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Norbornene Based-Sulfide-Stabilized Silylium Ions: Synthesis, Structure and Application in Catalysis

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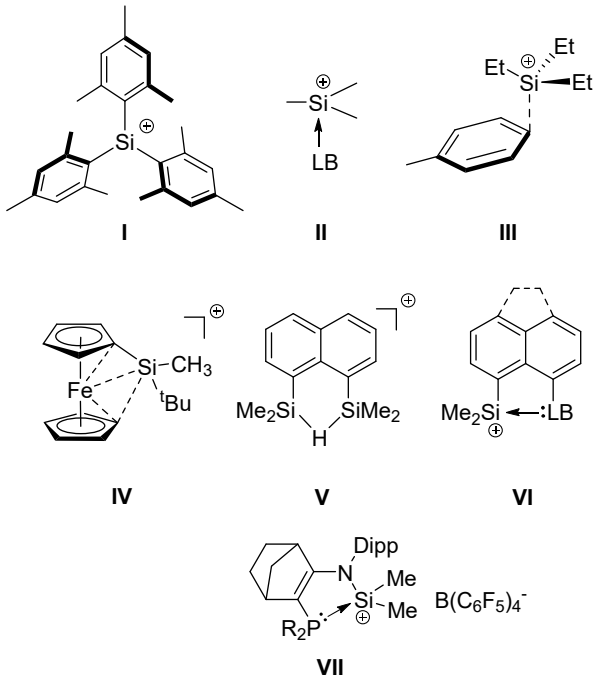
A norbornene-based sulfide stabilized silylium ion **4** has been synthesized. The S-Si interaction was studied in solution and in the solid state by NMR spectroscopy and X-ray diffraction analysis as well as DFT calculations. Unlike the previously reported phosphine-stabilized silylium ion **VII**, behaving as a Lewis pair, calculations predict that **4** should behave as a Lewis acid toward acrylate derivatives. Indeed, the base-stabilized silylium ion **4** has emerged as an easy-to-handle silylium ion-based Lewis acid catalyst, particularly for the Diels-Alder cycloaddition, with poorly reactive dienes, and hydrodefluorination reactions.

Introduction

Since the report of the first stable free silylium ion **I** by Reed and Lambert,[1] the chemistry of silylium ions has received considerable attention as useful and new synthetic tools (Figure 1).[2] Their exceptionally high Lewis acid character and extreme reactivity are highly sought-after criteria, but at the same time this has been a huge obstacle to their development due to the obvious difficulty of handling them. Of special interest, the formation of complexes with a donor ligand on the cationic silicon atom (**II**) has proven to be an excellent stabilization strategy[3] to make these species easier to handle and useful synthetic tools (Figure 1).[4] Strong silicon-based Lewis acids are efficient catalysts for Diels-Alder reactions.[5] Indeed, Sawamura et al. successfully shown that the triethylsilylium ion-toluene complex **III** is able to catalyze the cycloaddition between the poorly reactive cyclohexadiene and various dienophiles in good yields.[6] Oestreich also demonstrated the importance of stabilization by intermolecular coordination of weak Lewis bases for their catalytic activity with the ferrocenium-stabilized silylium ion **IV**,[7] showing not only the significantly improved reaction rates but also the broadened scope of reactions probably due to its increased persistence.[8] This model also provided the first hints of an asymmetric version of silylium ion catalysts.[9] Base-stabilized silylium ions are also able to effectively catalyze the hydrodefluorination reaction.[10] Silylium ions **V**[10b] and **VI**[10j] together with Ozerov's silylium-carborane systems[10c] are among the most efficient catalysts for C-F activation.[11] Obviously, the stability/reactivity balance of these species is strongly related to the choice of Lewis base ligand, and this is a crucial factor for their catalytic activity.



I II III IV V VI VII

Figure 1. Free silylium ion **I** and Lewis base-stabilized silylium ions **II-VII**.

