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Reaction of N-Heterocyclic Silylenes with Thioketone: Formation of Silicon–Sulfur Three- (Si-C-S) and Five- (Si-C-C-C-S) Membered Ring Systems

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Abstract: Three- and five-membered rings that bear the (Si-C-S) and (Si-C-C-C-S) unit have been synthesized by the reactions of **L**SiCl (**1**; **L** = PhC(N*t*Bu)$_2$) and **L**′Si (**2**; **L**′ = CH{(C=CH$_2$)(CMe)(2,6-*i*Pr$_2$C$_6$H$_3$N)$_2$}) with the thioketone 4,4′-bis(dimethylamino)thiobenzophenone. Treatment of 4,4′-bis(dimethylamino)thiobenzophenone with **L**SiCl at room temperature furnished the [1+2]-cycloaddition product silathiacyclopropane **3**. However, reaction of 4,4′-bis(dimethylamino)thiobenzophenone with **L**′Si at low temperature afforded a [1+4]-cycloaddition to yield the five-membered ring product **4**. Compounds **3** and **4** were characterized by NMR spectroscopy, EIMS, and elemental analysis. The molecular structures of **3** and **4** were unambiguously established by single-crystal X-ray structural analysis. The room-temperature reaction of 4,4′-bis(dimethylamino)thiobenzophenone with **L**′Si resulted in products **4** and **5**, in which **4** is the dearomatized product and **5** is formed under the 1,3-migration of a hydrogen atom from the aromatic phenyl ring to the carbon atom of the C−S unit. Furthermore, the optimized structures of probable products were investigated by using DFT calculations.

Keywords: cycloaddition · density functional calculations · silylenes · small-ring systems · thioketones

Introduction

Silylenes are divalent silicon atom containing species that contain silicon atoms and are considered to be silicon analogues of carbenes.[1] After the first report of stable N-heterocyclic silylene (NHSi) by West et al.[2] in 1994, many stable NHSi compounds as well as other substituted silylenes have been isolated.[1b–f,3] Stable silylenes have been the subject of interest in terms of both theoretical and experimental aspects.[4] The reactivities of NHSi compounds are to some extent comparable with those of N-heterocyclic carbenes (NHCs). The latter find widespread applications in different fields of chemistry.[5,6] The reactivity of silylenes is associated with the presence of both a lone pair of electrons and a vacant p orbital at the silicon atom. Thus, silylenes undergo reactions with Lewis acids and bases.[4] Owing to the ambiphilic nature of NHSi compounds, extensive research is being carried out on insertion,[7] addition reactions,[8] and metal complex formations.[9,10] Silylenes are highly reactive and provide an alternative route to new, previously inaccessible organosilicon compounds that are difficult to prepare by conventional methods. Furthermore, three-membered ring compounds that possess higher-coordinated silicon at the position adjacent to the heteroatom have attracted the attention of chemists because of their unique structure and their application in synthetic chemistry.[11] Three-membered ring compounds bearing a silicon atom are interesting on account of their high strain and novel bonding arrangement within the ring.[12] In the case of the sulfur-supported Brook rearrangement, the transition state has been proposed as a three-membered ring compound bearing a pentacoordinate silicon at the position adjacent to the sulfur atom.[13] The first structurally characterized silathiacyclopropane was reported by Ando et al., obtained by the reaction of dimesitylsilylene with 1,1,3,3-tetramethyl-2-indanethione.[14a] In 1994, Brook et al. isolated silathiacyclopropane from the reaction of silene with elemental sulfur.[14b] Owing to the high ring strain of the three-membered ring, only a few silicon compounds with heteroatoms have been reported so far.[1b–f] Currently we are interested in the chemistry of silylenes. The diverse properties of **L**SiCl (**1**; **L** = PhC(N*t*Bu)$_2$) and **L**′Si (**2**; **L**′ = CH{(C=CH$_2$)(CMe)(2,6-*i*Pr$_2$C$_6$H$_3$N)$_2$}) with organic substrates inspired us to further explore their chemistry. Among them, reactions with ketones are quite interesting, and the choice of silylene plays a key role in the product formation.[1b–f] We were curious to explore the reactivity of silylenes with thioketones. Herein, we report for the first time on the reactivity of a thioketone with stable N-hetero-

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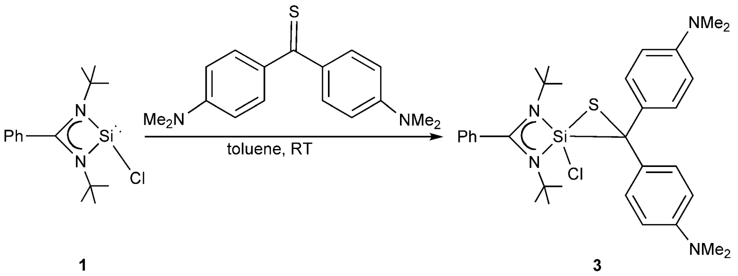
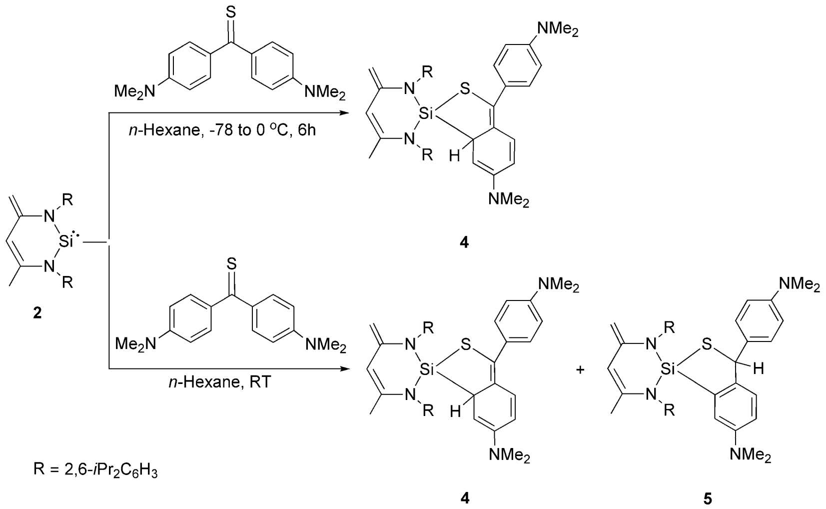
cyclic silylenes **1** and **2**, which lead to three- and five-membered rings that contain silicon and sulfur.

