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One Pot Synthesis of Disilatricycloheptene Analogue and Jutzi's Disilene

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The reaction of LiN(TMS)$_2$ (TMS = Me$_3$Si) with dichlorosilane (Me$_5$C$_5$)SiHCl$_2$ (**1**) in a molar ratio of 3:2 at ambient temperature leads to the formation of the disilatricycloheptene analogue (**2**). Compound **2** consists of three (three-, four-, and five-membered) fused rings that together form a six-membered heterocyclic ring. However, the reaction of **1** with KN(TMS)$_2$ affords the formation of disilene of composition *E*-[(TMS)$_2$N](η^1-Me$_5$C$_5$)Si=Si(η^1-Me$_5$C$_5$)[N(TMS)$_2$] (**3**) in good yield. This is a convenient and facile route for the synthesis of **3** in a single step and supports the formation of (Me$_5$C$_5$)SiN(TMS)$_2$ as an intermediate.

Introduction

The sterically encumbered cyclopentadienyl (Cp) and pentamethylcyclopentadienyl (Cp*) are two of the most fundamental organic in organometallic chemistry. The parent compound CpH was known for 100 years and came to the fore in 1951 when T. J. Kealy and R. L. Pauson discovered the first sandwich complex "ferrocene" (η^5-C$_5$H$_5$)$_2$Fe.[1] This epoch-making synthesis enthroned Cp as the pre-eminent ligand for transition and f-block metals due to its steric shielding and its capability to bind in different coordination modes to the metal center, which resulted in the formation of numerous fascinating organometallic compounds.[2−6] Advancement of related compounds with main group elements was somewhat slow, and it was also assumed that Cp* would be more effective in low-valent main group chemistry compared to Cp because the former is a better electron donor and provides more steric shielding. The Cp* as a ligand in the realm of the main group was initially introduced by Jutzi et al.[7a,b] and further established by the same group through the successful isolation of decamethylsilicocene (η^5-Me$_5$C$_5$)$_2$Si(II).[7c] This was further extended by Carmona and co-workers when they outlined the synthesis of decamethyldizincocene, a stable compound of Zn(I) with a Zn−Zn bond using the same ancillary ligand.[8a] In view of these results, it is understandable that chemistry with low-valent main group elements can be further explored using Cp* as an auxiliary ligand. Jutzi et al. developed the chemistry of (Me$_5$C$_5$)$_2$Si as well as the first cation of composition (Me$_5$C$_5$)Si$^+$,[8b] which is a stable derivative of HSi$^+$. However, (Me$_5$C$_5$)SiCl is still elusive. Our

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(1) (a) Kealy, T. J.; Pauson, P. L. *Nature* **1951**, *168*, 1039–1040. (b) Wilkinson, G.; Rosenblum, M.; Whiting, M. C.; Woodward, R. B. *J. Am. Chem. Soc.* **1952**, *74*, 2125–2126.

(2) (a) Janiak, C.; Schumann, H. *Adv. Organomet. Chem.* **1991**, *33*, 291–393. (b) Jutzi, P.; Burford, N. *Chem. Rev.* **1999**, *99*, 969–990 and references therein. (c) Edelmann, F. T. *Angew. Chem.* **1995**, *107*, 2647–2669. Edelmann, F. T. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2466–2488.

(3) (a) Dohmeier, C.; Schnöckel, H.; Robl, C.; Schneider, U.; Ahlrichs, R. *Angew. Chem.* **1993**, *105*, 1714–1716. Dohmeier, C.; Schnöckel, H.; Robl, C.; Schneider, U.; Ahlrichs, R. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1655–1657. (b) Sitzmann, H.; Lappert, M. F.; Dohmeier, C.; Üffing, C.; Schnöckel, H. *J. Organomet. Chem.* **1998**, *561*, 203–208. (c) von Hänisch, C. K. F.; Üffing, C.; Junker, M. A.; Ecker, A.; Kneisel, B. O.; Schnöckel, H. *Angew. Chem.* **1996**, *108*, 3003–3005. von Hänisch, C. K. F.; Üffing, C.; Junker, M. A.; Ecker, A.; Kneisel, B. O.; Schnöckel, H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2875–2877. (d) Loos, D.; Baum, E.; Ecker, A.; Schnöckel, H.; Downs, A. J. *Angew. Chem.* **1997**, *109*, 894–896. Loos, D.; Baum, E.; Ecker, A.; Schnöckel, H.; Downs, A. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 860–862. (e) Qing, Y.; Purath, A.; Donchev, A.; Schnöckel, H. *J. Organomet. Chem.* **1999**, *584*, 94–97.

