Chiral Cations

Easy Access to Enantiomerically Pure Heterocyclic Silicon-Chiral Phosphonium Cations and the Matched/Mismatched Case of Dihydrogen Release

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Abstract: Phosphonium ions are widely used in preparative organic synthesis and catalysis. The provision of new types of cations that contain both functional and chiral information is a major synthetic challenge and can open up new horizons in asymmetric cation-directed and Lewis acid catalysis. We discovered an efficient methodology towards new *Si*-chiral four-membered CPSSi* heterocyclic cations. Three synthetic approaches are presented. The stereochemical sequence of anchimerically assisted cation formation with $B(C_6F_5)_3$ and subsequent hydride addition was fully elucidated and proceeds with excellent preservation of the chiral information at the stereogenic silicon atom. Also the mechanism of dihydrogen release from a protonated hydrosilane was studied in detail by the help of *Si*-centered chirality as stereochemical probe. Chemoselectivity switch (dihydrogen release vs. protodesilylation) can easily be achieved through slight modifications of the solvent. A matched/mismatched case was identified and the intermolecularity of this reaction supported by spectroscopic, kinetic, deuterium-labeling experiments, and quantum chemical calculations.

In recent years, numerous inspiring examples of phosphorus-containing cations with promising applications in synthesis and catalysis have been reported.[1,2] Chiral quaternary phosphonium ions have proven to be important synthetic targets for applications in asymmetric ion-pairing catalysis.[3,4] Studies on silyl phosphonium ions have gained great interest in view of modulating structure and reactivity of frustrated Lewis pairs (FLPs).[5] Functionalized chiral cationic phosphorus compounds are interesting synthetic targets not only for a use in counter-ion-directed asymmetric catalysis; in case of an additionally present Lewis acidic center, new activation modes can open up. Due to their exceptionally strong Lewis acidity,[6] silylium ions have emerged as versatile reagents.[7,8] However, well-balanced inter- or intramolecular electronic stabilization of the electron-deficient silicon center by a Lewis base is generally required to tame such reactive species for broad synthetic utilizations.[9]

Pioneering work on applications of cationic silicon-based Lewis acids has been done by Müller, Oestreich, Ozerov, and others during the last two decades.[9–15] Silylium ions have been employed as powerful highly electrophilic Lewis acid catalysts,[9] for example, for demanding low-temperature Diels–Alder reactions,[10] hydrodefluorinations,[11] and C–C bond-forming reactions,[12] and used in frustrated Lewis pair combinations for the activation of dihydrogen,[5b,13] carbon dioxide,[5b,d,14] and carbon monoxide.[15] Neutral, frustrated silicon/phosphorus Lewis pairs with highly electrophilic silicon atoms were reported by Mitzel et al.[16] The strongly electron-withdrawing perfluorinated ethyl groups[17] in $(C_2F_5)_3SiCH_2P(tBu)_2$ led to the activation of CO_2 and SO_2 while forming a higher-coordinate silicon center.[16a] Quite recently, the same group also reported a zwitterionic four-membered heterocycle with a pentacoordinate silicon center (Figure 1 a).[16b]

Compounds with asymmetrically substituted silicon atoms have found use as stereochemical probes,[18] and many intriguing strategies for their stereoselective synthesis have been reported over the past few years.[19,20] However, the synthesis of Lewis base-stabilized silylium ions with silicon-centered chirality is challenging and the understanding of chiral memory in *Si*-stereogenic silylium ions is still in its infancy.[21] Very recently, Robert, Landais, and co-workers thoroughly investigated the chiral memory in highly strained four-membered silyl pyridini-