Results and Discussion

The reaction of equimolar amounts of 4,4′-bis(dimethylamino)thiobenzophenone with **1** leads to the [1+2]-cycloaddition product **3** (Scheme 1), which is similar to that of **1** with 2-adamantanone.[8c] Treatment of **2** with 4,4′-bis(dimethylamino)thiobenzophenone at low temperature resulted in the [1+4]-cycloaddition product **4** (Scheme 2).



Scheme 1. Synthesis of **3**.



Scheme 2. Synthesis of **4** and **5**.

Compound **3** is soluble in toluene and benzene. It is stable in the solid state as well as in solution without any decomposition under an inert gas atmosphere. The ^{29}Si NMR spectrum of **3** exhibits a single resonance at $\delta = -104.42$ ppm, which is upfield-shifted relative to that of **1** ($\delta = 14.6$ ppm).[3a] The *t*Bu protons of **3** in the ^{1}H NMR spectrum show a singlet that is observed at $\delta = 1.12$ ppm and is downfield-shifted relative to that of **1** ($\delta = 1.08$ ppm). In addition, compound **3** exhibits its fragment ion $[M^{+}-\mathrm{Cl}]$ in the mass spectrum at *m*/*z* 544.

The molecular structure of compound **3** was unambiguously established by single-crystal X-ray structural analysis. Compound **3** crystallizes in the triclinic space group $P\bar{1}$, and the molecular structure is shown in Figure 1. We suggest that the reaction of **1** with 4,4′-bis(dimethylamino)thiobenzophenone followed the [1+2]-cycloaddition reaction. Here the new three-membered ring is formed; it comprises carbon, sulfur, and silicon atoms. The silicon atom shows a distorted trigonal-bipyramidal (TBP) coordination geometry, which is made up of two nitrogen atoms, a sulfur atom, a carbon atom, and a chlorine atom. 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 a perfect square-based pyramid)[15] is 0.60, thus indicating a deviation from the regular TBP geometry. There is little change in the N-Si-N bite angle at the silicon atom with the backbone amidinate ligand. In **3** it is 70.53(12)°, whereas in **1** it is 71.15(7)°. There is a shortening of the Si−Cl bond length (2.0855(15) Å) in **3** relative to that of **1** (Si−Cl of **1** is 2.156(1) Å). The angles of the newly formed SSiC three-membered ring are S-Si-C (55.55(12)°), Si-C-S (70.58(13)°), and C-S-Si (53.86(12)°). Correspondingly, the bond lengths within the three-membered ring are Si−S (2.1781(19) Å), S−C (1.905(3) Å), and Si−C (1.865(4) Å). These values are comparable with the SSiC three-membered ring reported in the literature.[14]

The reaction of 4,4′-bis(dimethylamino)thiobenzophenone with **2** at low temperature afforded the [1+4]-cycloaddition product **4**. Compound **4** is soluble in *n*-hexane, *n*-pentane, toluene, and benzene. In addition, it is stable both in the solid state as well as in solution. The ^{29}Si NMR spectrum of **4** shows a single resonance ($\delta = 2.88$ ppm), which is shifted upfield relative to that of **2** ($\delta = 88.4$ ppm).[3c] The γ-C*H* proton for compound **4** in the ^{1}H NMR spectrum is observed at $\delta = 5.51$ ppm. The NCCH_2 protons in **4** exhibit sharp singlets at $\delta = 3.49$ and 4.04 ppm ($\delta =$ for **2** is 3.32 and 3.91 ppm). The dearomatized product has been clearly established by using ^{1}H NMR spectroscopy. A considerable shift is observed for the hydrogen atom ($\delta = 6.31$–6.35 ppm) present in the former benzene ring. The dearomatized ring shows further multiplets centered at $\delta = 5.74$ (1H), 6.52 (1H), and 7.00 ppm (2H), respectively, in its ^{1}H NMR spectrum. These values support the dearomatization of the benzene ring, which is in agreement with those reported in the literature.[8a,b] Compound **2** exhibits its molecular ion in the mass spectrum at *m*/*z* 728.4. In contrast, the room-temperature reaction of 4,4′-bis(dimethylamino)thiobenzophenone with **2** resulted in two products that were evidenced by ^{29}Si NMR

