Main-Group Chemistry

Deutsche Ausgabe: DOI: 10.1002/ange.201511493
Internationale Ausgabe: DOI: 10.1002/anie.201511493

1,3-Diazasilabicyclo[1.1.0]butane with a Long Bridging N–N Bond

Xu-Qiong Xiao[+], Zhaowen Dong[+], Zhifang Li, Chenting Yan, Guoqiao Lai, and Mitsuo Kira**

Abstract: *A 1,3-diazasilabicyclo[1.1.0]butane (**1**) is synthesized as thermally stable crystals by using the cycloaddition reaction of an isolable dialkylsilylene with aziadamantane. The bridge N–N bond length of **1** (1.70 Å) is the longest among those of known N–N singly-bonded compounds, including side-on bridged transition-metal dinitrogen complexes. The compound **1** is intact in air but moisture sensitive. No reaction occurs with hydrogen, even under pressure at 0.5 MPa. Irradiation of **1** with light gives an isomer quantitatively by N–N and adamantyl C–C bond cleavage. The origin of the remarkable N–N bond elongation is ascribed to significant interaction between a Si–C σ* and N–N π and σ orbitals as determined by DFT calculations of model compounds.*

1,3-Diazabicyclo[1.1.0]butanes and their congeners with main-group element bridges have not been reported until now, while related side-on bridging bimetallic dinitrogen complexes have been well-documented for many years in connection with nitrogen activation using transition-metal complexes.[1] Several siladiaziridine derivatives have been synthesized by Klingebiel et al. since 1982.[2] The first siladiaziridine (**2**; Figure 1) was obtained by the reaction of lithiated 1,2-bis(trimethylsilyl)hydrazine with di(*tert*-butyl)difluorosilane, and **2** was a glassy solid and unsuitable for X-ray analysis.[2c] Attempts to synthesize siladiaziridine derivatives through the reactions of transient silylenes with azobenzene have failed until recently. Ando et al. reported that the irradiation of hexamesitylcyclotrisilane or tetramesityldisilene with azobenzene gave **3** and **4**, which are formed by the hydrolysis of the corresponding siladiaziridine and by the addition of tetramesityldisilene to azobenzene, respectively.[3] During the photolysis of 2,2-diarylhexamethyltrisilanes [$(Me_3Si)_2SiAr_2$; Ar = mesityl, 2,4,6-triisopropylphenyl (TIP)] in the presence of azobenzene, Weidenbruch et al. obtained two diaziridine-derived products, **5** and **6**, but no evidence for the intermediary formation of the corresponding siladiaziridine was obtained.[4] So et al. described the reaction of a base-coordinated silylsilylene with diazobenzene gave a 1,2-diaza-3,4-disilacyclobutane via a siladiaziridine.[5] Eventually, Roesky et al. synthesized the siladiaziridine **7**, having a penta-

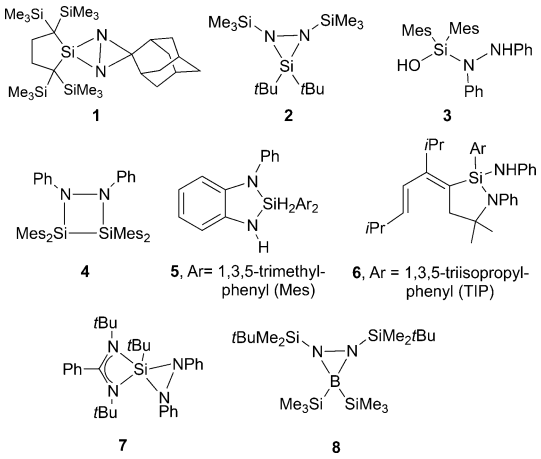
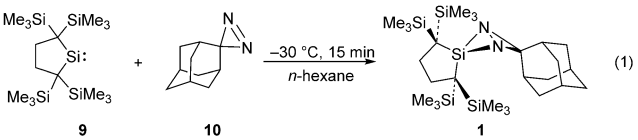


Figure 1. Siladiaziridine and related compounds studied.

