Stable Phosphonium Sila-ylide with Reactivity as a Sila-Wittig Reagent

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The Wittig reaction, which was first reported in 1954,[1] describes the transformation of the ubiquitous carbonyl functionality into a carbon−carbon double bond with high regio- and stereoselectivity[2] using a phosphonium ylide, **I** (often called a "Wittig reagent"), and is widely recognized as one of the most important reactions in organic synthesis.[3,4]
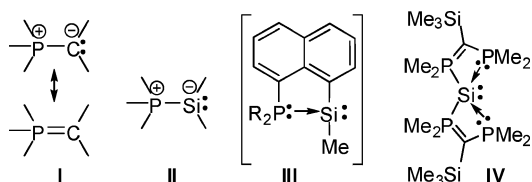
In marked contrast, the chemistry of the corresponding heavier silicon homologue, the phosphonium sila-ylide **II**, has not been developed nearly as fully. Sila-ylides are usually only short-lived reactive intermediates and were first postulated in 1978 to explain the improved [1 + 2] cycloaddition of transient silylenes with ketones in the presence of a phosphine.[5] In that article, the authors made the following statement: "The strong Si−O covalent bond energy and the reluctance of a silicon−carbon double bond to form very likely serve to steer the decomposition in the direction of oxasilirane formation so that a Wittig-type process does not occur". More recently, Tamao and co-workers[6] reported the reactions of the transient phosphonium sila-ylide **III** with diphenylacetylene, indicating an ylide character similar to that of ylide **I**, whereas the structurally similar transient ammonium sila-ylides exhibit a silylene-like reactivity.[7] However, the most typical and useful reaction of phosphonium ylides, the Wittig reaction, has never been demonstrated for phosphonium sila-ylides **II**.[8] Furthermore, as experimental evidence for existence of **II**, only the detection at 77 K by UV spectroscopy in a soft matrix system has been described to date,[9] although several stable silylene−Lewis base adducts, such as silylene−isocyanide[10] or −imine[11] complexes as well as **IV**, a four-coordinate silicon(II) compound stabilized by phosphines,[12] have been already synthesized. Herein, we report the synthesis of the first stable and isolable phosphonium sila-ylide, **2**, with reactivity as a sila-Wittig reagent.

The reaction of racemic 2-phosphino enamine **1** with 1 equiv of magnesium in THF at room temperature (rt) resulted in the clean formation of the desired cyclic phosphonium sila-ylide **2**, which was isolated as pale-yellow solid (61%, mp 187 °C) (Scheme 1). Sila-ylide **2** was obtained as a mixture of two diastereomers (**2a**/**2b** = 85:15), as indicated by the presence of two sets of signals, in the same ratio, in the NMR spectra [^{31}P NMR, 70.4 and 68.0 ppm; ^{29}Si NMR, −17.7 and −13.9 ppm, $^1J_{P-Si}$ = 157 and 141 Hz]. The

Scheme 1. Synthesis of Phosphonium Sila-ylides **2a** and **2b**
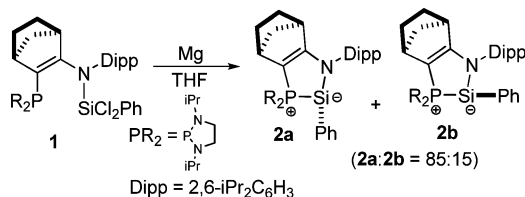
chemical shift of **2** in the ^{31}P{^{1}H} NMR spectrum is at a relatively high field compared with that of **1** (102.4 ppm). The Si−P coupling constants are much larger than that observed for the silylated phosphonium cation $(Me_3Si)_4P^+$ ($^1J_{P-Si}$ = 1.4 Hz).[13] The observation of two diastereomers (**2a** and **2b**) is consistent with a pyramidalized, chiral silicon center without inversion on the NMR time scale. Theoretical calculations predicted that **2a**, in which the phenyl group on the silicon is located on the side with less hindrance due to the asymmetric bicyclic fragment, is slightly more stable (by 2.2 kcal/mol) than **2b**.
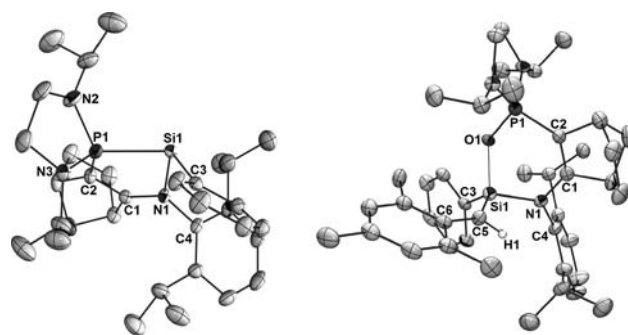

Figure 1. Molecular structures of (left) sila-ylide **2a** and (right) silene-donor adduct **5**. Thermal ellipsoids represent 30% probability, and H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg) for **2a**: P1−Si1, 2.304(5); Si1−C3, 1.906(2); P1−C2, 1.731(2); C2−C1, 1.381(3); C1−N1, 1.351(3); N1−Si1, 1.846(2); N1−C4, 1.456(2); P1−Si1−N1, 88.35(7); P1−Si1−C3, 106.23(16); N1−Si1−C3, 104.12(17); Si1−P1−C2, 92.34(8); P1−C2−C1, 114.86(16); C2−C1−N1, 124.22(19); C1−N1−Si1, 113.60(15); C4−N1−Si1, 125.02(16); C4−N1−C1, 121.38(18). For **5**: Si1−C5, 1.755(4); Si1−C3, 1.869(4); C5−C6, 1.450(5); Si1−O1, 1.729(3); P1−O1, 1.549(3); P1−C2, 1.731(2); C1−C2, 1.450(5); C1−N1, 1.351(3); C3−Si−C5, 126.32(19); N1−Si−C3, 107.09(18); N1−Si1−C3, 105.87(18); Si−C5−C6, 138.4(3).