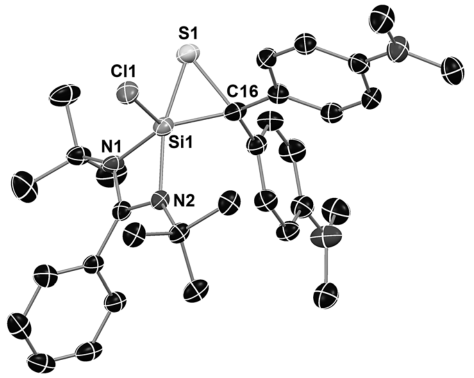


Figure 1. Molecular structure of **3**. The anisotropic displacement parameters are depicted at the 50 % probability level. Hydrogen atoms are omitted for clarity. Selected experimental bond lengths [Å] and angles [°] (theoretical BP86-D2/def2-SVP values are given in square brackets): Si1−N2 1.916(3) [1.9751], Si1−N1 1.802(3) [1.8363], Si1−Cl1 2.0855(15) [2.1209], S1−C16 1.905(3) [1.9525], Si1−C16 1.865(4) [1.8913], S1−Si1 2.1781(19) [2.1826]; C16-S1-Si1 53.86(12) [54.06], S1-C16-Si1 70.58(13) [69.18], N1-Si1-C16 126.03(15) [116.71], N1-Si1-N2 70.53(12) [69.29], C16-Si1-N2 108.87(15) [103.46], N1-Si1-Cl1 110.21(12) [113.63], C16-Si1-Cl1 123.34(11) [129.64], N2-Si1-Cl1 94.52(10) [95.06], N1-Si1-S1 109.59(11) [106.81], C16-Si1-S1 55.55(12) [56.73], N2-Si1-S1 161.82(9) [156.75], Cl1-Si1-S1 102.15(8) [107.06].

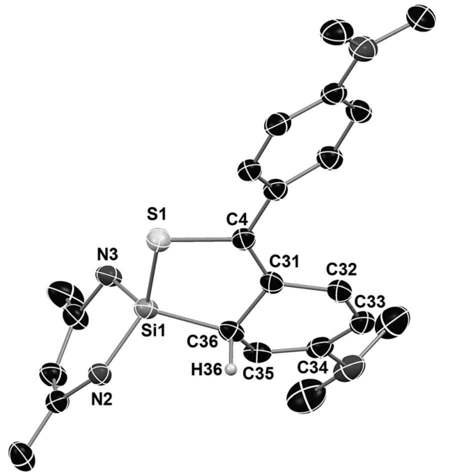


Figure 2. Molecular structure of **4**. The anisotropic displacement parameters are depicted at the 50 % probability level. Hydrogen atoms and diisopropylphenyl (dipp) groups are omitted for clarity, except for H36, which was refined freely from the F_o-F_c map. Diisopropylphenyl protection groups at N2 and N3 have also been omitted for clarity. Selected experimental bond lengths [Å] and angles [°] (theoretical BP86-D2/def2-SVP values are given in square brackets): N2−Si1 1.737(2) [1.7533], N3−Si1 1.715(2) [1.7627], S1−Si1 2.1292(13) [2.1759], C4−S1 1.794(3) [1.8083], C36−Si1 1.858(3) [1.8855], C4−C31 1.354(4) [1.3821], C31−C32 1.449(4) [1.4497], C31−C36 1.511(4) [1.5184], C32−C33 1.344(4) [1.3693], C33−C34 1.461(4) [1.4697], C34−C35 1.345(4) [1.3736], C35−C36 1.499(4) [1.5032]; N3-Si1-N2 104.53(12) [103.38], C36-Si1-S1 95.83(10) [95.10], C4-C31-C32 126.1(3) [124.76], C4-C31-C36 119.7(3) [119.58], C35-C36-Si1 118.8(2) [117.07], C31-C36-Si1 109.6(2) [108.63], C4-S1-Si1 94.18(10) [92.99], N3-Si1-C36 119.78(13) [118.57], N2-Si1-C36 110.33(12) [112.73], N3-Si1-S1 111.03(9) [112.34].

spectroscopy. The ^{29}Si NMR spectrum of the room-temperature reaction shows two sharp singlets at $\delta = 2.88$ (**4**) and −4.18 ppm (**5**). We surmised that the reaction proceeds like **2** with benzophenone,[8e] and the resonance at $\delta = -4.18$ ppm corresponds to product **5**, whereas that at $\delta = 2.88$ ppm is assigned to **4** (Scheme 2). Unfortunately, we were not able to isolate and characterize the pure product **5**, even when the reaction was performed at slightly elevated temperatures.

The formation of dearomatized compound **4** was unambiguously identified by single-crystal X-ray structural analysis. Compound **4** crystallizes in the monoclinic space group $P2_1/c$; the molecular structure is shown in Figure 2. The silicon atom, which is part of the C_3N_2Si six-membered ring, acts as a reaction center to form a new C_3SSi silicon/sulfur-bridged five-membered ring with the 4,4′-bis(dimethylamino)thiobenzophenone keeping the six-membered ring intact and leading to the spirocyclic compound **4**. In **4**, the six- and five-membered rings are fused together by the silicon atom, and the resulting rings are arranged nearly orthogonal to each other. The dihedral angle between the planes of the six- and five-membered rings is 90.5°. Furthermore, the dearomatized benzene ring is not planar, which is similar to those observed in the reaction of **2** with benzophenone[8e] and with diphenylhydrazone.[8b] The silicon atom of **4** is in a distorted tetrahedral geometry that consists of two nitrogen atoms from a chelating ligand, a carbon atom, and a sulfur atom. The silicon atom is shifted out of the plane defined by N2, C1, C2, C3, and N3 significantly (by 0.4253(30) Å). A slight variation of bonds can be observed between the silicon atom and the nitrogen atoms of the supporting ligand. The bond length between Si−N_{av} in **4** is 1.726(2) Å, whereas in **2** it is 1.7345(10) Å. In addition, there is an appreciable change in the N-Si-N bite angle at the silicon atom with the backbone ligand. In **4** it is 104.53(12)°, whereas in **2** it is 99.317(54)°. The bond lengths of Si1−S1 and Si1−C36 are 2.1292(13) and 1.858(3) Å, thus indicating single-bond character. The bond lengths between adjacent carbon atoms in the dearomatized six-membered benzene ring (C31, C32, C33, C34, C35, C36) of compound **4** possess both single- and double-bond character. The bond lengths between C31−C32, C33−C34, C35−C36, and C31−C36 are 1.449(4), 1.461(4), 1.499(4), and 1.511(4) Å, respectively, thus indicating C−C single bonds. The bond lengths between C32=C33 and C34=C35 are 1.344(4) and 1.345(4) Å, thereby representing C=C double bonds. The bond length between C4=C31 is 1.354(4) Å, which reflects a C=C double bond.[16]