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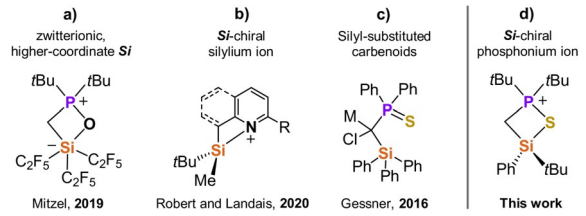
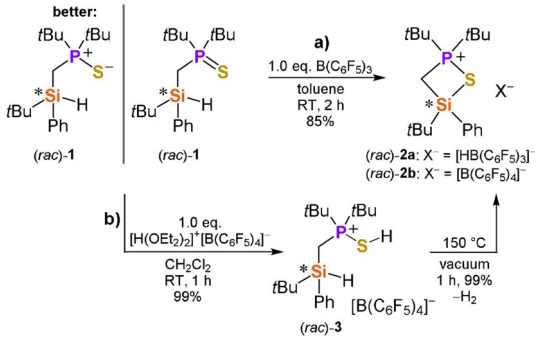


Figure 1. a) Zwitterionic heterocycle with a pentacoordinate highly Lewis acidic silicon center. b) Chiral memory studies in silyl pyridinium and quinolinium cations. c) Silyl-substituted metal carbenoids. d) *Si*-chiral heterocyclic silyl phosphonium sulfide reported herein.

um and quinolinium rings stabilized through intramolecular N–Si interaction (Figure 1 b).[21b] Silyl-substituted phosphine sulfides have recently been used for generating alkali metal carbenoids (Figure 1 c),[22] but the stereochemical implications of a P=S moiety on the stabilization of silylium ions have not yet been reported. Eventually, we got inspired by the idea to disclose a new class of small cationic heterocyclic rings having a Lewis acidic, chiral, and configurationally stable silicon atom for potential use in asymmetric cation-directed or Lewis acid-catalyzed reactions (Figure 1 d).

Herein, we report on a convenient route toward small and configurationally stable, highly enantiomerically enriched silicon-chiral phosphonium sulfide cations that have a $[P{-}S{-}Si]^+$ motif (Figure 1 d). The neighboring group participation of the P=S moiety led to complete conservation of the chiral information at the stereogenic silicon atom during *S*-silyl phosphonium cation formation/hydride addition. Furthermore, a synthetic approach toward the cationic species via dihydrogen release or protodesilylation starting from protonated intermediates was discovered. Experimental, computational, and stereochemical findings revealed a hitherto unknown intermolecular process for generating stabilized silylium ion-like species.

Sulfur-stabilized silyl cations have already proven to be relevant species in synthetically valuable reactions and the nature of this interaction has gained great interest.[11f,21c,23] However, detailed structural information on this type of interaction is still lacking. We therefore chose a phosphine sulfide-functionalized hydrosilane (**1**) as attractive starting system and performed our initial investigations with racemic compounds (Scheme 1). (*rac*)-**1** was synthesized by reaction of *t*BuPhHSiCl with $LiCH_2P(S)(tBu)_2$ (see the Supporting Information). Hydride abstraction from (*rac*)-**1**, assisted by intramolecular attack of the P=S group at the silicon atom, was achieved using $B(C_6F_5)_3$, which was Lewis acidic enough for irreversible formation of the *S*-silylated phosphonium hydroborate (*rac*)-**2 a** (Scheme 1, route **a**).[24] As an alternative, we opened up a route toward ion pair (*rac*)-**2 b** (with $[B(C_6F_5)_4]^-$ as counteranion) through Brønsted acid-promoted dehydrogenation,[25] and we were fortunate to be able to isolate and crystallize a protonated intermediate [(*rac*)-**3**] before the release of dihydrogen at 150 °C under neat conditions (Scheme 1, route **b**).



Scheme 1. Synthesis of racemic heterocyclic *S*-silyl phosphonium sulfides [(*rac*)-**2**] starting from hydrosilane (*rac*)-**1** either via hydride abstraction using $B(C_6F_5)_3$ (route **a**) or via protonation followed by liberation of dihydrogen from intermediate (*rac*)-**3** (route **b**).