(4) (a) Jutzi, P.; Möhrke, A. *Angew. Chem.* **1990**, *102*, 913–914. Jutzi, P.; Möhrke, A. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 893–894. (b) Jutzi, P.; Bunte, E. A. *Angew. Chem.* **1992**, *104*, 1636–1638. Jutzi, P.; Bunte, E. A. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1605–1607. (c) Jutzi, P.; Kroos, R.; Müller, A.; Bögge, H.; Penk, M. *Chem. Ber.* **1991**, *124*, 75–81. (d) Jutzi, P.; Bunte, E.-A.; Holtmann, U.; Neumann, B.; Stammler, H.-G. *J. Organomet. Chem.* **1993**, *446*, 139–147. (e) Jutzi, P.; Brusdeilins, N.; Stammler, H.-G.; Neumann, B. *Chem. Ber.* **1994**, *127*, 997–1001. (f) Jutzi, P.; Neumann, B.; Reumann, G.; Stammler, H.-G. *Organometallics* **1998**, *17*, 1305–1314.

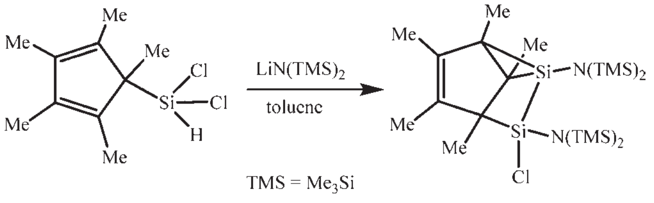
(5) (a) Schulz, S.; Roesky, H. W.; Koch, H. J.; Sheldrick, G. M.; Stalke, D.; Kuhn, A. *Angew. Chem.* **1993**, *105*, 1828–1830. Schulz, S.; Roesky, H. W.; Koch, H. J.; Sheldrick, G. M.; Stalke, D.; Kuhn, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1729–1731. (b) Schulz, S.; Andruh, M.; Pape, T.; Heinze, T.; Roesky, H. W.; Häming, L.; Kuhn, A.; Herbst-Irmer, R. *Organometallics* **1994**, *13*, 4004–4007. (c) Schulz, S.; Häming, L.; Herbst-Irmer, R.; Roesky, H. W.; Sheldrick, G. M. *Angew. Chem.* **1994**, *106*, 1052–1054. Schulz, S.; Häming, L.; Herbst-Irmer, R.; Roesky, H. W.; Sheldrick, G. M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 969–970.

(6) (a) Weiss, J.; Stetzkamp, D.; Nuber, B.; Fischer, R. A.; Boehme, C.; Frenking, G. *Angew. Chem.* **1997**, *109*, 95–97. Weiss, J.; Stetzkamp, D.; Nuber, B.; Fischer, R. A.; Boehme, C.; Frenking, G. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 70–72. (b) Cowley, A. H.; Lomelí, V.; Voigt, A. *J. Am. Chem. Soc.* **1998**, *120*, 6401–6402.

(7) (a) Jutzi, P; Seufert, A. *Chem. Ber.* **1979**, *112*, 2481–2487. (b) Jutzi, P. *Chem. Rev.* **1986**, *86*, 983–996. (c) Jutzi, P.; Kanne, D.; Krüger, C. *Angew. Chem.* **1986**, *98*, 163–164. Jutzi, P.; Kanne, D.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 164.

(8) (a) Resa, I.; Carmona, E.; Puebla, E. G.; Monge, A. *Science* **2004**, *305*, 1136–1138. (b) Jutzi, P.; Mix, A.; Rummel, B; Schoeller, W. W.; Neumann, B.; Stammler, H.-G. *Science* **2004**, *305*, 849–851.