To complement the experimental findings, theoretical calculations were carried out on the systems under study. The structures of compounds **3**–**5** together with the corresponding precursor molecules were optimized at the BP86/def2-SVP level of theory, including DFT-D2 dispersion corrections.[17] The free energy of reaction $\Delta G_x(298.15\,\mathrm{K})$ for each of the products ($x = $ **3**–**5**) was computed by adding thermal and zero-point energy corrections (BP86-D2/def2-SVP) and recomputing the electronic energy at the DF-SCS-MP2/cc-pVTZ level of theory.[18] All DFT calculations were carried out with the ORCA program package,[17e] and the MP2 calculations were carried out with the Molpro2010.1 package.[18d]

The computed values are $\Delta G_1 = -18.5$, $\Delta G_2 = -20.9$, and $\Delta G_3 = -51.1\ \mathrm{kcal\,mol^{-1}}$, which show that the reactions that lead to compounds **3** and **4** are almost isoenergetic. Relative to the reactions shown in Scheme 2, we find that compound **5** should be the thermodynamic product. The difference of $30.2\ \mathrm{kcal\,mol^{-1}}$ (at 298.15 K) in the computed free energies is quite significant. Given the experimental observation that **4** is formed preferably, it should correspond to the kinetic product with a lower activation barrier. The formation of **5** in solution has been observed when the temperature increases, which again suggests that the latter corresponds to the thermodynamic product.

The difficulty found in crystallizing compound **5** can also be explained on the basis of our computational results. The crystal structure of **4** reveals close intermolecular contacts between 1,3-diisopropyl groups. This contact is allowed because the 4-dimethylaminophenyl group stretches along the plane of the five-membered ring, thereby allowing for an unhindered contact. The proton migration in **5**, however, generates an sp^3 carbon at this connection, thus leading to a bend in the 4-dimethylaminophenyl moiety (Figure 3). The latter builds an intermolecular contact with one of the diisopropyl groups, effectively shielding it from intermolecular interactions. We have also computed the interaction energy between two diisopropyl groups at the DF-SCS-MP2/cc-pVTZ level of theory on the basis of the crystal-structure coordinates. Each contact should stabilize the crystal by about $4.6\ \mathrm{kcal\,mol^{-1}}$.

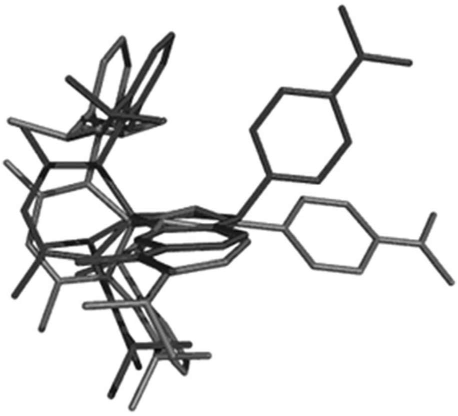


Figure 3. Superimposed structures of **4** (gray) and **5** (black). Hydrogen atoms have been removed for clarity. Upon proton migration, the 4-dimethylaminophenyl moiety bends towards the top of the plane formed by the five-membered ring.

Having considered products **4** and **5** for the reaction of **2**, one could also question the possibility of forming a three-membered ring, in analogy to compound **3**. One indeed obtains a stable minimum with a free reaction energy of $-12.5\ \mathrm{kcal\,mol^{-1}}$. This is somewhat higher than $\Delta G_2 = -20.9\ \mathrm{kcal\,mol^{-1}}$ and explains why such a byproduct has not been observed. Further details about the calculations can be found in the Supporting Information.

Conclusion

In summary, we report for the first time that the reaction of stable N-heterocyclic silylenes **L**SiCl and **L′**Si with thioketone 4,4′-bis(dimethylamino)thiobenzophenone leads to CSiS three- and C_3SiS five-membered rings. The CSiS three-membered ring is stable at room temperature under an inert atmosphere. The reaction of **L′**Si results in temperature-dependent product formation. At low temperature, the dearomatized C_3SiS five-membered ring is formed, whereas at room temperature an additional migration of a proton from the aromatic to the nonaromatic carbon occurred to yield a mixture of compounds of **4** and **5**. The experimental results are supported by DFT calculations.

Experimental Section

All manipulations were carried out in an inert atmosphere of dinitrogen using standard Schlenk techniques and in a dinitrogen-filled glovebox. Solvents were purified using an MBRAUN SPS-800 solvent purification system. All chemicals were purchased from Aldrich and used without further purification. **L**SiCl[3b] and **L′**Si[3c] were prepared as reported in the literature. ^{1}H and ^{29}Si NMR spectra were recorded using a Bruker Avance DRX 500 spectrometer with C_6D_6 as solvent. Chemical shifts (δ) are given relative to $SiMe_4$. EIMS spectra were obtained using a Finnigan MAT 8230 instrument. Elemental analyses were performed by the Institut für Anorganische Chemie, Universität Göttingen.