coordinate silicon atom, and characterized the structure by X-ray crystallography.[6] No siladiaziridine derivative having a tetracoordiante silicon atom in the ring has been reported to date, but the boradiazacyclopropane **8** was synthesized by Klingebiel et al. in 1986.[2b,7] We report herein the synthesis, structure, and reactions of the 1,3-diaza-2-silabicyclo-[1.1.0]butane **1** as the first 1,3-diazabicyclo[1.1.0]butane derivative containing a bridging main-group element. Interestingly, the N–N bond in **1** is extremely long with the length of 1.698(5) Å, and it is even longer than that of **8** (1.67 Å)[7] and the side-on bridged transition-metal/N_2 complexes (< 1.64 Å).[8] The origin of the long N–N bond is discussed in terms of the interaction between a Si–C σ* orbital and N–N π and σ orbitals.

During the course of our study on the reactions of the isolable dialkylsilylene **9**[9,10] with multiply-bonded heteroatom compounds such as imines,[11a] nitriles,[11b] carbon dioxide,[11c] and diazo compounds,[11d] we have found that **1** is obtained by the thermal [1+2] cycloaddition reaction of **9** with aziadamantane (**10**). When **9** was treated with an equimolar amount of **10** in *n*-hexane at −30 °C, the orange-yellow color of the solution turned to pale yellow within 15 minutes. The usual workup gave **1** in 90% yield, upon isolation, as light yellow crystals. No reaction took place between **9** and azobenzene, probably because of the severe steric repulsion between the reagents.



(1)

[*] Dr. X.-Q. Xiao,[+] Z. Dong,[+] Prof. Z. Li, C. Yan, Prof. G. Lai, Prof. M. Kira
Hangzhou Normal University, Key Laboratory of Organosilicon Chemistry and Material Technology of Ministry of Education
No. 58 Haishu Rd. Hangzhou, 311121, Zhejiang (China)
E-mail: zhifanglee@hznu.edu.cn
mkira@m.tohoku.ac.jp

[+] These authors contributed equally to this work.

Supporting information for this article (experimental details, NMR spectra, and X-ray crystallography of **1**, **12**, and **13**, and the details of the DFT calculations) can be found under http://dx.doi.org/10.1002/anie.201511493.

The structure of **1** was determined by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy, high-resolution mass spectrometry, and X-ray crystallography.[12] The molecular structure of **1** determined by X-ray crystallography is shown in Figure 2 with the pertinent structural parameters. The N–N bond

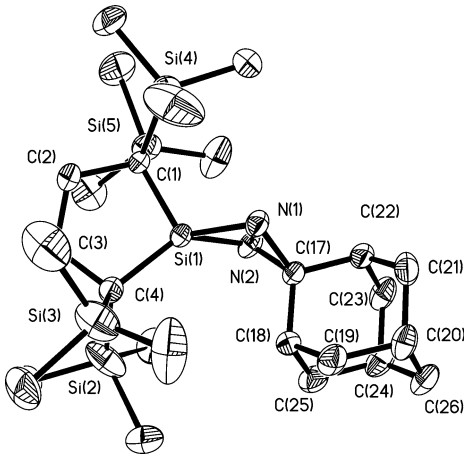


Figure 2. Molecular structure of **1**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level. Selected bond lengths [Å], bond angles [°] and dihedral angles [°]: N1-N2 1.698(5), Si1-N1 1.761(4), Si1-N2 1.753(4), N1-C17 1.458(5), N2-C17 1.459(5); N2-Si1-N1 57.79(18), C17-N1-N2 54.5(2), C17-N1-Si1 101.9(3), N2-N1-Si1 60.88(18), C17-N2-N1 54.4(2), C17-N2-Si1 102.2-(3), N1-N2-Si1 61.33(17), N1-C17-N2 71.2(3), Si1-N1-N2-C17 133.4(2), N1-Si1-C17-N2 116.1(3).

length of **1** [1.698(5) Å] is exceptionally long in comparison with those of related cyclic and noncyclic hydrazine derivatives, and transition-metal complexes with a side-on bridged N_2 ligand. Some reported N–N bond lengths for hydrazine derivatives are 1.449(4) (hydrazine),[13] 1.477(7) (**4**), [3] and 1.5240(18) Å (**7**),[6] and those for side-on bridging bimetallic dinitrogen complexes are found in the range of 1.38–1.64 Å.[8] The origin of the N–N bond elongation of **1** is discussed in a later section. The dihedral angle between the Si1-N1-N2 and C17-N1-N2 planes is 133.4(2)°, which is much smaller than those found in the related transition-metal complexes (146.7°–180.0°).[8] The structural parameters around diazasilabicyclobutane ring were nearly in accord with those of the model molecule **1′**, calculated at the B3LYP/6-31+G(d, p) level[14] (Figure 4 and Table 1).