Scheme 1. Preparation of **2**



1 **2**

recent success in synthesizing stable monomeric chlorosilylene $[PhC(NtBu)_2SiCl]$[9a] and N-heterocyclic carbene-stabilized dichloro silylene ($LSiCl_2$, L = 1,3-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene)[9b] prompted us to pursue such a target. Moreover, very recently, we demonstrated a new and convenient route to access $PhC(NtBu)_2SiCl$ in 90% yield by utilizing $LiN(TMS)_2$ as a dehydrochlorinating agent,[10] instead of using hazardous chemicals like KC_8, Na-naphthalene, etc. The same technique was also used by Driess and co-workers for the facile synthesis of heterofulvene-type germylene.[11] The advantage of using $MN(TMS)_2$ (M = Li, Na, K) is (i) it is cheap and commercially available and (ii) the side products are MCl and $HN(TMS)_2$, which can easily be removed from the reaction mixture through filtration and evaporation. To prepare $(Me_5C_5)SiCl$, we opted for this route by treating $(Me_5C_5)SiHCl_2$ with $LiN(TMS)_2$, and surprisingly it afforded a new type of tricyclic silicon compound instead of yielding silylene. Such a type of tricyclic silicon containing cage structures has been of interest in recent days owing to its unique structures and nonclassical bonding patterns. Moreover, unlike bicyclic compounds, the examples of tricyclic silicon derivatives are rare.[12] To gain further insight into the reaction, we also tried other metal amides, e.g., $KN(TMS)_2$ and $NaN(TMS)_2$, and surprisingly we observed the formation of disilene *E*-$[(TMS)_2N](\eta^1\text{-}Me_5C_5)Si{=}Si(\eta^1\text{-}Me_5C_5)[N(TMS)_2]$[8b] with both of them. Herein, we report the facile synthesis of the disilatricycloheptene analogue in good yield, a new addition in the family of silicon-substituted strained ring compounds and a new and convenient route to Jutzi's disilene in a one-pot reaction.

Result and Discussion

Dichlorosilane $(Me_5C_5)SiHCl_2$ (**1**)[13] was treated with $LiN(TMS)_2$ in a molar ratio of 2:3 in toluene at ambient temperature under stirring overnight. After removal of the solvent under vacuum, *n*-pentane was added and LiCl was filtered off through Celite (Scheme 1). The solution was concentrated and stored at −30 °C in a freezer for crystallization, which afforded colorless needle-shaped crystals of **2**. The structure of **2** was confirmed by NMR spectroscopy, EI-MS spectrometry, elemental analysis, and X-ray crystallography.

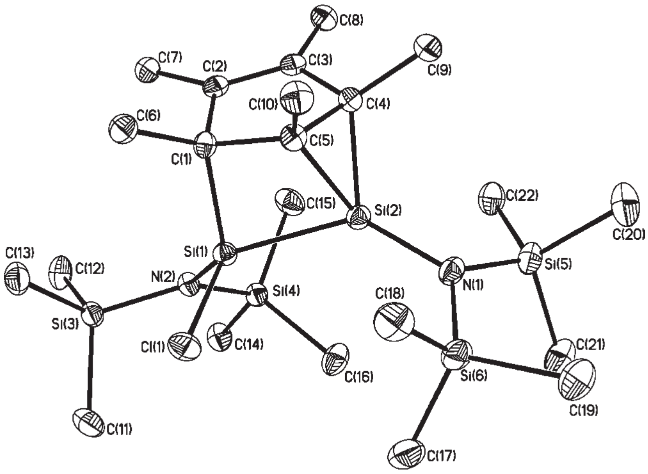


Figure 1. Anisotropic displacement parameters of **2**, depicted at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Si(1)−Si(2) 2.2915(8), Cl(1)−Si(1) 2.1047(8), Si(1)−N(2) 1.7294(17), Si(2)−N(1) 1.7238(17), Si(1)−C(1) 1.922(2), Si(2)−C(5) 1.899(2), Si(2)−C(4) 1.888(2), C(1)−(C2) 1.525(3), C(2)−(C3) 1.341(3), C(3)−(C4) 1.498(3), C(1)−C(5) 1.583(3), C(4)−C(5) 1.560(3); N(2)−Si(1)−C(1) 125.10(8), N(2)−Si(1)−Cl(1) 106.90(6), C(1)−Si(1)−Cl(1) 105.98(6), N(2)−Si(1)−Si(2) 129.64(6), C(1)−Si(1)−Si(2) 79.52(6), Cl(1)−Si(1)−Si(2) 105.86(3), N(1)−Si(2)−C(4) 123.55(9), N(1)−Si(2)−C(5) 132.46(9), C(4)−Si(2)−C(5) 48.66(8), N(1)−Si(2)−Si(1) 135.71(7), C(4)−Si(2)−Si(1) 100.73(6), C(5)−Si(2)−Si(1) 76.52(6).