We recently reported the synthesis of phosphine-stabilized silylium ions **VII** with a particular norbornene-based framework that links the silylium ion and the phosphine ligand (Figure 1).[12] Interestingly, due to the flexibility of the ligand framework and its strong nucleophilic character, phosphine-stabilized silylium

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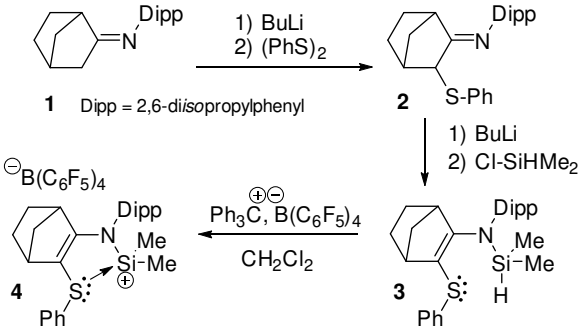
ions **VII** behave as a Lewis pair instead of a simple Lewis acid and undergo ambiphilic type reactions with an aldehyde or methyl acrylate leading to seven- to nine-membered heterocycles. However, these species **VII** do not behave as silylium ion Lewis acid catalysts. In order to improve the Lewis acid character, and to prevent the Lewis pair reactions, we have considered the replacement of the phosphine moiety by a less nucleophilic sulfide ligand.[13] Here we report the synthesis of sulfide-stabilized silylium ion **4**, which is an easy-to-handle and efficient catalyst for Diels-Alder and hydrodefluorination reactions.

Results and discussion

Using a similar synthetic strategy to that of phosphine-stabilized silylium ions **VII**,[12] the iminosulfide **2** was prepared by the reaction of lithiated imine with diphenyldisulfide. Subsequent lithiation of **2** and treatment with chlorodimethylsilane afforded the hydrosilane derivative **3**. Contrary to the silylium ion **VII**, prepared by halide abstraction following Kira and Sakurai's methodology,[14] silylium ion **4** was obtained *via* the classical Joyce Corey reaction, ie hydride abstraction from hydrogenosilane **3**, using trityl tetrakis(pentafluorophenyl)-borate,[15] and was isolated as an air-sensitive pale-brown solid in 78% yield (Scheme 1). The base-stabilized silylium ion **4** is stable in CH_2Cl_2 at room temperature, demonstrating its tamed reactivity.



Scheme 1. Synthesis of sulfide-stabilized silylium ion **4.**

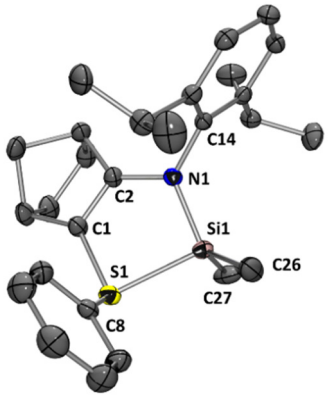


Figure 2. Molecular structure of cationic part of sulfonium borate **4**. Thermal ellipsoids represent 30% probability. H atoms and counterion $[B(C_6F_5)_4]^-$ were omitted for clarity. Selected bond lengths [Å] and angles [°]: N1−Si1 1.737(2), Si1−S1 2.280(1), S1−C1 1.753(3), C1−C2 1.357(4), C2−N1 1.387(4), N1−C14 1.451(3), S1−C8 1.803(3), Si1−C27 1.823(3), Si1−C26 1.826(4); N1−Si1−S1 94.0(1), Si1−S1−C1 89.1(1), S1−C1−C2 118.0(2), C1−C2−N1 123.0(3), C2−N1−Si1 112.4(2), C8−S1−Si1 106.1(1), C8−S1−C1 106.7(1), N1−Si1−C27 116.1(2), N1−Si1−C26 113.2(1), C27−Si1−C26 117.7(2), C2−N1−C14 121.4(2), C14−N1−Si1 125.7(2).

Sulfide-stabilized silylium ion **4** was fully characterized by NMR spectroscopy. In the ^{29}Si NMR spectrum, a characteristic signal is observed at δ = 54.3 ppm, reminiscent of other sulfide-stabilized silylium ions (42-70 ppm).[3h,10j] In the ^{1}H-NMR spectrum, the Si-methyl groups are non-equivalent and appear as two singlet signals at δ = 0.45 and 0.98 ppm, suggesting a hindered free rotation of silylium ion moiety due to the coordination to the sulfide ligand. Only one set of signals observed in all NMR spectra indicates that the silylium ion **4** exists as a single diastereomer.