Despite the fact that the bicyclobutane ring was found to be significantly bent in the solid state, a single peak representing four eqivalent trimethylsilyl groups in **1** was observed at $\delta = 0.33$, 3.09, and 3.39 ppm in the ^{1}H, ^{13}C, and ^{29}Si NMR spectra (C_6D_6), respectively, thus suggesting facile bicyclobutane ring flipping in solution at room temperature. The ^{29}Si NMR resonance resulting from the bridge silicon of **1** was observed at $\delta = 58.8$ ppm, which is at seemingly low field in light of the ^{29}Si resonance observed at $\delta = -30.7$ ppm for the ring silicon of the siladiaziridine **2**[2a,7] (Figure 1). While the origin of the upfield shift of the ^{29}Si chemical shift in **2** was attributed to the feature of small silacycles,[2a] the rule may not be applicable for the ^{29}Si NMR chemical shift for

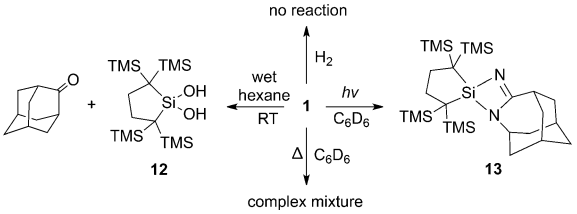
Table 1: Selected structural parameters, Wiberg's Bond Indices, and ^{29}Si NMR chemical shifts of diazabicyclo[1.1.0]butanes and related compounds calculated at the B3LYP/6-31+G(d,p) level of theory.

Compounds		Bond Length [Å] N–N	N–Si	Dihedral Angle[a] [°]	WBI (N–N)[b]	$\delta(^{29}Si)$ [ppm][c]
diazasila-	**1′**	1.696	1.769	131.1	–[d]	53.2
bicyclobutanes	**11**	1.664	1.775	120.2	0.922	18.9
	14	1.740	1.732	122.3	0.898	–[d]
diazadisila-	**15**	1.858	1.748	137.6	0.937	16.6
bicyclobutanes	**16**	1.962	1.720	136.9	0.918	–[d]
others	**17**	1.577	1.749	–	1.012	−43.9
	18	1.480	1.796	–	1.023	39.8
	19	1.500	–	–	–	–
	20	1.492	–	–	0.993	–
	21	1.533	–	114.1	0.926	–

[a] Angle between two three-membered ring planes. [b] Wiberg bond index (WBI) between two bridgehead nitrogen atoms.[16] [c] Calculated at the GIAO/B3LYP/6-311+(2d,p)//B3LYP/6-31+G(d,p) level. [d] Not calculated.

silabicyclobutane ring compounds. Actually, the shifts, of the model 1,3-diazasilabicyclobutanes **1′** and **11** (Figure 4), calculated by the GIAO calculations at the B3LYP/6-311+G-(2d,p)//B3LYP/6-31+G(d,p) level were $\delta = 53.2$ and 18.9 ppm, respectively.

The compound **1** can be stored without decomposition in dry air for several months at room temperature, while treatment of **1** with a trace amount of water in *n*-hexane provided **12**[12] in good yield together with adamantanone (Scheme 1).[15] Heating of **1** in C_6D_6 at 120 °C in a sealed NMR



Scheme 1. Reactivity of **1**.

tube gave a mixture of unidentified products. No reaction occurred when **1** was treated with hydrogen under either the normal flow condition or a pressure of 0.5 MPa (Scheme 1).