The ^1H NMR spectrum exhibits resonances for five methyl groups attached to the five-membered ring at δ 1.24, 1.39, 1.47, 1.53, and 1.71 ppm, which shows that all methyl groups are in chemically different environments. A broad resonance at δ 0.31 ppm indicates the presence of 36 TMS protons. The ^{29}Si NMR spectrum exhibits four resonances (δ 6.98, 7.79, −22.04, and −47.49 ppm) which confirm the presence of four chemically different silicon atoms. The former two resonances are assigned to silicon atoms of the trimethylsilyl group. A sharp singlet appeared at δ −22.04 ppm that corresponds to the silicon atom attached to chlorine. The remaining Si atom resonates at δ −47.49 ppm. This minor upfield shift of the latter silicon atom with respect to the former is presumably due to strong shielding in the strained three-membered ring. Similar behavior was also observed in the cases of three-membered $\{(TMS)_2Si\}_3$ and four-membered $\{(TMS)_2Si\}_4$ ring systems, where a resonance at δ −164 ppm appears in ^{29}Si NMR for the former one and the latter exhibits a signal at δ −91 ppm.[14] The molecular ion is observed in the EI-MS spectrum as the most abundant peak with the highest relative intensity at *m*/*z* 546. Compound **2** is easily soluble in common organic solvents and surprisingly stable at room temperature under an inert atmosphere.

The molecular structure of **2** is shown in Figure 1.[15] Compound **2** crystallizes in the monoclinic space group

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(9) (a) So, C.-W.; Roesky, H. W.; Magull, J.; Oswald, R. B. *Angew. Chem.* **2006**, *118*, 4052–4054. So, C.-W.; Roesky, H. W.; Magull, J.; Oswald, R. B. *Angew. Chem., Int. Ed.* **2006**, *45*, 3948–3950. (b) Ghadwal, R. S.; Roesky, H. W.; Merkel, S.; Henn, J.; Stalke, D. *Angew. Chem.* **2009**, *121*, 5793–5796. Ghadwal, R. S.; Roesky, H. W.; Merkel, S.; Henn, J.; Stalke, D. *Angew. Chem., Int. Ed.* **2009**, *48*, 5683–5686.

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

(11) Driess, M.; Yao, S.; Brym, M.; van Wüllen, C. *Angew. Chem.* **2006**, *118*, 4455–4458. Driess, M.; Yao, S.; Brym, M.; van Wüllen, C. *Angew. Chem., Int. Ed.* **2006**, *45*, 4349–4352.

(12) (a) Lee, V. Y.; Yokoyama, T.; Takanashi, K.; Sekiguchi, A. *Chem.—Eur. J.* **2009**, *15*, 8401–8404. (b) Ando, W.; Yoshida, H.; Kurishima, K.; Sugiyama, M. *J. Am. Chem. Soc.* **1991**, *113*, 7790–7792. (c) Ueba-Ohshima, K.; Iwamoto, T.; Kira, M. *Organometallics* **2008**, *27*, 320–323.

(13) (a) Cowley, A. H.; Ebsworth, E. A. V.; Mehrotra, S. K.; Rankin, D. W. H.; Walkinshaw, M. D. *J. Chem. Soc., Chem. Commun.* **1982**, 1099–1100. (b) Jutzi, P.; Kanne, D.; Hursthouse, M.; Howes, A. J. *Chem. Ber.* **1988**, *121*, 1299–1305.

(14) (a) Chen, Y.; Gasper, P. P. *Organometallics* **1982**, *1*, 1410–1412. (b) Fischer, R.; Konopa, T.; Baumgartner, J.; Marschner, C. *Organometallics* **2004**, *23*, 1899–1907. (c) Klinkhammer, K. W. In *Organosilicon Chemistry III: From Molecules to Materials*; Auner, N., Weis, J., Eds.; Wiley-VCH: Weinheim, Germany, 1998.

(15) (a) Kottke, T.; Stalke, D. *J. Appl. Crystallogr.* **1993**, *26*, 615–619. (b) Stalke, D. *Chem. Soc. Rev.* **1998**, *27*, 171–178. (c) Schulz, T.; Meindl, K.; Leusser, D.; Stern, D.; Ruf, M.; Sheldrick, G. M.; Stalke, D. *J. Appl. Crystallogr.* **2009**, *42*, 885–891.