Synthesis of 3: Toluene (60 mL) was added to a 100 mL Schlenk flask that contained **L**SiCl (**1**; 0.29 g, 0.98 mmol) and 4,4′-bis(dimethylamino)thiobenzophenone (0.29 g, 1.02 mmol). The reaction mixture was stirred at room temperature for 12 h. The solvent was reduced under vacuum to about 20 mL and stored at −32 °C in a freezer for 5 d to obtain single crystals of **3** (0.42 g, 74 %). For elemental analysis, **3**•0.25 toluene was treated under vacuum for six hours to remove the toluene molecules. ^{1}H NMR (500 MHz, C_6D_6, 25 °C): $\delta = 1.12$ (s, 18 H; $C(CH_3)_3$), 2.58 (s, 12 H; NCH_3), 6.71–6.93 ppm (m; ArH); ^{29}Si{^{1}H} NMR (99.36 MHz, C_6D_6, 25 °C): $\delta = -104.42$ ppm; EIMS: m/z: 544.0 [$M^+ - Cl$]; elemental analysis calcd (%) for $C_{32}H_{43}ClN_4SSi$ (579.31): C 66.34, H 7.48, N 9.67; found: C 66.24, H 7.45, N 9.58.

Synthesis of 4: A solution of **L′**Si (**2**; 0.24 g, 0.54 mmol) in n-hexane (20 mL) at −78 °C was added to a cooled solution of 4,4′-bis(dimethylamino)thiobenzophenone (0.16 g, 0.56 mmol) in n-hexane (20 mL) at −78 °C. After the addition, the reaction mixture was allowed to warm slowly to 0 °C and stirring was continued for a further 6 h at 0 °C. The solvent was reduced and stored in a freezer at −32 °C for 12 h to obtain yellow single crystals of **4** (0.26 g, 66 %). For elemental analysis, **4**•hexane was treated under vacuum for 6 h to remove the hexane molecules. ^{1}H NMR (500 MHz, C_6D_6, 25 °C): $\delta = 1.28$ (d, $J = 7$ Hz, 6 H; $CH(CH_3)_2$), 1.31 (d, $J = 7$ Hz, 6 H; $CH(CH_3)_2$), 1.39 (d, $J = 7$ Hz, 3 H; $CH(CH_3)_2$), 1.44 (d, $J = 7$ Hz, 6 H; $CH(CH_3)_2$), 1.45 (s, 3 H; $NCCH_3$), 1.57 (d, $J = 7$ Hz, 3 H; $CH(CH_3)_2$), 2.35 (s, 9 H; NCH_3), 2.38 (s, 3 H; NCH_3), 3.49 (s, 1 H; $NCCH_2$), 3.54 (m, 1 H; $CH(CH_3)_2$), 3.60 (m, 1 H; $CH(CH_3)_2$), 3.85 (m, 2 H; $CH(CH_3)_2$), 4.04 (s, 1 H; $NCCH_2$), 5.52 (s, 1 H; γ-CH), 5.74 (m, 1 H; CH), 6.25 (m, 2 H; CH), 6.52 (m, 1 H; CH), 6.99–7.01 (m; ArH), 7.10–7.22 ppm (m; ArH); ^{29}Si{^{1}H} NMR (99.36 MHz, C_6D_6, 25 °C): $\delta = 2.88$ ppm; EIMS: m/z: 728.4 [M^+]; elemental analysis calcd (%) for $C_{46}H_{60}N_4SSi$ (729.15): C 75.77, H 8.29, N 7.68; found: C 75.85, H 8.18, N 7.64.

Synthesis of 4 and 5: *n*-Hexane (60 mL) was added to a 100 mL Schlenk flask that contained **L′**Si (0.30 g, 0.67 mmol) and 4,4′-bis(dimethylamino)-thiobenzophenone (0.19 g, 0.67 mmol). The reaction mixture was stirred at room temperature for 12 h. The solvent was reduced under vacuum to obtain the mixture of compounds **4** and **5**. ^{29}Si{^{1}H} NMR (99.36 MHz, C_6D_6, 25 °C): $\delta = 2.88, -4.18$ ppm.

Crystal structure determination: Suitable single crystals for X-ray structural analysis of **3** and **4** were mounted at low temperature in inert oil under an argon atmosphere by using an X-Temp2 device.[19] The data were collected using a Bruker D8 three-circle diffractometer equipped with a SMART APEX II CCD detector and an INCOATEC Mo microfocus source with INCOATEC Quazar mirror optics.[20] The data were integrated with SAINT[21] and a semiempirical absorption correction with SADABS[22] 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).[23] 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 1.5 U_{eq} of their pivot atoms for terminal sp^3-carbon atoms and 1.2 times for all other carbon atoms. In **4**, H36 (attached to C36) was refined freely. The severely disordered solvent molecules and the disorder of the CH_2/CH_3 groups on the CH{(C=CH_2)(CMe)(2,6-iPr$_2C_6H_3$N)$_2$} ligand were refined using restraints on the distances and the anisotropic displacement parameters.

Compound 3: $M_r = 625.37$ g mol^{-1}; triclinic, space group $P\bar{1}$; $a = 11.073(5)$, $b = 12.294(6)$, $c = 13.696$ Å; $\alpha = 97.98(1)$, $\beta = 93.88(2)$, $\gamma = 112.96(9)$°; $V = 1684.9(13)$ Å^3; $Z = 2$; $\mu(\text{Mo}_{K\alpha}) = 0.242$ mm^{-1}; $T = 100(2)$ K; 24098 reflections measured; 4840 unique reflections; $R_{\text{int}} = 0.0565$, 425 parameters refined, $R1$ (all data) = 0.0845, $R1$ $(I > 2\sigma(I)) = 0.0462$, $wR2$ (all data) = 0.1065, $wR2$ $(I > 2\sigma(I)) = 0.0926$; GOF = 1.024; largest difference peak and hole 0.296 and −0.299 e Å^{-3}.

