *Chem. Commun.* **2010**, *46*, 5873–5875. (c) Gao, Y.; Zhang, J.; Hu, H.; Cui, C. *Organometallics* **2010**, *29*, 3063–3065. (d) Khan, S.; Sen, S. S.; Roesky, H. W.; Kratzert, D.; Michel, R.; Stalke, D. *Inorg. Chem.* **2010**, *49*, 9689–9693. (e) Yasuda, H.; Lee, V. Y.; Sekiguchi, A. *J. Am. Chem. Soc.* **2009**, *131*, 6352–6353. (f) Tavčar, G.; Sen, S. S.; Roesky, H. W.; Hey, J.; Kratzert, D.; Stalke, D. *Organometallics* **2010**, *29*, 3930–3935. (g) Atwell, W. H. *Organometallics* **2008**, *28*, 3573–3586. (h) Sen, S. S.; Khan, S.; Kratzert, D.; Roesky, H. W.; Stalke, D. *Eur. J. Inorg. Chem.* **2011**, 1370–1373. (i) Khan, S.; Sen, S. S.; Kratzert, D.; Tavčar, G.; Roesky, H. W.; Stalke, D. *Chem. Eur. J.* **2011**, *17*, 4283–4290.

(3) Sen, S. S.; Roesky, H. W.; Stern, D.; Henn, J.; Stalke, D. *J. Am. Chem. Soc.* **2010**, *132*, 1123–1126.

(4) (a) Sen, S. S.; Khan, S.; Roesky, H. W.; Kratzert, D.; Meindl, K.; Henn, J.; Stalke, D.; Demers, J.-P.; Lange, A. *Angew. Chem.* **2011**, *123*, 2370–2373; *Angew. Chem., Int. Ed.* **2011**, *50*, 2322–2325.

(5) (a) Evans, W. J.; Drummond, D. K.; Chamberlain, L. R.; Doedens, R. J.; Bott, S. G.; Zhang, H.; Atwood, J. L. *J. Am. Chem. Soc.* **1988**, *110*, 4983–4994; (b) Bonyhady, S. J.; Green, S. P.; Jones, C.; Nembenna, S.; Stasch, A. *Angew. Chem.* **2009**, *121*, 3017–3021; *Angew. Chem., Int. Ed.* **2009**, *48*, 2973–2977. (c) Cui, C.; Olmstead, M. M.; Fettinger, J. C.; Spikes, G. H.; Power, P. P. *J. Am. Chem. Soc.* **2005**, *127*, 17530–17541. (d) Sen, S. S.; Kratzert, D.; Stern, D.; Roesky, H. W.; Stalke, D. *Inorg. Chem.* **2010**, *49*, 5786–5788.

(6) (a) Sakakibara, A.; Kabe, Y.; Shimizu, T.; Ando, W. *J. Chem. Soc., Chem. Commun.* **1991**, 43–44. (b) Zhang, S.-H.; Yeong, H.-X; So, C.-W. *Chem. Eur. J.* **2011**, *17*, 3490–3494.

(7) Weidenbruch, M.; Olthoff, S.; Saak, W.; Marsmann, H. *Eur. J. Inorg. Chem.* **1998**, 1755–1758.

(8) Jana, A.; Samuel, P. P.; Roesky, H. W.; Schulzke, C. *J. Am. Chem. Soc.* **2010**, *132*, 10164–10170.

(9) (a) Walker, R. H.; Miller, K. A.; Scott, S. L.; Cygan, Z. T.; Bartolin, J. M.; Kampf, J. W.; Holl, M. M. B. *Organometallics* **2009**, *28*, 2744–2755. (b) Hartmann, M.; Haji-Abdi, A.; Abersfelder, K.; Haycock, P. R.; White, A. J. P.; Scheschkewitz, D. *Dalton Trans.* **2010**, *39*, 9288–9295. (c) Nguyen, T.-I.; Scheschkewitz, D. *J. Am. Chem. Soc.* **2005**, *127*, 10174–10175. (d) Abersfelder, K.; Scheschkewitz, D. *J. Am. Chem. Soc.* **2008**, *130*, 4114–4121.