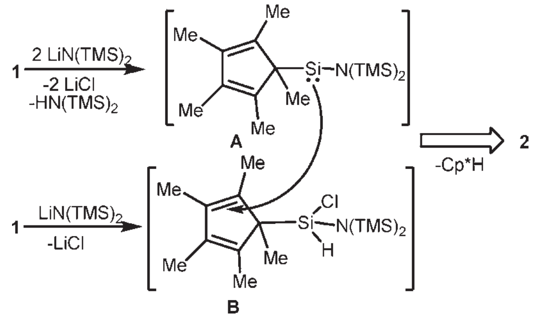
Table 1. Crystallographic Data for the X-Ray Structural Analyses of Compounds **2** and **3**

parameter	**2**	**3**
empirical formula	$C_{22}H_{51}ClN_2Si_6$	$C_{32}H_{66}N_2Si_6$
fw	547.64	647.41
T (K)	100(1)	100(2)
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$
a (Å)	21.707(3)	17.655(3)
b (Å)	9.2762(13)	10.1597(15)
c (Å)	16.985(3)	23.368(4)
α (deg)	90	90
β (deg)	110.554(3)	110.668(2)
γ (deg)	90	90
V, Å^3	3202.3(8)	3921.9(10)
Z	4	4
ρ_{calc}, Mg m^{-3}	1.136	1.096
μ, mm^{-1}	0.357	0.235
F(000)	1192.0	1424
reflns collected	66112	102129
data/restraints/params	7329/0/297	9365/0/383
GoF	1.056	1.057
$R1$, w$R2[I > 2\sigma(I)]^{a,b}$	0.0392	0.0404
$R1$, w$R2$ (all data)	0.0943	0.1060
largest diff peak, hole (e Å^{-3})	0.420/−0.326	0.546/−0.324

^{a} $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} w$R2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{0.5}$.

$P2_1/c$ (Table 1). The molecular structure of **2** displays three different rings (three-, four-, and five-membered) fused together, looking like a basket cavity. One of the silicon atoms (Si2) is fused between a three-membered silacyclopropane and a four-membered disilacyclobutane ring; this resulted in the formation of a unique, strained, fused 1,2-disiletane derivative with a short Si−Si bond. The Si−Si bond is involved in the formation of a strained six-membered heterocyclic ring with a short Si−Si single bond distance (2.29 Å) that is similar to those reported for strained ring systems.[16] The central Si−Si bond distance is only about 0.05 Å shorter than the sum of the Si covalent radii (2.34 Å)[17] and about 0.07 Å shorter than the Si−Si single bond distance in α-silicon (2.36 Å).[18] Thus, it is evident that the strained four-membered ring formation brings two silicon atoms at their lowest possible distance, which is at the verge of the Si−Si double bond range (Si−Si double bonds range from 2.14 to 2.29 Å).[19] It is quite clear from the structure that the five-membered pentamethylcyclopentadienyl ring has lost its planarity, and π bonding is located between two carbon atoms C2 and C3. The C(2)−C(3) bond length (1.34 Å) confirms the double bond character whereas the bond lengths C(1)−C(5) and C(4)−C(5) are 1.58 Å and 1.56 Å, respectively, which are in good accordance with the C−C single bond length reported in the literature.[20]

Scheme 2. Suggested Mechanism for the Formation of **2**



Both of the silicon atoms are tetra-coordinate with distorted tetrahedral geometry. One of the silicon atoms (Si1) is attached to chlorine Cl1, a neighboring silicon atom (Si2), C1, and N2 to complete the tetra-coordination with bond distances of Si1−Cl1 = 2.10, Si1−C1 = 1.92, and Si(1)−N(2) = 1.72 Å and bond angles of Cl(1)−Si(1)−Si(2) = 105.86°, C(1)−Si(1)−Cl(1) = 105.98°, N(2)−Si(1)−Cl(1) = 106.90°, and C(1)−Si(1)−Si(2) = 79.52°. Another silicon atom (Si2) is completing its tetra-coordination geometry through nitrogen N1, silicon Si1, and carbon atoms C5 and C4 with bond distances of Si2−C4 = 1.88, Si2−C5 = 1.89, and Si1−Si2 = 2.29 Å and bond angles N(1)−Si(2)−Si(1) = 135.71°, N(1)−Si(2)−C(4) = 123.55°, C(4)−Si(2)−C(5) = 48.66°, and C(5)−Si(2)−Si(1) = 76.52°.