Compounds (*rac*)-**1**, (*rac*)-**2 a**, and (*rac*)-**3** were characterized by single-crystal X-ray diffraction analysis (Figure 2; for details on (*rac*)-**1**, see the Supporting Information). (*rac*)-**2 a** crystallized from pentane in the space group $P\bar{1}$. The cation of (*rac*)-**2 a** forms an almost planar four-membered highly strained CPSSi heterocycle [sum of angles: 358.8(4)°] with the P–S distance of 2.0755(6) Å being elongated only by 0.11 Å compared to the same bond in the starting compound (*rac*)-**1** [1.9693(4) Å].[26] The P–S bond length of 2.0815(16) Å in the sulfur-protonated ion pair (*rac*)-**3** (space group $P2_1/c$) does not differ significantly from that in (*rac*)-**2 a**. The relative unaffected nature of the P–S bond when comparing all three compounds is also reflected by the almost identical ^{31}P NMR chemical shifts of (*rac*)-**2 a** [$\delta(^{31}P) = 89.0$ ppm] and (*rac*)-**3** [$\delta(^{31}P) = 88.6$ ppm], which are only slightly downfield-shifted with respect to (*rac*)-**1** [$\delta(^{31}P) = 76.8$ ppm].

In general, the spectroscopic data are quite the same for the cations in both compounds (*rac*)-**2 a**/**b**, thus indicating that the $[HB(C_6F_5)_3]^-$ counterion in (*rac*)-**2 a** is not being coordinated via an Si···H···B interaction in solution.[27] An interaction with the solvent CD_2Cl_2 can also be safely excluded.[10b] ^{29}Si NMR spectroscopy of compounds (*rac*)-**2 a** and **b** in CD_2Cl_2 shows a signal at $\delta = 13.7$ and 13.6 ppm, respectively. We were indeed surprised about this relatively small downfield-shift with respect to (*rac*)-**1** [$\delta(^{29}Si) = -2.0$ ppm]. Since the ^{29}Si NMR chemical shift turned out to be a powerful diagnostic tool for estimating the Lewis acidity of silicon centers,[10b] we came to the conclusion that the P=S moiety enables a significant electronic stabilization of the cationic silicon center resulting in a strong S–Si interaction and a high level of rigidity. This agrees well with a strong electrovalent nature of the P=S bond in (*rac*)-**1** and should therefore be better formulated as a zwitterionic $P^+{-}S^-$ bond with hyperconjugative multiple bond character (Scheme 1).[28] This is in line with the natural bond orbital (NBO) analysis of compound **1** and the cations of compounds **2** and **3**, performed on the M062X/6–31+G(d) level of theory (for details on the NBO calculations, see the Supporting Information).

The next step was to examine this type of $[P{-}S{-}Si]^+$ interaction within the strained CPSSi* heterocyclic cation more closely with regard to its stereochemical behavior. For this purpose we first had to provide highly enantiomerically enriched hydrosilanes (Scheme 2). (*rac*)-**1** was converted to diastereomers

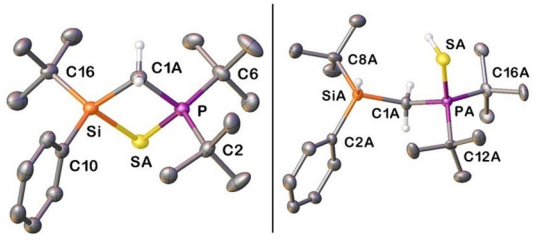
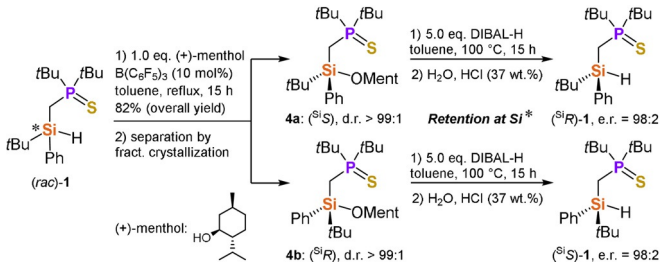


Figure 2. Molecular structures of (*rac*)-**2 a** (left) and (*rac*)-**3** (right) in the crystal (displacement ellipsoids set at the 50% probability level, counteranions and hydrogen atoms, except for the CH_2 and SH groups are omitted for clarity).

