ORGANOMETALLICS

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A New Synthetic Route for Silacyclopropanes: Reactions of a Bromosilylenoid with Olefins

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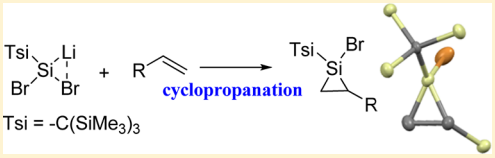
Supporting Information

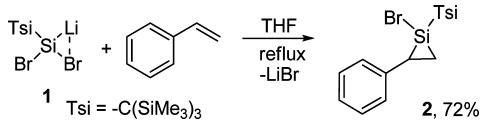
ABSTRACT: Stable 1-bromo-1-silacyclopropanes were synthesized in high yields from the reaction of the stable bromotrisylsilylenoid **1** (trisyl = $C(SiMe_3)_3$) with olefins such as styrene, trimethylvinylsilane, triethylvinylsilane, and dimethylphenylvinylsilane, a new synthetic route for silacyclopropanes. The structure of bromosilacyclopropane **5** was confirmed by X-ray analysis. In the presence of excess MeOH the phenyl-substituted bromosilacyclopropane **2** underwent regioselective ring opening to give the corresponding product **6**. In contrast, the reaction of silyl-substituted bromosilacyclopropane **5** with MeOH gave only the product of nucleophilic substitution at the silicon atom, 1-methoxy-1-silacyclopropane **7**, without any ring opening. Furthermore, the bromosilacyclopropane **2** extruded bromosilylene **8** through a thermal cycloreversion reaction.



Silylenoids (R_2SiMX), silicon analogues of carbenoids, are species in which an electropositive metal (M, usually an alkali metal) and a leaving group (X, usually a halogen) are bound to the same silicon atom and show amphiphilic (nucleophilic and electrophilic) properties.[1−7] Silylenoids and silylenes (R_2Si:) have been postulated as key intermediates in oligosilane and polysilane syntheses.[1] The reactivities of silylenoids are often similar to those of silylenes (R_2Si:). It is well-known that silylenes react with carbon−carbon double bonds to form silacyclopropanes,[8] the corresponding [1 + 2] cycloadducts.[9] Only a few stable silylenoids, including (*t*BuO)-Ph_2SiLi,[2] $(Mes)_2Si(SMes)Li$,[3] $(Me_3Si)_2Si(OMe)K$·crown ether,[4] $(R_3Si)_2SiFLi$[5] (R_3Si = *t*-Bu_2MeSi), and the halosilylenoid $TsiSiBr_2Li$[6] (Tsi (trisyl) = $C(SiMe_3)_3$), and their reactivities have been reported, but there has been no report on their reactivities with olefins. In this paper we report unprecedented examples of reactions of the stable bromotrisylsilylenoid **1** with olefins such as styrene, trimethylvinysilane, triethylvinylsilane, and dimethylphenylvinylsilane, to yield the corresponding 1-bromo-1-silacyclopropanes. Halogen-substituted silacyclopropanes could be very useful because of their high synthetic potential. In addition, their reactivity toward MeOH and their thermal stability are reported.

The stable bromosilylenoid **1**, having a bulky Tsi group, was prepared by the reduction of tribromotrisylsilane with 2 equiv of lithium naphthalenide.[6] To the solution was added an excess of styrene at −78 °C. When the reaction mixture was slowly warmed to room temperature, no reaction took place. However, stirring for 1 h at reflux temperature successfully gave 1-bromo-2-phenyl-1-silacyclopropane **2** in 72% yield (Scheme 1).

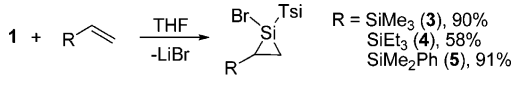
Scheme 1. Synthesis of 2



The structure of silacyclopropane **2** was characterized by ^1H, ^{13}C, and ^{29}Si NMR, GC/MS, and HRMS. In ^1H and ^{13}C NMR, resonances (^1H NMR, 2.69, 1.46 ppm; ^{13}C NMR, 22.7, 10.1 ppm) derived from CH and CH_2 of the three-membered ring were observed. The ^{29}Si NMR signal of the center silicon atom in **2** was observed at −38.0 ppm, which is in the same range as reported values (−48.9, −43.9, −33.8 ppm) for 1,l-di-*tert*-butyl-2-benzyl-1-silacyclopropane,[10] 1,l-di-*tert*-butyl-*trans*-2,3-dimethyl-1-silacyclopropane,[1b] and (*Z*)-1,2-dimethyl-4,4,7,7-tetrakis-(trimethylsilyl)-3-silaspiro[2.4]heptane.[11]

The syntheses were successfully extended to the cyclopropanation of silyl-substituted olefins. Treatment of **1** with trimethylvinylsilane, triethylvinylsilane, and dimethylphenylvinylsilane furnished cyclic products **3**−**5** in 90%, 58%, and 91% yields, respectively (Scheme 2). Cyclopropanes **3**−**5** were