Irradiation of **1** in C_6D_6 using a high-pressure mercury arc lamp (300 W) at 0 °C for 8 hours afforded the isomer **13** quantitatively (Scheme 1). The structure of **13** was characterized using multinuclear NMR spectroscopy and X-ray analysis.[12] The molecular structure of **13** determined by X-ray crystallography is shown in Figure 3. The C17–N2 bond length of 1.293(2) Å is indicative of the double-bond character between these two atoms. The Si1-N1-C17-N2 four-membered ring is planar with the sum of inner angles of 360.0°. The C1-Si1-C4 and N1-Si1-N2 planes are almost perpendicular to each other with a dihedral angle of 89.7°. The photochemical reaction is quite unique because a rela-

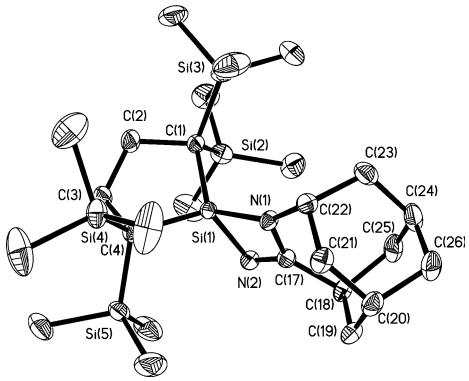
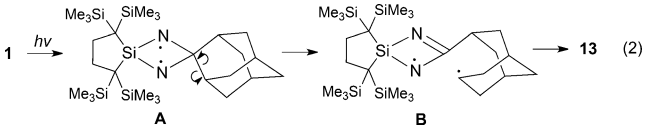


Figure 3. Molecular structure of **13**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level. Selected interatomic distances [Å] and angles [°]: Si1-N1 1.7890(15), Si1-N2 1.7791(17), N1-C17 1.394(2), N2-C17 1.293(2); N2-Si1-N1 77.16(7), C17-N1-Si1 83.87(11), C17-N2-Si1 87.21(12), N2-C17-N1 111.75(17).

tively inactive adamantyl C–C bond is cleaved. The compound **13** would be produced by the initial photochemical N–N bond cleavage, thus giving the biradical **A** followed by the cleavage of the adamantyl C–C bond, which may be prompted by the C=N bond formation in **B**. The intramolecular recombination of **B** will then form **13** [Eq. (2)].



To elucidate the origin of the extremely long N–N bond in **1**, DFT calculations at the B3LYP/6-31 + G(d,p) level of theory were performed for several model and reference compounds shown in Figure 4.[14] As shown in Table 1, all the 1,3-diazasilabicyclo[1.1.0]butanes, **1′**, **11**, and **14**, have an extremely long N–N bond and the feature is markedly enhanced in the 1,3-diaza-2,4-disilabicyclo[1.1.0]butanes **15** and **16**. Remarkably, the N–N bond length of **14** and **16** with difluorosilylene bridge is 0.076 and 0.104 Å longer than that of **11** and **15**, respectively. The N–N bond length of **16** is expected theoretically to be either 1.96 Å, that is, 0.43 Å longer than that of the corresponding carbon-bridged system

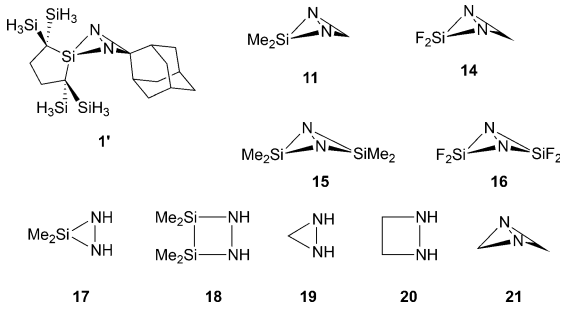


Figure 4. Model compounds used for the DFT calculations.

21. Similar but less significant elongation of the N–N bond is found in the siladiaziridine **17**. The elongation of the N–N bond occurs together with decreasing its WBI value and shortening of the Si–N bond, as seen by comparing the data of **11** and **14**–**16**.