X-ray diffraction analysis of diastereomer **2a** showed the presence of a racemic mixture of the two enantiomers in the unit cell ($P2_1/n$). The P−Si bond distances are quite long (2.304 and 2.302 Å) for a double bond (2.05−2.09 Å)[14] but comparable to that for a P−Si single bond (2.31 Å), as observed for the tetrakis(trimethylsilyl)phosphonium cation (Figure 1).[13] Moreover, the value of the sum of the bond angles about silicon ($\sum Si_\alpha$ = 298.8°) is in

agreement with a strongly pyramidalized center. However, the bond-angle sum about silicon is much larger than the computed value ($\sum Si_\alpha = 268°$) for the parent molecule H_3P-SiH_2,[15] probably for steric reasons. These structural features suggest a highly polarized P−Si ylidic bond with little or no P═Si π character, in marked contrast to the carbon congener **I**, which features a shortened P−C bond (~1.68 Å) compared with that in phosphonium salts (1.78−1.80 Å) and a nearly planar carbon center due to the P−C negative hyperconjugation.[16] Indeed, Wiberg bond orders[17] calculated for **2** (P−Si, 0.856) indicate that the P−Si bond has no noticeable double-bond character. Moreover, the relatively short C1−N1 (1.351 Å) and P1−C2 (1.731 Å) bonds and the elongated C1−C2 bond (1.381 Å) reveal good delocalization of the enamine π electrons toward the positively charged phosphonium center.

Although the phosphonium sila-ylide **2** is stable in solution as well as in the solid state at rt under inert atmosphere, it was found to be highly reactive. Indeed, the reaction of **2** with H_2O immediately led to the corresponding 2-phosphoxide enamine derivative **4** (Scheme 2). The silicon fragment [$HOSi(Ph)H_2$] could not be analyzed because of its rapid oligomerization accompanied by the release of H_2. Although we could not detect the possible intermediate **3**, the formation of the phosphine oxide, which formally arises from deprotonation of H_2O by the negatively charged silicon center followed by nucleophilic attack of the resulting hydroxyl anion on the phosphorus atom, strongly indicates the α,β-ambiphilic character (nucleophilic Si and electrophilic P) of the sila-ylide function of **2**.[18]

Scheme 2. Reactions of **2** with H_2O and Mesitylaldehyde
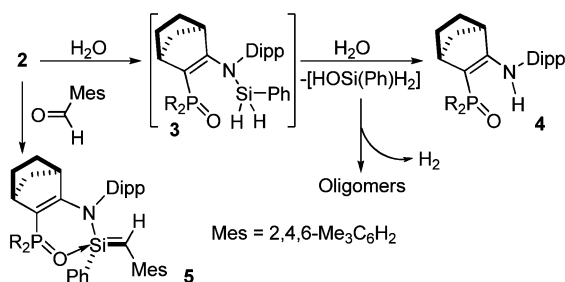
Furthermore, the α,β-ambiphilic character of **2** can also be exploited in the sila-Wittig reaction with a carbonyl derivative. The addition of 1 equiv of mesitylaldehyde to **2** in ether at rt resulted in the formation of silene derivative **5**. The spectroscopic data for the silene function (^{13}C NMR, 39.6 ppm; ^1H NMR, 2.80 ppm) show upfield shifts compared with those for other silenes,[19] indicating an interaction between the silicon center and the P═O fragment. As a consequence, the chemical shift in the ^{29}Si NMR spectrum is typical for a silene−Lewis base adduct [−18.7 ppm (d, $^2J_{SiP} = 7.0$ Hz)]. The structure of silene **5** was unambiguously confirmed by X-ray diffraction analysis and reveals the silene with a trans configuration (Figure 1). Derivative **5** appears as a Lewis base adduct in which the phosphoxide coordinates in an intramolecular fashion to the strongly Lewis acidic silicon center with a Si−O distance of 1.549 Å. This interaction induces an elongation of the Si−C bond (Si1−C5, 1.755 Å)[8,20] and a slight pyramidalization around the silicon center ($\sum Si_\alpha = 339.3°$), which are features that have been reported previously for other silene−Lewis base adducts (silene−THF, 1.747 Å and 348.7°; silene−amine, 1.751 Å and 345.5°).[21,22] In view of the strong oxygen affinity of the Si atom,[23] the lability of P−Si bonds,[15a] and the previous report on the

reactivity of transient phosphonium sila-ylides **II** with ketones,[5] the results obtained here are rather surprising and reveal a very different behavior for **2** than for other silylene−Lewis base adducts.[5,10] Although the formation of the cis isomer of **5** was not detected, the stereoselectivity of the sila-Wittig reaction remains obscure because of the presence of the silene−phosphoxide interaction, which could decrease the rotation barrier around the Si−C1 bond, potentially inducing the isomerization reaction.

A suitable kinetically and thermodynamically stabilizing system enables the synthesis of stable phosphonium sila-ylides with reactivity similar to that of classical phosphonium ylides **I**. The results shown here demonstrate that the concept of Wittig reagents can be applied to heavier silicon-centered phosphonium ylides. This might be an important first step in further extending the application range of the Wittig reaction. The detailed mechanism of the sila-Wittig reaction is under active investigation.

Supporting Information Available: Experimental details regarding the synthesis and spectroscopic data of **2**, **4**, and **5**; crystallographic data for **2a** and **5** (CIF); and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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