Although the mechanism for the formation of compound **2** is still unknown, we propose that the initial step involves the formation of $N(TMS)_2$ substituted silylene **A**, which is not stable enough and immediately attacks another possible intermediate, **B**, to give the final product **2** with the elimination of one Cp*H molecule (Scheme 2). Silylenes are well-known in the literature to react with different unsaturated[21a−d] molecules to change their formal oxidation state from +2 to +4. We presume that the $N(TMS)_2$ substituted silylene **A** displays *in situ* oxidative addition to form cycloaddition product **2**. An alternative route is also suggested for the formation of **2** through the insertion of intermediate silylene **A** into the Si−Cl bond[21e,f] of **B** as an initial step and then subsequent elimination of one Cp*H molecule to give the final product **2** (Scheme 3). The formation of the proposed intermediate **A** is further supported by the reaction given in Scheme 4.

To exploit further the facile formation of **2**, we turned our attention to different metal amides and probed the reactions of **1** with them. Accordingly, we treated **1** with $KN(TMS)_2$ in a molar ratio of 1:2 at ambient temperature in toluene (Scheme 4). In contrast to the formation of **2**, the corresponding reaction of $KN(TMS)_2$ with **1** is much faster and the color of the solution changes from colorless to bright yellow immediately. The reaction mixture was stirred overnight and was investigated by multinuclear NMR spectroscopy. The appearance of only two new resonances (δ 2.06 and 15.06 ppm) in the ^{29}Si NMR spectrum indicates the formation of a new compound. Compound **3** is isolated as deep yellow colored crystals in 68% yield,

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(16) (a) Fischer, G.; Huch, V.; Mayer, P.; Vasisht, S. K.; Veith, M.; Wiberg, N. *Angew. Chem.* **2005**, *117*, 8096–8099. Fischer, G.; Huch, V.; Mayer, P.; Vasisht, S. K.; Veith, M.; Wiberg, N. *Angew. Chem., Int. Ed.* **2005**, *44*, 7884–7887. (b) Scheschkewitz, D. *Angew. Chem.* **2005**, *117*, 3014–3016. Scheschkewitz, D. *Angew. Chem., Int. Ed.* **2005**, *44*, 2954–2956.

(17) Corey, J. Y. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, U. K., 1989; Vol. 1, Chapter 1

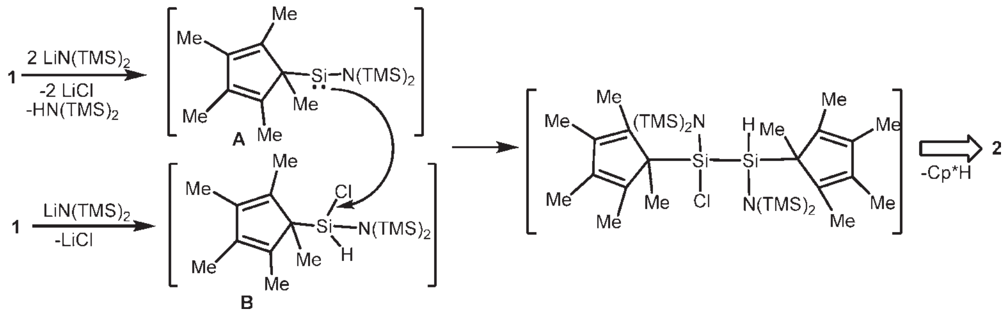
(18) Nesper, R.; Currao, A.; Wengert, S. In *Organosilicon Chemistry II: From Molecules to Materials*; Auner, N., Weis, J., Eds.; VCH: Weinheim, Germany, 1996; p 469.

(19) Weidenbruch, M. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, U. K., 2001; Vol. 3, Chapter 5.

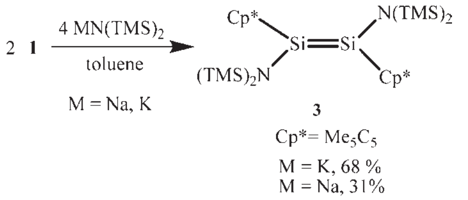
(20) (a) Pauling, L.; Brockway, L. O.; Beach, J. Y. *J. Am. Chem. Soc.* **1935**, *57*, 2705–2709. (b) Pauling, L. In *The Nature of the Chemical Bond*, 3rd ed.; Cornell: Ithaca, NY, 1960; pp 224−233.

(21) (a) Haaf, M.; Schmedake, T. A.; West, R. *Acc. Chem. Res.* **2000**, *33*, 704–714. (b) Gehrhus, B.; Lappert, M. *Polyhedron* **1998**, *17*, 999–1000. (c) Nagendran, S.; Roesky, H. W. *Organometallics* **2008**, *27*, 457–492. (d) Mizuhata, Y.; Sasamori, T.; Tokitoh, N. *Chem. Rev.* **2009**, *109*, 3479–3511. (e) Ishida, S.; Iwamoto, T.; Kabuto, C.; Kira, M. *Silicon Chemistry* **2003**, *2*, 137–140. (f) Ishida, S.; Iwamoto, T.; Kabuto, C.; Kira, M. *Nature* **2003**, *421*, 725–727.