The extremely long N–N bridge bond of **1** indicates that **1** would be classified as a long-bond isomer of the bicyclo-[1.1.0]butane systems, but the origin seems to be substantially different from that of well-documented bicyclo-[1.1.0]tetrasilane and 1,3-disilabicylo[1.1.0]butane systems.[17,18] While the origin of the elongation of the latter systems has been attributed to the inverted sigma bridge bond,[18b] the N–N bond elongation in the present systems is similar to the σ* aromaticity first proposed by Clark et al. to explain a small but significant C=C bond elongations and shortenings of the C–X bond (X = P or Si) of substituted 1*H*-phosphirenium cations and silacyclpropenes,[19] though the extent is much smaller than that for the N–N bond elongation.

In a simplified MO model of the model diazasilabicyclo-[1.1.0]butane **11**, two nitrogen atoms have a total of ten valence electrons but four of them are used to make four peripheral covalent bonds and the remaining six electrons reside on two nitrogen atoms as lone-pairs and as one N–N in σ bond orbitals (Figure 5a). The π_S and σ_S orbitals that are

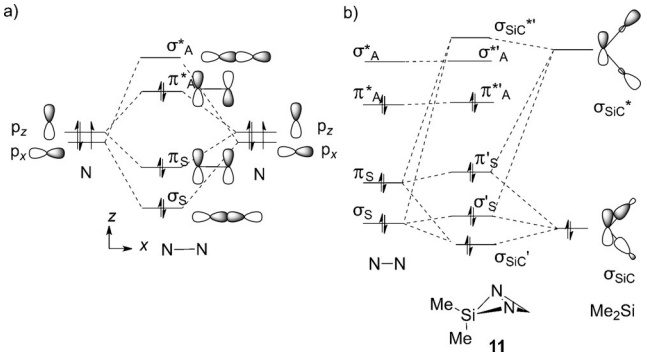


Figure 5. Schematic MO diagram for the 1,3-diazasilabicyclobutane **11**. a) Simplified Frontier MOs of the N–N bond constructed from the two p orbitals on each nitrogen atom ($2p_x$ and $2p_y$). Contribution of 2s orbitals on N is ignored for simplicity. b) Schematic representation of the frontier orbitals of **11** constructed by the interaction between Si–C σ and σ* orbitals and N–N π_S and σ_S orbitals.

symmetric to the symmetry plane bisecting the N–N bond and through the bridge atoms, can interact mainly with a bonding (σ_{SiC}) and an antibonding (σ_{SiC}*) orbital of the Me_2Si fragment, and hence, the frontier MOs of **11** would be schematically given as shown in Figure 5b.[20] Because raising the energy of the π_S and σ_S orbitals through π_S–σ_{SiC} and σ_S–σ_{SiC} interactions is compensated by lowering the energy of the σ_{SiC} orbital at the first approximation, only π_S–σ_{SiC}* and σ_S–σ_{SiC}* interactions contribute to stabilizing the system and the N–N bond elongation. The frontier Kohn–Sham orbitals of **11** (Figure 6) are basically in accord with the above qualitative model. The HOMO and HOMO−1 have a π_A*′ and π_S′ nature and the HOMO−2 and HOMO−3 appear to be constructed

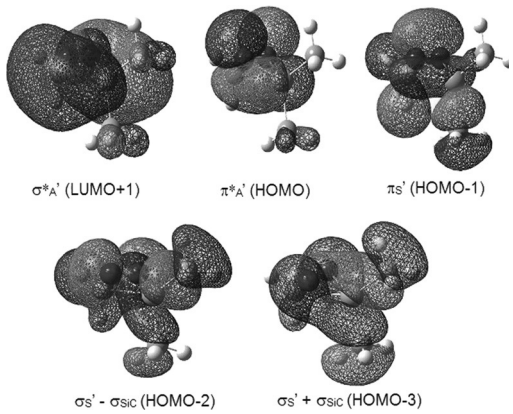


Figure 6. Frontier Kohn–Sham MOs of 1,3-diazasilabicyclobutane **11**.

mainly by mixing σ_S and σ_{SiC}. The LUMO + 1 corresponds to σ_A*, while the LUMO is assigned to a low-lying methyl σ* orbital (see Figure S13 in the Supporting Information). It is hard to see visually the contribution of the σ_{SiC}* orbital in the HOMO−1, HOMO−2, and HOMO−3, because of the more effective mixing of the σ_{SiC} orbital than that of σ_{SiC}*. The NBO analysis of **11** reveals, however, that there is significant BD(NN)–BD*(SiC) and LP(N)–BD*(SiC) (BD = bonding and LP = lone pair) interaction with the second-order perturbation energies [*E*(2)] of 5.92 and 4.20 kcal mol^{-1}, respectively. The relative importance between π_S–σ_{SiC}* and σ_S–σ_{SiC}* interactions for the N−N bond elongation remains unclear.