(10) All manipulations were carried out under an inert atmosphere of dinitrogen using standard Schlenk techniques and in a dinitrogen-filled glovebox. Solvents were purified with the MBRAUN solvent purification system MB SPS-800. Compound **1** was prepared according to the literature method,[3] and diazobenzene purchased from Aldrich was used without further purification. ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded in THF-d_8 with Bruker Avance DRX 500 spectrometer. The chemical shifts δ are given relative to SiMe$_4$. The EI-MS spectrum was obtained using a Finnigan MAT 8230 instrument. The IR spectrum was recorded on a Bio-Rad Digilab FTS7 spectrometer in the range 4000–350 cm^{-1}. Elemental analyses were performed by the Institut für Anorganische Chemie, Universität Göttingen. The melting point was measured in a sealed glass tube on a Büchi B-540 melting point apparatus. To a solution of **1** (0.293 g, 1 mmol) in toluene (30 mL) was added a solution of PhNNPh (0.06 g, 0.33 mmol) in toluene (20 mL) slowly at room temperature. The mixture was stirred for 12 h and the resulting greenish yellow solution was concentrated in vacuo to 5 mL and stored at room temperature to yield block-shaped yellow crystals of **2** (0.14 g, 20%). Mp: 168 °C. ^{1}H NMR (500 MHz, THF-d_8, 25 °C): δ 0.94 (s, 18H, *t*Bu), 1.46 (s, 18H , *t*Bu), 6.30 (s, 1H, Si-*H*), 6.67–6.77 (m, 2H, *Ph*), 7.16–7.66 (m, 14H, *Ph*), 7.92–7.97 (m, 2H, *Ph*) ppm. $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (125.75 MHz, THF-d_8, 25 °C): δ 31.21-(C*Me*$_3$), 32.13(C*Me*$_3$), 54.69 (*C*Me$_3$), 55.61(*C*Me$_3$), 115.43, 116.43, 128.30, 128.91, 130.06, 130.71, 131.03, 131.12, 135.41, 136.29, 153.78, 153.98 (*Ph*), 172.11, 172.87 (NCN) ppm. $^{29}\mathrm{Si}\{^{1}\mathrm{H}\}$ NMR (99.36 MHz, THF-d_8, 25 °C): δ −94.28 (d, ^{1}J(Si–H) = 280.42 Hz), −86.7 ppm. EI-MS: m/z: 734 $[\mathrm{M}^+]$ (100%). IR (Nujol, cm^{-1}): $\bar{\nu}$ 2086 (Si–H). For elemental analysis **2**·(toluene) was treated under vacuum overnight to remove the toluene molecule. Anal. Calcd for $C_{42}H_{55}ClN_6Si_2$ (734.37): C, 68.58; H, 7.54; N, 11.43. Found: C, 68.17; H, 7.23; N, 10.77.

(11) X-ray investigation of **2**: the data sets were collected from oil coated shock-cooled crystals ((a) Stalke, D. *Chem. Soc. Rev.* **1998**, *27*, 171–178. (b) Kottke, T.; Lagow, R. J.; Stalke, D. *J. Appl. Crystallogr.* **1996**, *29*, 465–468. (c) Kottke, T.; Stalke, D. *J. Appl. Crystallogr.* **1993**, *26*, 615–619.) on a Bruker SMART-APEX diffractometer with a D8 goniometer (Mo Kα radiation, λ = 0.71073 Å) equipped with an Incoatec microfocus source (Schulz, T.; Meindl, K.; Leusser, D.; Stern, D.; Graf, J.; Michaelsen, C.; Ruf, M.; Sheldrick, G. M.; Stalke, D. *J. Appl. Crystallogr.* **2009**, *42*, 885–891.) and a low-temperature device in ω-scan mode at 100(2) K. The data were integrated with SAINT (*SAINT v7.68A*; Bruker, Madison, WI, 2009) and an empirical absorption correction was applied with SADABS (Sheldrick, G. M. *SADABS 2008/1*; Universität Göttingen, Göttingen, Germany, 2008). The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares methods against F^2 (SHELXL-97, Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.). CCDC no 819818 contains the supplementary crystallographic data for this paper. Crystal data for **2**·(toluene): $C_{49}H_{63}N_6Si_2Cl$, M_r = 827.68, triclinic, space group $P\bar{1}$, a = 9.3427(11) Å, b = 10.7563(13) Å, c = 12.2182(15) Å, α = 94.310(2)°, β = 97.304(2)°, γ = 108.196(2)°, V = 1148.4(2) Å^3, Z = 1, ρ_{calcd} = 1.197 Mg/m^3, μ = 0.176 mm^{-1}, 27 534 reflections measured, 4737 independent reflections, R1($I > 2\sigma(I)$) = 0.0611, wR2($I > 2\sigma(I)$) = 0.1343. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

(12) (a) Mitzel, N. W. *Z. Naturforsch., B* **2003**, *58*, 369–375. (b) Hemme, I.; Klingebiel, U. *Adv. Organomet. Chem.* **1996**, *39*, 159–192. (c) Glidewell, C.; Rankin, D. W. H.; Robiette, A. G.; Sheldrick, G. M. *J. Chem. Soc. A* **1970**, 318–320. (d) Veith, M.; Rammo, A. *Z. Anorg. Allg. Chem.* **2001**, *627*, 662–668.

(13) (a) Sen, S. S.; Tavčar, G.; Roesky, H. W.; Kratzert, D.; Hey, J.; Stalke, D. *Organometallics* **2010**, *29*, 2343–2347. (b) Kaftory, M.; Kapon, M.; Botoshansky, M. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, U.K., 1998; Vol. 2, Chapter 5.

(14) (a) Jana, A.; Schulzke, C.; Roesky, H. W. *J. Am. Chem. Soc.* **2009**, *131*, 4600–4601. (b) Sadow, A. D.; Tilley, T. D. *J. Am. Chem. Soc.* **2005**, *127*, 643–656. (c) Sadow, A. D.; Tilley, T. D. *J. Am. Chem. Soc.* **2002**, *124*, 6814–6815.