Scheme 2. Synthesis of 3−5



Received: June 15, 2012
Published: July 17, 2012

dx.doi.org/10.1021/om3005349 | *Organometallics* 2012, 31, 5227−5230

characterized by multinuclear NMR, GC/MS, and HRMS. The ^{29}Si NMR signals attributed to the center silicon atoms in compounds **3**–**5** resonate at −41.3, −41.2, and −42.4 ppm, respectively. To the best of our knowledge, only two examples of stable silacyclopropanes having halogen(s) substituted at the silicon atom have been reported until now. Seyferth and Duncan synthesized 1,1-difluoro-2,2,3,3-tetramethyl-1-silacyclopropane via a ring-closing reaction,[12] and Tokitoh and coworkers obtained 7-bromo-7-Bbt-7-silabicyclo[4.1.0]heptanes (Bbt = 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl) from the reaction of 1,2-diaryl-1,2-dibromodisilene with cyclohexene.[8b]

Colorless crystals of bromosilacyclopropane **5** were obtained from a cold hexane solution (−40 °C), and the structure was confirmed by X-ray analysis,[13] giving the first molecular structure of a halosilacyclopropane (Figure 1). The endocyclic

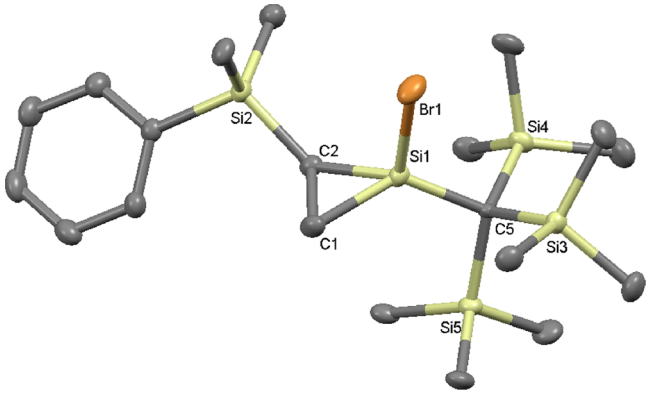


Figure 1. ORTEP drawing of **5** with 30% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Si1–Br1 = 2.235(1), Si1–C1 = 1.825(4), Si1–C2 = 1.831(4), Si1–C5 = 1.860(4), C1–C2 = 1.601(5), Si3–C5 = 1.923(3); C1–Si1–C2 = 52.0(2), Si1–C2–C1 = 63.7(2), Si1–C1–C2 = 64.3(2), Si1–C2–Si2 = 131.9(2), Br1–Si1–C2 = 111.6(1), Br1–Si1–C1 = 109.7(1), Br1–Si1–C5 = 114.5(1).

bond angles of Si1, C2, and C1 (52.0(2), 63.7(2), and 64.3(2)°) imply the strained nature of the silacyclopropane. The torsion angles C5–Si1–C2–Si2 = 137.0(2)° and Br1–Si1–C2–Si2 = 11.2(3)° indicate the trans orientation of the Tsi group and the dimethylphenylsilyl group and cis orientation of the bromine atom and the dimethylphenylsilyl group, respectively. This stereoselectivity is possibly due to the bulky substituent. The Si1–C2 bond length (1.831(4) Å) is within the range of reported values (1.825–1.880 Å).[14,15] The C1–C2 bond length (1.601(5) Å) in the three-membered ring is longer than reported distances (1.508–1.576 Å)[14] in 2,3-alkyl- or hydrogen-substituted 1-silacyclopropanes, except for that (1.643 Å)[15] in 2,3-silyl-substituted 1-silacyclopropane. The Si1–Br1 (2.235(1) Å), Si1–C5 (1.860(4) Å), and Si1–C2 bond lengths (1.831(4) Å) are shorter than the corresponding Si1–Br (2.265(2) Å), Si1–C9 (1.890(7) Å), and Si1–C1 lengths (1.885(7) Å) in acyclic compound **6** (Figure 2).

In order to investigate the reactivity of silacyclopropanes toward nucleophiles, excess methanol was added to **2** at room temperature. The reaction mixture gave the ring-opened and methoxy-substituted product **6** in 80% yield (Scheme 3). As expected, the Si–C bond was cleaved due to ring strain in the silacyclopropane, resulting in the insertion of MeOH into the

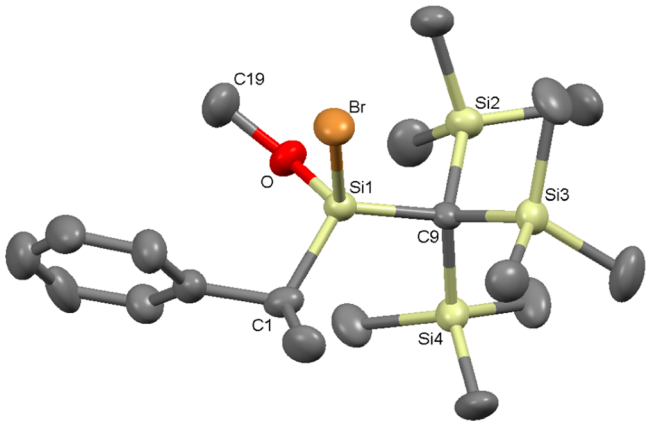
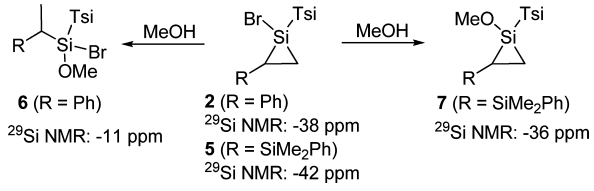