Compound 4: $M_r = 772.22$ g mol^{-1}; monoclinic, space group $P2_1/c$; $a = 15.696(8)$, $b = 16.291(6)$, $c = 18.109$ Å; $\beta = 102.05(2)$°; $V = 4529(4)$ Å^3; $Z = 4$; $\mu(\text{Mo}_{K\alpha}) = 0.135$ mm^{-1}; $T = 100(2)$ K; 63635 reflections measured, 6532 unique reflections, $R_{\text{int}} = 0.0509$, 554 parameters refined, $R1$ (all data) = 0.0749, $R1$ $(I > 2\sigma(I)) = 0.0520$, $wR2$ (all data) = 0.1403, $wR2$ $(I > 2\sigma(I)) = 0.1290$; GOF = 1.062; largest difference peak and hole 0.620 and −0.358 e Å^{-3}.

CCDC-889037 (**3**) and 889038 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] a) P. P. Gaspar, R. West in *The Chemistry of Organic Silicon Compounds, Vol. 2* (Eds.: Z. Rappoport, Y. Apeloig), Wiley, Chichester, **1998**, pp. 2463–2567; b) M. Haaf, T. A. Schmedake, R. West, *Acc. Chem. Res.* **2000**, *33*, 704–714; c) B. Gehrhus, M. F. Lappert, *J. Organomet. Chem.* **2001**, *617–618*, 209–223; d) S. S. Sen, S. Khan, P. P. Samuel, H. W. Roesky, *Chem. Sci.* **2012**, *3*, 659–682; e) M. Kira, *Chem. Commun.* **2010**, *46*, 2893–2903; f) S. Yao, Y. Xiong, M. Driess, *Organometallics* **2011**, *30*, 1748–1767; g) R. S. Ghadwal, R. Azhakar, H. W. Roesky, *Acc. Chem. Res.* DOI: 10.1021/ar300196u.

[2] M. Denk, R. Lennon, R. Hayashi, R. West, A. V. Belyakov, H. P. Verne, A. Haaland, M. Wagner, N. Metzler, *J. Am. Chem. Soc.* **1994**, *116*, 2691–2692.

[3] a) C.-W. So, H. W. Roesky, J. Magull, R. B. Oswald, *Angew. Chem.* **2006**, *118*, 4052–4054; *Angew. Chem. Int. Ed.* **2006**, *45*, 3948–3950; b) S. S. Sen, H. W. Roesky, D. Stern, J. Henn, D. Stalke, *J. Am. Chem. Soc.* **2010**, *132*, 1123–1126; c) M. Driess, S. Yao, M. Brym, C. van Wüllen, D. Lentz, *J. Am. Chem. Soc.* **2006**, *128*, 9628–9629; d) L. Kong, J. Zhang, H. Song, C. Cui, *Dalton Trans.* **2009**, 5444–5446; e) R. Azhakar, R. S. Ghadwal, H. W. Roesky, H. Wolf, D. Stalke, *Chem. Commun.* **2012**, *48*, 4561–4563; f) R. Azhakar, R. S. Ghadwal, H. W. Roesky, H. Wolf, D. Stalke, *Organometallics* **2012**, *31*, 4588–4592.

[4] a) R.-E. Li, J.-H. Sheu, M.-D. Su, *Inorg. Chem.* **2007**, *46*, 9245–9253; b) P. V. Bharatam, R. Moudgil, D. Kaur, *Inorg. Chem.* **2003**, *42*, 4743–4749; c) P. V. Bharatam, R. Moudgil, D. Kaur, *Organometallics* **2002**, *21*, 3683–3690; d) P. W. Percival, J.-C. Brodovitch, M. Mozafari, A. Mitra, R. West, R. S. Ghadwal, R. Azhakar, H. W. Roesky, *Chem. Eur. J.* **2011**, *17*, 11970–11973; e) R. Azhakar, G. Tavčar, H. W. Roesky, J. Hey, D. Stalke, *Eur. J. Inorg. Chem.* **2011**, 475–477; f) R. S. Ghadwal, R. Azhakar, H. W. Roesky, K. Pröpper, B. Dittrich, S. Klein, G. Frenking, *J. Am. Chem. Soc.* **2011**, *133*, 17552–17555; g) R. S. Ghadwal, R. Azhakar, H. W. Roesky, K. Pröpper, B. Dittrich, G. Catharina, G. Frenking, *Chem. Commun.* **2012**, *48*, 8186–8188; h) A. Jana, R. Azhakar, S. P. Sarish, P. P. Samuel, H. W. Roesky, C. Schulzke, D. Koley, *Eur. J. Inorg. Chem.* **2011**, 5006–5013.

[5] a) S. P. Nolan, *N-Heterocyclic Carbenes in Synthesis*, Wiley-VCH, Weinheim, **2006**; b) F. Glorius, *N-Heterocyclic Carbenes in Transition Metal Catalysis*, Springer, Berlin, **2007**; c) C. Vollmer, C. Janiak, *Coord. Chem. Rev.* **2011**, *255*, 2039–2057; d) A. Jana, R. Azhakar, G. Tavčar, H. W. Roesky, I. Objartel, D. Stalke, *Eur. J. Inorg. Chem.* **2011**, 3686–3689; e) L. Benhamou, E. Chardon, G. Lavigne, S. Bellemin-Laponnaz, V. César, *Chem. Rev.* **2011**, *111*, 2705–2733.

[6] a) D. P. Mills, L. Soutar, W. Lewis, A. J. Blake, S. T. Liddle, *J. Am. Chem. Soc.* **2010**, *132*, 14379–14381; b) C.-H. Yang, J. Beltran, V. Lemaur, J. Cornil, D. Hartmann, W. Sarfert, R. Fröhlich, C. Bizzari, L. D. Cola, *Inorg. Chem.* **2010**, *49*, 9891–9901; c) H.-J. Park, K. H. Kim, S. Y. Choi, H.-M. Kim, W. I. Lee, Y. K. Kang, Y. K. Chung, *Inorg. Chem.* **2010**, *49*, 7340–7352; d) R. S. Crees, M. L. Cole, L. R. Hanton, C. J. Sumby, *Inorg. Chem.* **2010**, *49*, 1712–1719; e) C. Dash, M. M. Shaikh, R. J. Butcher, P. Ghosh, *Inorg. Chem.* **2010**, *49*, 4972–4983; f) C.-F. Fu, C.-C. Lee, Y.-H. Liu, S.-M. Peng, S. Warsink, C. J. Elsevier, J.-T. Chen, S.-T. Liu, *Inorg. Chem.* **2010**, *49*, 3011–3018.

