Siletanylmethyllithium: an ambiphilic organosilane†

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Received (in Bloomington, IN, USA) 2nd March 2005, Accepted 18th April 2005
First published as an Advance Article on the web 6th May 2005
DOI: 10.1039/b503110a

The adjacent centres of electrophilicity and nucleophilicity lead to interesting chemical reactivity in the title reagent.

Siletanes (silacyclobutanes) are an emerging class of silane reagents that attract attention by virtue of their "*strain-release Lewis acidity*".[1] Strained silacycles complex readily with nucleophiles to form hypervalent silicate complexes, which are less strained than the neutral tetracoordinate silanes.[2] This siletane electrophilicity provides an advantage in aldol[3] and allylation[4] reactions. Ring opening of siletanes has been used to trigger anionic polymerization,[5] transition metal-catalyzed coupling reactions,[6] and carbosilane oxidation.[7]

With the exception of anionic polymerization, all of these organosilane reactions parallel organoboron chemistry. Much of the chemistry of these two metalloids (silicon and boron) is similar, with boron reagents tending to be more reactive and silanes being generally more stable. In many ways, siletanes combine attractive features of organoboranes (mild reaction conditions, inherent Lewis acidity) and conventional organosilanes (stability in multistep reaction sequences, ease of purification and handling).

The similarities notwithstanding, silicon and boron chemistries diverge when it comes to metalloid-derived nucleophiles. It is difficult to integrate the Lewis acidity of boranes with nucleophilic functionality. For example, the boron analog[8] of the Peterson olefination[9] is limited to highly hindered organoborane reagents. Siletane reagents, which incorporate features reminiscent of boranes but with enhanced stability, may be particularly attractive in this context.

We therefore became interested in the synthesis and properties of siletane-derived nucleophiles. Such compounds were expected to display ambiphilic character and reactivity not seen in other systems. We consider the organometallic reagents **1** and **2** to be "pseudo-ylides" (Fig. 1). Whereas a traditional ylide[10] contains formal positive and negative charges on adjacent atoms, siletanylmethyl anions (*e.g.*, **2**) present adjacent nucleophilic and electrophilic centres.

We describe herein the synthesis and characterization of stannane **1** and efforts to generate and trap **2**. Reagent **2**, if it is immune to self-annihilation, should have novel ambiphilic properties derived from its pseudo-ylide nature.

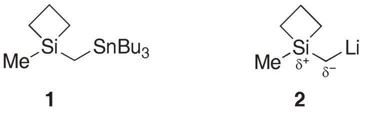
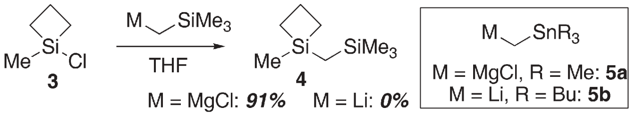


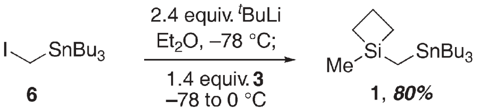
Fig. 1 Siletane ambiphiles.



Scheme 1 Nucleophilic addition to **3**.

Our synthetic approach to **1** was based on addition to chlorosiletane **3**.[11] We first examined silyl-based nucleophiles as models (Scheme 1). The results are fully consistent with past experience: Grignard reagents react efficiently with **3**, whereas alkyllithiums[12] afford little or none of the desired product.

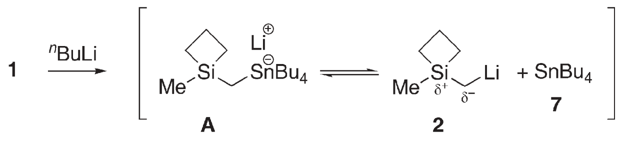
Stannyl-based nucleophiles did not follow this trend, as attempts to couple **5a**[13] with **3** failed to provide significant amounts of stannane product analogous to **4**. In contrast, **5b**[14] (generated from **6**[15] by halogen–metal exchange) couples surprisingly well with **3**, providing multigram quantities of **1** after distillation [eqn. (1)]. This is a dramatic illustration of subtle differences between silane and stannane reagents.



(1)

The next phase of research focused on synthesis and applications of **2**. It was not clear at the outset whether ^{n}BuLi would react faster with the siletane or stannane functionality of **1**. Attack at silicon would likely result in anionic polymerization, leading to polymer-bound stannane.[5] However, stannanes react rapidly with ^{n}BuLi to form "ate" complexes (*e.g.*, **A**, Scheme 2),[16] which in the case of **A** would formally release siletanylmethyllithium **2**.

It is the latter process—transmetallation—that predominates, as evidenced by trapping experiments with tribenzylsilyl chloride (Bn_3SiCl, Table 1). Treating **1** with an equimolar amount of ^{n}BuLi at −78 °C for 30 min, followed by addition of Bn_3SiCl, provides **8** in 52% yield based on **1** (entry 1) or 57–59% based on Bn_3SiCl (entries 2 and 3). This chemical reactivity is consistent with that expected for siletanylmethyllithium intermediate **2**. Increasing the amount of **1** (and ^{n}BuLi) relative to Bn_3SiCl is detrimental (entry 4), probably due to alkyllithium-induced decomposition of



Scheme 2 Transmetallation to generate **2**.