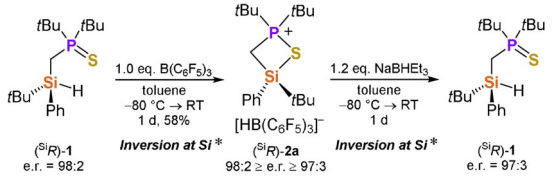


Scheme 2. Synthesis of highly enantiomerically enriched hydrosilanes (^{Si}R)-**1** and (^{Si}S)-**1** via catalytic dehydrogenative Si–O coupling of (*rac*)-**1** and (+)-menthol, separation of diastereomers **4a,b** by fractional crystallization, followed by stereospecific Si–O cleavage using DIBAL-H.

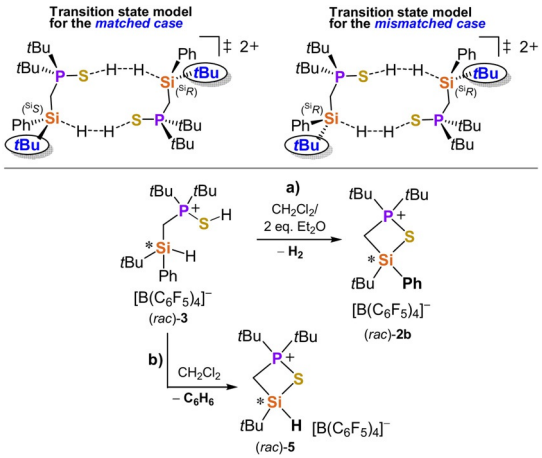
4a,b by Lewis acid-catalyzed dehydrogenative Si–O coupling with (+)-menthol, followed by fractional crystallization of the two diastereomers, each of them being isolated in diastereomerically pure form. The absolute configurations of menthoxysilanes **4a** (^{Si}S) and **4b** (^{Si}R) were determined by single-crystal X-ray diffraction analysis. Reaction of **4a,b** with DIBAL-H resulted in stereospecific Si–O cleavage with retention at the silicon atom.[29] Hydrosilanes (^{Si}R)-**1** and (^{Si}S)-**1**, respectively, were obtained in excellent enantiomeric ratios of e.r. = 98:2 in each case, measured by chiral HPLC. Recrystallization of (^{Si}R)-**1** (e.r. = 98:2) gave optically pure single-crystals (e.r. > 99:1), suitable for X-ray diffraction analysis and determination of the absolute configuration at the silicon stereocenter (for details concerning X-ray crystallography, see the Supporting Information).

In order to further investigate the applicability of this new type of cation as a potential chiral auxiliary, information on the configurational stability of the silicon atom is essential. Hydrosilane (^{Si}R)-**1** (e.r. = 98:2) was used to elucidate the stereochemical course and chiral memory during the sequence of cation formation and subsequent hydride addition (Scheme 3). Reaction of (^{Si}R)-**1** with $B(C_6F_5)_3$ in toluene at −80 °C immediately led to phase separation indicating the formation of *S*-silyl phosphonium hydroborate **2a**. It is important to note that the ion pair formed was stirred for one day at room temperature prior to isolation. **2a** was then converted back into the hydrosilane **1** with $NaBHEt_3$, for which an enantiomeric ratio of e.r. = 97:3 was determined by chiral HPLC. An overall retention of configuration at silicon was identified over two steps. Since it is obvious that the hydride abstraction takes place with the anchimeric assistance[30] of the P=S moiety, we can with great certainty assume a stereochemical course with double inversion[18d,21b] at the silicon center passing through a silyl phosphonium cation with ^{Si}R-configuration. The overall process [(^{Si}R)-**1**→(^{Si}R)-**2a**→(^{Si}R)-**1**] thus proceeds with excellent preservation of the stereochemical identity. The isolable *S*-silyl phosphonium hydroborate (^{Si}R)-**2a** shows exceptional configurational stability, which, in comparison to the silyl pyridinium and quinolinium systems,[21b] remains unaffected even for one day at room temperature. This further supports a strong [P–S–Si]$^+$ interaction, which prevents ring opening and racemization of the *Si*-stereogenic center very efficiently.