[7] a) R. Azhakar, S. P. Sarish, H. W. Roesky, J. Hey, D. Stalke, *Organometallics* **2011**, *30*, 2897–2900; b) R. Azhakar, R. S. Ghadwal, H. W. Roesky, J. Hey, D. Stalke, *Dalton Trans.* **2012**, *41*, 1529–1533; c) A. Jana, P. P. Samuel, G. Tavčar, H. W. Roesky, C. Schulzke, *J. Am. Chem. Soc.* **2010**, *132*, 10164–10170; d) F. Antolini, B. Gehrhus, P. B. Hitchcock, M. F. Lappert, J. C. Slootweg, *Dalton Trans.* **2004**, 3288–3294; e) R. Azhakar, R. S. Ghadwal, H. W. Roesky, M. Granitzka, D. Stalke, *Organometallics* **2012**, *31*, 5506–5510; f) Y. Xiong, S. Yao, M. Driess, *Organometallics* **2009**, *28*, 1927–1933; g) B. Gehrhus, P. B. Hitchcock, M. F. Lappert, J. C. Slootweg, *Chem. Commun.* **2000**, 1427–1428.

[8] a) R. Azhakar, S. P. Sarish, G. Tavčar, H. W. Roesky, J. Hey, D. Stalke, D. Koley, *Inorg. Chem.* **2011**, *50*, 3028–3036; b) A. Jana, H. W. Roesky, C. Schulzke, P. P. Samuel, *Organometallics* **2009**, *28*, 6574–6577; c) R. Azhakar, R. S. Ghadwal, H. W. Roesky, J. Hey, D. Stalke, *Organometallics* **2011**, *30*, 3853–3858; d) R. Azhakar, H. W. Roesky, R. S. Ghadwal, J. J. Holstein, B. Dittrich, *Dalton Trans.* **2012**, *41*, 9601–9603; e) Y. Xiong, S. Yao, M. Driess, *Chem. Eur. J.* **2009**, *15*, 5545–5551; f) Y. Xiong, S. Yao, M. Driess, *Organometallics* **2010**, *29*, 987–990; g) S. B. Clendenning, B. Gehrhus, P. B. Hitchcock, J. F. Nixon, *Chem. Commun.* **1999**, 2451–2452; h) B. Gehrhus, P. B. Hitchcock, *Organometallics* **2004**, *23*, 2848–2849; i) S. Ishida, T. Iwamoto, M. Kira, *Organometallics* **2010**, *29*, 5526–5534; j) J. Heinicke, B. Gehrhus, *J. Organomet. Chem.* **1992**, *423*, 13–21; k) P. P. Samuel, R. Azhakar, R. S. Ghadwal, S. S. Sen, H. W. Roesky, M. Granitzka, J. Matussek, H. I. Regine, D. Stalke, *Inorg. Chem.* **2012**, *51*, 11049–11054; l) R. Azhakar, K. Pröpper, B. Dittrich, H. W. Roesky, *Organometallics* **2012**, *31*, 7586–7590.

[9] a) T. A. Schmedake, M. Haaf, B. J. Paradise, A. J. Millevolte, D. Powell, R. West, *J. Organomet. Chem.* **2001**, *636*, 17–25; b) J. D.

Feldman, G. P. Mitchell, J.-O. Nolte, T. D. Tilley, *J. Am. Chem. Soc.* **1998**, *120*, 11184–11185; c) B. Gehrhus, P. B. Hitchcock, M. F. Lappert, H. Maciejewski, *Organometallics* **1998**, *17*, 5599–5601; d) S. H. A. Petri, D. Eikenberg, B. Neumann, H.-G. Stammler, P. Jutzi, *Organometallics* **1999**, *18*, 2615–2618; e) T. A. Schmedake, M. Haaf, B. J. Paradise, D. Powell, R. West, *Organometallics* **2000**, *19*, 3263–3265; f) J. M. Dysard, T. D. Tilley, *Organometallics* **2000**, *19*, 4726–4732; g) S. B. Clendenning, B. Gehrhus, P. B. Hitchcock, D. F. Moser, J. F. Nixon, R. West, *J. Chem. Soc. Dalton Trans.* **2002**, 484–490; h) D. Amoroso, M. Haaf, G. P. A. Yap, R. West, D. E. Fogg, *Organometallics* **2002**, *21*, 534–540; i) A. G. Avent, B. Gehrhus, P. B. Hitchcock, M. F. Lappert, H. Maciejewski, *J. Organomet. Chem.* **2003**, *686*, 321–331; j) M. Denk, R. K. Hayashi, R. West, *J. Chem. Soc. Chem. Commun.* **1994**, 33–34; k) A. Meltzer, C. Präsang, M. Driess, *J. Am. Chem. Soc.* **2009**, *131*, 7232–7233.