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† Electronic supplementary information (ESI) available: procedures and data for **1** and **8**. See http://www.rsc.org/suppdata/cc/b5/b503110a/
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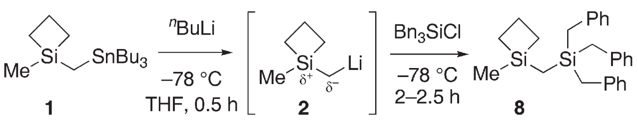
Table 1 Formation and trapping of lithium **2**



Entry	Equivalents **1**/^{n}BuLi	Equivalents Bn$_3$SiCl	Yield[a] (%)
1	1.0	1.2	52
2	1.2	1.0	57
3	1.5	1.0	59
4	2.0	1.0	26

[a] Isolated yield of **8** following chromatographic purification.

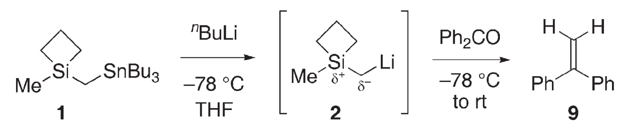
the product (**8**).[5] It thus appears that the carbanionic nature of **2** (or **A**) shields the siletane ring against nucleophilic attack.

Having concluded that siletane **2** is a viable chemical species, we next examined its ambiphilic character and behaviour as a pseudo-ylide species. Discussion of ylide chemistry calls to mind the Wittig olefination.[17] The Peterson olefination with silylmethyl anions is a well-known complementary method, but this is a two-step process in which β-hydroxysilanes are isolated and then eliminated regioselectively.[9]

Silylmethyl anions are more reactive toward a range of ketones than are phosphorus ylides, but they require an extra elimination step, often involving acid or strong base, to complete the olefination process. We expected: (1) that ambiphilic siletane **2** would maintain the high nucleophilicity associated with silylmethyl anions, and (2) that the siletane electrophilicity would promote elimination under mild conditions. Table 2 summarizes our observations on the reaction of pseudo-ylide **2** (generated from **1** as described above) with benzophenone (Ph$_2$CO).

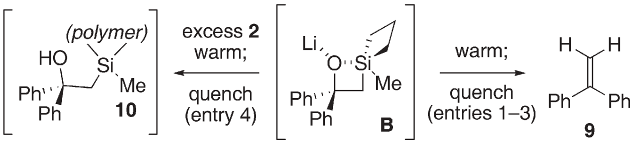
Addition of benzophenone to **2** affords 1,1-diphenylethylene (**9**), which is obtained along with **7** as the sole identifiable products in entries 1 and 3 (tributylmethyltin was produced in the experiment described in entry 2). This one-step olefination stands in contrast to the traditional silane reactivity.[18] Modest yields may reflect inefficiencies in the transmetallation event (**1** → **2**). Nonetheless, this reaction is interesting from a mechanistic perspective and for the insight it provides into the ambiphilic nature of **2**.

Table 2 Reaction of **2** with benzophenone



Entry	Equivalents **1**/^{n}BuLi	Equivalents Ph$_2$CO	Yield [a](%)
1	1.0	1.0	33
2[b]	1.0	1.0	36
3	1.0	1.5	40[c]
4	1.2	1.0	0 → 42[d]

[a] Isolated yield of **9** following chromatographic purification. [b] In entry 2, MeLi was used in place of ^{n}BuLi for generating **2**. [c] Bu$_4$Sn (**7**) was isolated and quantified in this experiment. It was obtained in 74% yield. [d] None of the expected product (**9**) was observed in the crude reaction mixture by TLC or ^{1}H NMR analysis. Alkene **9** was obtained after stirring the crude product with silica gel in methylene chloride overnight.



Scheme 3 Presumed olefination intermediate **B**.

The reaction described in entry 4 (with an excess of siletanylmethyllithium **2**) takes a different course: **9** was not detected in the crude reaction mixture, but it forms gradually upon treatment with acidic silica gel. This observation, surprising at first, is consistent with our mechanistic hypothesis, which emphasizes the importance of the siletane ring (Scheme 3).

We interpret these results as follows: nucleophilic attack of **2** on the carbonyl generates a lithium alkoxide, which, although inert to most vicinal silanes, coordinates with the electrophilic siletane.[19] This intermediate (**B**) eventually decomposes into alkene **9**.[20] In entry 4, the residual **2** likely promotes anionic polymerization[5] of silicate **B**. The resulting polymer-bound β-hydroxysilane (**10**) is no longer activated by the silacycle strain-release Lewis acidity, and therefore requires further treatment with acidic silica gel overnight to promote elimination. In conclusion, this communication describes the synthesis and ambiphilic reactivity of novel organometallic reagents (**1** and **2**) derived from strained silacycles.

Stannane **1** is prepared conveniently and in high yield on a multigram scale. The reactivity of **1** with ^{n}BuLi suggests that the presence of the stannyl moiety suppresses polymerization of the siletane ring. The ambiphilic properties of **2** present new avenues for organosilicon chemistry that warrant further investigation. Potential applications include the use of **2** for olefination or as a synthetic equivalent of hydroxymethyllithium (in conjunction with the siletane oxidation[7] reported previously). Efforts aimed at generating reagents of type **2** more efficiently by halogen–metal exchange or by using the complex-induced proximity effect[21] are underway.

We thank the FSU Department of Chemistry and Biochemistry for supporting this research.

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