These results prompted us to take a closer look at route **b** of Scheme 1 from a mechanistic point of view by using the chiral information on silicon as stereochemical probe. When we performed the dehydrogenation reaction at 150 °C starting from neat (^{Si}R)-**3** (e.r. = 98:2), a complete loss of configurational identity at the stereogenic silicon center occurred (see the Supporting Information). Instead, what caught our particular interest was the fact that a diethyl ether-containing solution of the racemic phosphonium borate (*rac*)-**3** in CD_2Cl_2 was slowly converted to (*rac*)-**2b** with liberation of dihydrogen even at room temperature, which was unambiguously proven by the characteristic ^{1}H NMR signals of the heterocyclic cation and H_2 (δ = 4.61 ppm). Interestingly, when using highly enantiomerically enriched (^{Si}R)-**3** (e.r. = 98:2), no reaction was observed even after four days.[31] NMR monitoring of the reaction progress of previously isolated (*rac*)-**3** and highly enantiomerically enriched (^{Si}R)-**3** (e.r. = 98:2), followed by a thorough kinetic analysis, showed a decrease of the reaction rate of dihydrogen release by 65% when using (^{Si}R)-**3** instead of (*rac*)-**3**. Based on these results, we proposed an intermolecular mechanism in which two cations of **3** must be involved for the release of dihydrogen, which in the case of chiral molecules would inevitably lead to matched or mismatched transition state combinations (Scheme 4, top). The intermolecularity is also supported by the fact that the rate of the reaction from (*rac*)-**3** to (*rac*)-**2b** was slowed down by 80% when the initial concentration of (*rac*)-**3** was decreased from 0.2 M to 0.1 M. A deuterium labeling experiment gave additional support of the intermolecularity of the reaction (see the Supporting Information).



Scheme 3. Elucidation of chiral memory in the stereochemical process of anchimerically assisted cation formation [(^{Si}R)-**1**→(^{Si}R)-**2a**] and subsequent hydride addition [(^{Si}R)-**2a**→(^{Si}R)-**1**].



Scheme 4. Transition state models for the matched/mismatched case of intermolecular dehydrogenation (top). Chemoselectivity switch (dihydrogen release, path **a**; protodesilylation, path **b**) by changing the solvent (bottom).

DFT calculations [M062X/6-31 + G(d)] on intermolecularly stabilized, eight-membered intermediates after hydrogen elimination gave a simplified but plausible estimate ($\Delta H = +28\ kJ\,mol^{-1}$) of the energy difference between a centrosymmetric (matched) and an asymmetric (mismatched) case, which should also be reflected in the energy of the transition state combinations (see the Supporting Information). During our mechanistic studies on compound **3**, a second reaction pathway was observed that could be useful for alternative synthetic approaches to generate functionalized silylium ions (Scheme 4, bottom). In the absence of diethyl ether, a switch from dihydrogen release to protodesilylation was identified leading chemoselectively to the hydrosilyl phosphonium borate **5**, which is an interesting species for future reactivity studies. In a similar kinetic study, a matched/mismatched case could also be proven for the protodesilylation (lowering of the reaction rate by 90% when using (^{Si}R)-**3** instead of (*rac*)-**3**) (for details, see the Supporting Information).

In conclusion, our findings shed light on fundamental questions regarding the configurational stability of chiral, Lewis acidic silicon centers in silyl phosphonium sulfide cations. Dehydrogenative cation formation from a protonated intermediate was achieved and an intermolecular mechanism with two molecules involved was unambiguously identified by combining various experimental, stereochemical, and quantum chemical methods. Chemoselectivity switch between dihydrogen release and protodesilylation was shown. The *Si*-chiral heterocyclic silyl phosphonium sulfides described herein represent a new class of chiral, functionalized cations that might enable future use in asymmetric synthesis and catalysis. Modulating the Lewis acidity of the *Si*-stereogenic center by varying the strength of the P–S–Si interaction and increasing the degree of functionality by changing the substituents are just two of the adjusting screws that are being addressed in our ongoing studies. A major advantage of our cation type is the ability to easily functionalize the phosphoryl group over a wide range and also to incorporate phosphorus-centered chirality[32] in the molecular design.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: chemoselectivity · chiral memory · Lewis acids · phosphonium cations · silylium ions

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