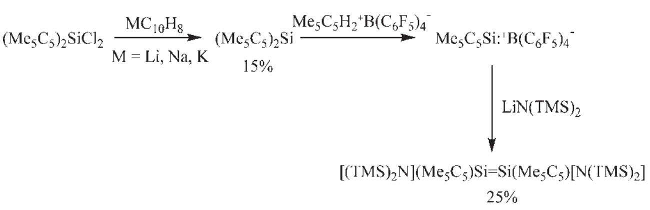
Scheme 3. Alternative Route for the Formation of **2**



Scheme 4. Synthesis of Compound **3**



Scheme 5. Multistep Synthesis of **3**



and single crystals suitable for X-ray analysis were obtained by storing a concentrated *n*-pentane solution at −32 °C in a freezer.

The X-ray crystallographic data confirmed the formation of *E*-[$(TMS)_2N](\eta^1\text{-}Me_5C_5)Si{=}Si(\eta^1\text{-}Me_5C_5)[N(TMS)_2]$[8b] (**3**), which was previously reported by Jutzi et al. by a multistep reaction sequence with an overall yield of 10% (Scheme 5).

Our new synthetic method will definitely develop a more convenient protocol to access the disilene **3** in a one-step reaction and, more importantly, in good yield. Moreover, the formation of **3** in this method further corroborates our proposed mechanism. Like in the previous reaction, $(Me_5C_5)SiN(TMS)_2$ (**A**) is formed as an intermediate which subsequently dimerizes to form the disilene **3**. A similar type of mechanism was also suggested by Jutzi et al., who reported a reversible equilibrium between **A** and **3** and explained it by steric strain in the solid disilene and flexibility in bonding modes (σ or π) of a silicon-bound pentamethylcyclopentadienyl (Cp*) substituent.[22] The experimental observations were also supported by theoretical calculations.[22]

The formation of two different products with two different amides [$MN(TMS)_2$, M = K, Li] encouraged us to study the reaction with $NaN(TMS)_2$. Accordingly, **1** is reacted with $NaN(TMS)_2$ under the same conditions and affords **3**, however, in less yield. We presume that the formation of different products with different metal amides is probably due to the difference in size of the metal cations, which increases down the group with the result that the basicity of the amide increases.

Conclusion

In conclusion, the reaction of $LiN(TMS)_2$ with dichlorosilane $(Me_5C_5)SiHCl_2$ (**1**) in a molar ratio of 3:2 at ambient temperature leads to the formation of an analogue of disilatricycloheptene (**2**). However, the reaction of **1** with $KN(TMS)_2$ results in the formation of disilene (**3**) in good yield in a single step and supports the mechanism for the formation of **2**. The composition and constitution of compounds **2** and **3** have been supported by NMR spectroscopy, EI-MS spectrometry, and single-crystal X-ray diffraction studies.

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 with the MBRAUN solvent purification system MB SPS-800. Compounds **1** and **3** were prepared using the literature method.[13] All chemicals purchased from Aldrich were used without further purification. ^1H, ^{13}C, and ^{29}Si NMR spectra were recorded in C_6D_6 with Bruker Avance DPX 200 or Bruker Avance DRX 500 spectrometers. The chemical shifts δ are given relative to $SiMe_4$. EI-MS spectra were obtained using a Finnigan MAT 8230 instrument. Elemental analyses were performed at 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.