Figure 2. ORTEP drawing of **6** with 30% probability thermal ellipsoids. Hydrogen atoms and the disorder of three trimethylsilyl groups are omitted for clarity. Selected bond lengths (Å) and angles (deg): Si1–Br = 2.265(2), Si1–O = 1.621(6), Si1–C1 = 1.885(7), Si1–C9 = 1.890(7), C9–Si2 = 1.951(8), C9–Si3 = 1.928(8), C9–Si4 = 1.943(8); C1–Si1–C9 = 118.8(3), Si1–O–C19 = 134.4(5).

Scheme 3. Reactions of 2 and 5 with MeOH



6 (R = Ph)
^{29}Si NMR: -11 ppm

2 (R = Ph)
^{29}Si NMR: -38 ppm
5 (R = $SiMe_2Ph$)
^{29}Si NMR: -42 ppm

7 (R = $SiMe_2Ph$)
^{29}Si NMR: -36 ppm

Si–C bond to form **6**. Regioselective rupture of the Si–C bond could be explained by previous reports that the less hindered silicon–carbon bond in a three-membered ring was preferentially cleaved by MeOH.[16]

In the ^{1}H NMR of **6**, the resonance derived from OMe was observed at 2.48 ppm, shifted unexpectedly upfield in comparison with the normal chemical shift (3.0–3.5 ppm) of SiOMe groups. The abnormal shift may be understood from the X-ray crystallographic characterization of **6**. The molecular structure of **6** (Figure 2) shows that the methyl group of OMe is below the plane of the phenyl group. This arrangement possibly caused the shielding of methyl protons in the OMe group due to the aromatic ring current. All trimethylsilyl groups in Tsi appeared to be disordered with nearly equivalent site occupation factors (0.51/0.49).

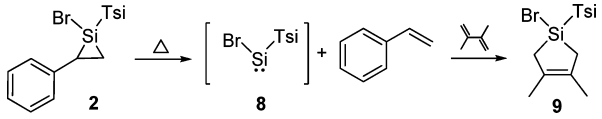
To compare the reactivity of a 2-silyl-substituted 1-silacyclopropane with that of a 2-phenyl-substituted 1-silacyclopropane, the reaction of **5** with MeOH in THF was carried out. Interestingly, the reaction mixture afforded only methoxy-substituted silacyclopropane **7** (Scheme 3). This is the first example of nucleophilic substitution on a silacyclopropane without ring cleavage. Compound **7** at room temperature was stable even in the air for a few days.[17] Those results indicate that the silyl substituent increased the stability of silacyclopropane toward MeOH in comparison with the phenyl group.[18]

Silacyclopropane **2** was thermally stable in THF or chloroform solvent at room temperature. However, about 50% of compound **2** decomposed after heating at 80 °C for 60 min in toluene solution, monitored by ^{1}H NMR. ^{1}H NMR signals of styrene also appeared downfield, and the intensities of ^{1}H NMR signals due to CH and CH_2 of the three-membered ring decreased (Figure S2, Supporting Information). This

dx.doi.org/10.1021/om3005349 | *Organometallics* 2012, 31, 5227–5230

observation implies that styrene was thermally eliminated from the silacyclopropane to afford bromotrisylsilylene **8**.[19] In order to trap the transient bromosilylene **8**, a toluene solution of **2** in the presence of excess 2,3-dimethyl-1,3-butadiene was heated to 80 °C for 1 h to afford the Br(Tsi)silylene-trapping product **9** (Scheme 4).[6] This result suggests strongly that halosilacyclopropanes can be promising precursors for halosilylenes.[20]

Scheme 4. Thermal Cycloreversion Reaction of 2



Our study demonstrated that stable silacyclopropanes at room temperature were synthesized from the reaction of the bromotrisylsilylenoid **1** with olefins, which extruded the halosilylene **8** through a thermal cycloreversion reaction. These results provide new synthetic pathways for synthesizing halosilacyclopropanes and generating halosilylenes. No ring cleavage of bromosilacyclopropane **5** in the presence of methanol was observed. Further studies on the reactivity of functionalized silacyclopropanes for synthetic applications are in progress.

■ ASSOCIATED CONTENT

Supporting Information

CIF files giving crystal data for **5** and **6** and text, tables, and figures giving details of the synthesis and characterization data of **2**–**9** and crystallographic data of **5** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2010-0024877). We thank Professor Robert West, distinguished Professor in the WCU program, for valuable discussions.

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