[10] a) G. Tavčar, S. S. Sen, R. Azhakar, A. Thorn, H. W. Roesky, *Inorg. Chem.* **2010**, *49*, 10199–10202; b) R. Azhakar, S. P. Sarish, H. W. Roesky, J. Hey, D. Stalke, *Inorg. Chem.* **2011**, *50*, 5039–5043; c) R. S. Ghadwal, R. Azhakar, K. Pröpper, J. J. Holstein, B. Dittrich, H. W. Roesky, *Inorg. Chem.* **2011**, *50*, 8502–8508; d) R. Azhakar, R. S. Ghadwal, H. W. Roesky, H. Wolf, D. Stalke, *J. Am. Chem. Soc.* **2012**, *134*, 2423–2428; e) R. Azhakar, R. S. Ghadwal, H. W. Roesky, J. Hey, D. Stalke, *Chem. Asian. J.* **2012**, *7*, 528–533; f) R. Azhakar, H. W. Roesky, J. J. Holstein, B. Dittrich, *Dalton Trans.* **2012**, *41*, 12096–12100.

[11] a) *Chemistry of Heterocyclic Compounds: Heterocyclic Compounds with Three- and Four-Membered Rings, Vol. 19* (Ed.: A. Weissberger), Wiley, New York, **2008**; b) Small Silicon Ring Compounds: M. Weidenbruch in *Organosilicon Chemistry I: From Molecules to Materials* (Eds.: N. Auner, J. Weis), Wiley-VCH, Weinheim, **2008**.

[12] a) G. Magyarfalvi, P. Pulay, *Chem. Phys. Lett.* **1995**, *241*, 393–398; b) D. Cremer, J. Gauss, E. Cremer, *J. Mol. Struct.: THEOCHEM* **1988**, *169*, 531–561.

[13] A. G. Brook, *Acc. Chem. Res.* **1974**, *7*, 77–84.

[14] a) W. Ando, Y. Hamada, A. Sekiguchi, *Tetrahedron Lett.* **1983**, *24*, 4033–4036; b) A. G. Brook, R. Kumarathasan, A. J. Lough, *Organometallics* **1994**, *13*, 424–425.

[15] a) A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn, G. C. Verschoor, *J. Chem. Soc. Dalton Trans.* **1984**, 1349–1356; b) V. Chandrasekhar, R. Azhakar, T. Senapati, P. Thilagar, S. Ghosh, S. Verma, R. Boomishankar, A. Steiner, P. Kögerler, *Dalton Trans.* **2008**, 1150–1160.

[16] N. Kocher, J. Henn, B. Gostevskii, I. Kost, I. Kalikhman, B. Engels, D. Stalke, *J. Am. Chem. Soc.* **2004**, *126*, 5563–5568.

[17] a) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098–3100; b) J. P. Perdew, *Phys. Rev. B* **1986**, *33*, 8822–8824; c) A. Schaefer, H. Horn, R. Ahlrichs, *J. Chem. Phys.* **1992**, *97*, 2571–2577; d) S. Grimme, *J. Comput. Chem.* **2006**, *27*, 1787–1799; e) ORCA, version 2.8, F. Neese, U. Becker, D. Ganiouchine, S. Koßmann, T. Petrenko, C. Riplinger, F. Wennmohs, University of Bonn (Germany), **2010**.

[18] a) F. R. Manby, P. J. Knowles, A. W. Lloyd, *J. Chem. Phys.* **2001**, *115*, 9144–9148; b) S. Grimme, *J. Chem. Phys.* **2003**, *118*, 9095–9102; c) T. H. Dunning, *J. Chem. Phys.* **1989**, *90*, 1007–1023; d) MOLPRO, version 2010.1, H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz, P. Celani, T. Korona, R. Lindh, A. Mitrushenkov, G. Rauhut, K. R. Shamasundar, T. B. Adler, R. D. Amos, A. Bernhardsson, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, E. Goll, C. Hampel, A. Hesselmann, G. Hetzer, T. Hrenar, G. Jansen, C. Köppl, Y. Liu, A. W. Lloyd, R. A. Mata, A. J. May, S. J. McNicholas, W. Meyer, M. E. Mura, A. Nicklaß, D. P. O'Neill, P. Palmieri, D. Peng, K. Pflüger, R. Pitzer, M. Reiher, T. Shiozaki, H. Stoll, A. J. Stone, R. Tarroni, T. Thorsteinsson, M. Wang, **2010**.

[19] a) D. Stalke, *Chem. Soc. Rev.* **1998**, *27*, 171–178; b) T. Kottke, D. Stalke, *J. Appl. Crystallogr.* **1993**, *26*, 615–619.

[20] T. Schulz, K. Meindl, D. Leusser, D. Stern, J. Graf, C. Michaelsen, M. Ruf, G. M. Sheldrick, D. Stalke, *J. Appl. Crystallogr.* **2009**, *42*, 885–891.

[21] SAINT, Bruker AXS Inc., Madison, **2000**.

[22] SADABS, G. M. Sheldrick, Universität Göttingen, **2000**.

[23] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112–122.

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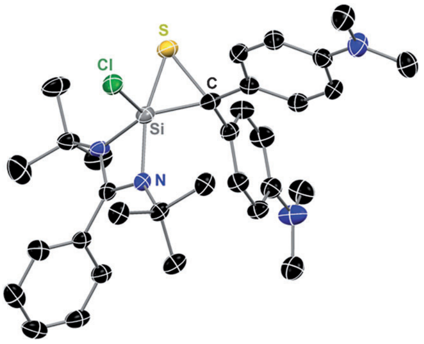
Rings 'n' things: Three- and five-membered rings (see figure) bearing the (Si-C-S) and (Si-C-C-C-S) units have been synthesized by the reactions of **L**SiCl (**L** = PhC(N*t*Bu)$_2$) and **L'**Si (**L'** = CH{(C=CH$_2$)(CMe)(2,6-*i*Pr$_2$C$_6$H$_3$N)$_2$}) with the thioketone 4,4'-bis(dimethylamino)thiobenzophenone.



Cycloaddition

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Reaction of N-Heterocyclic Silylenes with Thioketone: Formation of Silicon–Sulfur Three- (Si-C-S) and Five- (Si-C-C-C-S) Membered Ring Systems