Preparation of Compound 2. To a solution of **1** (0.234 g, 1 mmol) in toluene (30 mL) was slowly added a solution of $LiN(TMS)_2$ (0.250 g, 1.5 mmol) in toluene (20 mL) at room temperature. The mixture was stirred overnight, and the volatiles were removed *in vacuo*. *n*-Pentane (40 mL) was added to the residue. The solution was filtered through Celite to remove LiCl formed during the reaction. The solution was concentrated to 5 mL and stored at −30 °C in a freezer for two days to yield colorless needle-shaped crystals of **2** (0.150 g, 55%). Mp 68−70 °C. ^1H NMR (500 MHz, C_6D_6, 25 °C): δ 1.71 (s, 3 H, CH_3), 1.53 (s, 3 H, CH_3), 1.47 (s, 3 H, CH_3), 1.39 (s, 3 H, CH_3), 1.24 (s, 3 H, CH_3), 0.31 (br, 36 H, $SiMe_3$) ppm. $^{13}C\{^1H\}$ NMR (125.75 MHz, C_6D_6, 25 °C): δ 1.35 (Me_3Si), 4.83 (Me_3Si), 11.47 ($C_5\text{-}CH_3$), 12.51 ($C_5\text{-}CH_3$), 13.23 ($C_5\text{-}CH_3$), 14.48 ($C_5\text{-}CH_3$), 15.38 ($C_5\text{-}CH_3$), 43.63 ($C_5\text{-}CH_3$), 49.53 ($C_5\text{-}CH_3$), 54.94 ($C_5\text{-}CH_3$),131.75 ($C_5\text{-}CH_3$), 137.81 ($C_5\text{-}CH_3$) ppm. $^{29}Si\{^1H\}$ NMR (99.36 MHz, C_6D_6, 25 °C): δ 6.98 ($SiMe_3$), 7.79 ($SiMe_3$), −22.04 (*Si1*), −47.49 (*Si2*) ppm. EI-MS: *m*/*z* 546 [M^+] (100%). Anal. Calcd for $C_{22}H_{51}ClN_2Si_6$ (547.62): C, 48.25; H, 9.39; N, 5.12. Found: C, 48.91; H, 9.05; N, 5.01.

Preparation of Compound 3. To a solution of **1** (0.234 g, 1 mmol) in toluene (30 mL) was added slowly $KN(TMS)_2$ (0.398 g, 2 mmol) in toluene (20 mL) at room temperature. The mixture was stirred overnight, and the volatiles were removed *in vacuo*. *n*-Pentane (40 mL) was added to the residue. The solution was filtered through Celite to remove KCl formed during the reaction. The solution was concentrated to 3 mL and stored at −30 °C in a freezer for a few days to yield deep yellow crystals of **3** (0.21 g, 68%). ^1H

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[22] Jutzi, P.; Mix, A.; Neumann, B.; Rummel, B.; Schoeller, W. W.; Stammler, H.-G.; Rozhenko, A. B. *J. Am. Chem. Soc.* **2009**, *131*, 12137–12143.

NMR (200 MHz, C_6D_6, 25 °C): δ 1.90 (s, 30 H, CH_3), 0.23 (br, 36 H, TMS) ppm. $^{13}C\{^1H\}$ NMR (125.75 MHz, C_6D_6, 25 °C): 5.6 (*Me*$_3$Si), 6.1 (*Me*$_3$Si), 11.3 (*Me*$_5$C$_5$), 120.6 (Me$_5$*C*$_5$) ppm. $^{29}Si\{^1H\}$ NMR (99.36 MHz, C_6D_6, 25 °C): δ 15.06 (*Si*=*Si*), 2.06 (*Si*Me$_3$) ppm. EI-MS: *m*/*z*: 323 (M^+ −(Me$_5$C$_5$)SiN(TMS)$_2$), 278 (M^+ −(Me$_5$C$_5$)SiN(TMS)$_2$ −3Me), 220 (M^+ −(Me$_5$C$_5$)SiN(TMS)$_2$ −SiMe$_3$ −CH$_3$ −CH$_2$). Anal. Calcd for $C_{32}H_{66}N_2Si_6$ (646.38) C, 59.46; H, 10.28; N, 4.33. Found: C, 59.06; H, 9.98; N, 4.21.

Crystal Structure Determination. Shock-cooled crystals were selected and mounted under a nitrogen atmosphere using X-TEMP2.[15] The data for **2** and **3** were collected at 100(2) K on an INCOATEC Mo Microsource[15] with Quazar mirror optics and an APEX II detector on a D8 goniometer (see Table 1). The diffractometer was equipped with a low-temperature device and used Mo Kα radiation, $\lambda = 0.71$ Å. The data of **2** and **3** were integrated with SAINT, and an empirical absorption (SADABS) was applied.[23] The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares methods against F^2 (SHELXL-97).[24] 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 equal to 1.5 times the U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms. Disordered moieties were refined using bond length restraints and isotropic displacement parameters restraints.

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Supporting Information Available: CIF files for **2** and **3** and molecular structure of **3**. These materials are available free of charge via the Internet at http://pubs.acs.org.

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(23) Sheldrick, G. M. *SADABS 2008/2*; *University of Göttingen*: Göttingen, Germany, 2008.

(24) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.