Remarkable elongation of the N−N bond caused by the introduction of fluorine substituents on silicon is in good accord with the enhancement of the π_S–σ_{SiC}* and σ_S–σ_{SiC}* interaction resulting from the lower-lying σ_{SiF}* orbital relative to the σ_{SiC}* orbital. The significant but smaller N−N bond elongation found for the siladiaziridine **17** (Table 1) would be the result of the undesirable arrangement of the two nitrogen lone-pair orbitals in this system.

In summary, we have synthesized the first 1,3-diazasilabicyclo[1.1.0]butane **1**, having an extremely long N−N bond of 1.70 Å. Because the N−N bond elongation in side-on N_2-bridging transition-metal complexes has often been taken as a measure of the N−N bond reactivity towards hydrogen and hydrosilanes,[8] we may expect for **1**, and especially for the unknown the 1,3-diazadisilabicyclo-[1.1.0]butanes like **15**, to show relatively high reactivity to a variety of reagents. Further work is in progress.

Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (Nos. 21472032, 21101050).

Keywords: π interactions · bridging ligands · density-functional calculations · silylene · X-ray diffraction

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 3758–3762
Angew. Chem. **2016**, *128*, 3822–3826

[1] For reviews, see: a) B. K. Burgess, D. J. Lowe, *Chem. Rev.* **1996**, *96*, 2983–3012; b) M. D. Fryzuk, S. A. Johnson, *Coord. Chem. Rev.* **2000**, *200*, 379–409; c) B. A. MacKay, M. D. Fryzuk, *Chem. Rev.* **2004**, *104*, 385–402; d) R. R. Schrock, *Angew. Chem. Int. Ed.* **2008**, *47*, 5512–5522; *Angew. Chem.* **2008**, *120*, 5594–5605.
[2] a) J. Hluchy, U. Klingebiel, *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 301; *Angew. Chem.* **1982**, *94*, 292; *Angew. Chem. Suppl.* **1982**, 750–754; b) U. Klingebiel, S. Schmatz, E. Gellermann, C. Drost, M. Noltemeyer, *Monatsh. Chem.* **2001**, *132*, 1105–1124.
[3] A. Sakakibara, Y. Kabe, T. Shimizu, W. Ando, *J. Chem. Soc. Chem. Commun.* **1991**, 43–44.
[4] M. Weidenbruch, S. Olthoff, W. Saaka, H. Marsmann, *Eur. J. Inorg. Chem.* **1998**, 1755–1758.
[5] S.-H. Zhang, H.-X. Yeong, C.-W. So, *Chem. Eur. J.* **2011**, *17*, 3490–3499.
[6] R. Azhakar, H. W. Roesky, R. S. Ghadwal, J. J. Holstein, B. Dittrich, *Dalton Trans.* **2012**, *41*, 9601–9603.
[7] R. Boese, U. Klingebiel, *J. Organomet. Chem.* **1986**, *306*, 295–302.
[8] M. Hirotsu, P. P. Fontaine, P. Y. Zavalij, L. R. Sita, *J. Am. Chem. Soc.* **2007**, *129*, 12690–12692.
[9] M. Kira, S. Ishida, T. Iwamoto, C. Kabuto, *J. Am. Chem. Soc.* **1999**, *121*, 9722–9723.
[10] For reviews on the silylene **9**, see: a) M. Kira, *J. Organomet. Chem.* **2004**, *689*, 4475–4488; b) M. Kira, S. Ishida, T. Iwamoto, *Chem. Rec.* **2004**, *4*, 243–253; c) M. Kira, T. Iwamoto, S. Ishida, *Bull. Chem. Soc. Jpn.* **2007**, *80*, 258–275; d) M. Kira, *Chem. Commun.* **2010**, *46*, 2893–2903; e) M. Kira, *J. Chem. Sci.* **2012**, *124*, 1205–1215.
[11] a) W. Chen, L. Wang, Z. Li, A. Lin, G. Lai, X. Xiao, Y. Deng, M. Kira, *Dalton Trans.* **2013**, *42*, 1872–1878; b) L. Wang, W. Chen, Z. Li, X.-Q. Xiao, G. Lai, X. Liu, Z. Xu, M. Kira, *Chem. Commun.* **2013**, *49*, 9776–9778; c) X. Liu, X.-Q. Xiao, Z. Xu, X. Yang, Z. Li, Z. Dong, C. Yan, G. Lai, M. Kira, *Organometallics* **2014**, *33*, 5434–5439; d) Z. Dong, X. Q. Xiao, Z. Li, Q. Lu, G. Q. Lai, M. Kira, *Org. Biomol. Chem.* **2015**, *13*, 9471–9476.
[12] See the Supporting Information for the experimental, spectroscopic, and X-ray analysis details of **1**, **12**, and **13**. The X-ray data for **1**, **12**, and **13** are deposited with CCDC, whose numbers are 1056194, 1056197 and 1056196, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.
[13] Y. Morino, T. Iijima, Y. Murata, *Bull. Chem. Soc. Jpn.* **1960**, *33*, 46–48.
[14] See the Supporting Information for the calculation details with the full reference of Gaussian 09.
[15] While the details of the hydrolysis mechanism of **1** remains open, it may be supposed that the nucleophilic attack of water to the silicon atom of **1** give silandiol **12** and hydraziadamantane, the latter of which will be hydrolyzed to give adamantanone and hydrazine.
[16] K. B. Wiberg, *Tetrahedron* **1968**, *24*, 1083–1096.
[17] a) T. Dabish, W. W. Schoeller, *J. Chem. Soc. Chem. Commun.* **1986**, 896–898; b) P. v. R. Schleyer, A. F. Sax, J. Kalcher, R. Janoschek, *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 364–366; *Angew. Chem.* **1987**, *99*, 374–377; c) S. Collins, R. Dutler, A. Rauk, *J. Am. Chem. Soc.* **1987**, *109*, 2564–2569; d) S. Nagase, T. Kudo, *J. Chem. Soc. Chem. Commun.* **1988**, 54–56; e) J. A. Boatz, M. S. Gordon, *J. Phys. Chem.* **1988**, *92*, 3037–3042; f) J. A. Boatz, M. S. Gordon, *J. Phys. Chem.* **1989**, *93*, 2888–2891.
[18] a) T. Iwamoto, D. Yin, C. Kabuto, M. Kira, *J. Am. Chem. Soc.* **2001**, *123*, 12730–12731; b) M. Kira, *Organometallics* **2014**, *33*, 644–652, and references therein.
[19] a) A. Göller, H. Heydt, T. Clark, *J. Org. Chem.* **1996**, *61*, 5840–5846; b) A. Göller, T. Clark, *J. Mol. Model.* **2000**, *6*, 133–149;

c) S. Tsutsui, K. Sakamoto, C. Kabuto, M. Kira, *Organometallics* **1998**, *17*, 3819 – 3821.

[20] There are two Si–C bonds in the Me_2Si fragment and we may take one set of Si–C orbitals (σ_{SiC} and σ_{SiC}^*) as those antisymmetric to the symmetric plane (σ_v) bisecting the CSiC plane and the other set (σ_{SiC}' and $\sigma_{SiC}^{*\prime}$) as those symmetric to the σ_v. The two sets of orbitals may interact with both the π_S and σ_S orbitals, because the four-membered ring of **11** is not planar but bent. However, σ_{SiC} is higher-lying than σ_{SiC}', and σ_{SiC}^* is lower-lying than $\sigma_{SiC}^{*\prime}$. Hence, in the present qualitative MO model, the contribution of σ_{SiC}' and $\sigma_{SiC}^{*\prime}$ orbitals is neglected. Contribution of methylene σ and σ* orbitals is significant but relatively smaller than that of the Si–C orbitals, and hence, not considered in the discussion.

Received: December 10, 2015
Published online: February 8, 2016