The structure of **4** was determined by X-Ray diffraction analysis (Figure 2), which confirms the interaction between sulfur and silicon atoms. The S1-Si1 bond length [2.280(1) Å] is in the same range as those observed by Schulz (2.24-2.31 Å),[16] suggesting a relatively weak coordination of the sulfide ligand on the silicon atom. The weak S→Si electron donation was also suggested by the less pyramidalized silicon center ($\Sigma°_{Si}$ = 347.0°) than that observed in the corresponding phosphine-stabilized **VII** ($\Sigma°_{Si}$ = 334.3°).[12]

The electronic interaction between the sulfur and silicon atoms in cation **4'** (**4** without counter-anion) was studied by density functional calculations at the M06-2X/def-2tzvp level of theory. This level of theory is justified as the computed molecular structure parameters for the stabilized silylium ion **4'** are very close to the experimental values, i.e. the mean unsigned deviation of the computed bond lengths (Table S2 in the supplementary information) is only 1%. The coordination environment around the silicon atom is as expected for a sulfide-stabilized amino-substituted silylium ion. In detail, the silicon atom adopts a 3+1 coordination with the sulfide group as the additional fourth substituent. The sum of the bond angles around the silicon atom involving the amino substituent and the two methyl groups, $\sum\alpha(SiNC_2)$, is 342.2°, significantly smaller than the 360° expected for ideal trigonal planar coordination. The N–Si–S angle is almost 94°, which places the sulfide group in perfect orientation for electron donation to the silicon center. The Si–N bond in cation **4'** is typical for bonds between tetracoordinate silicon and tricoordinate nitrogen (**4'** 1.740 Å vs. the average value of 1.739 Å[17] and the coordination environment of the nitrogen atom is essentially trigonal planar ($\sum\alpha$(N) = 359.6°). As already pointed out, the Si-S bond is longer in **4'** (2.290 Å) than the Si-S covalent single bond calculated for (trimethylsilyl)phenylsulfide **5** (2.160 Å) and reaches almost the lengths of the Si-S bond in (trimethylsilyl)-diphenylsulfonium **6** (2.293 Å) (Figure 3).

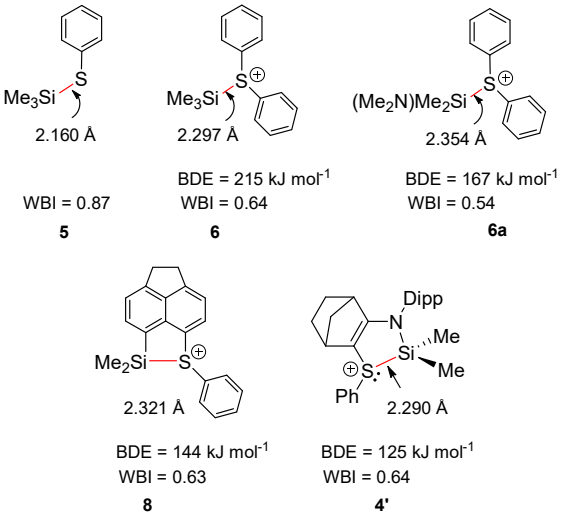
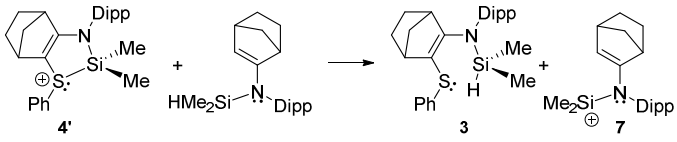


Figure 3. Comparison of the calculated parameters of Si–S bonds in cation **4'** (**4** without counter-anion) and related species (BDE: bond dissociation energy, WBI: Wiberg bond index; calculated at M062X/def2-tzvp).[10j]

The bond dissociation energy (BDE) for the newly formed Si–S bond is estimated using the hydride transfer reaction shown in Scheme 2. It compares the stability of silylcation **4'** with that of amino-substituted silylium ion **7**. This BDE is 125 kJ mol^{-1}, which is lower than that of the cyclic sulfide-stabilized silylium ion **8** (by 19 kJ mol^{-1}). This is due to the electron donating amino-substituent at the silicon atom. In general, an amino-substituent lowers the additional stabilization that a silylium ion gains through the extra coordination of diphenylsulfide. In the case of the two acyclic cations **6** and **6a**, the decrease is 48 kJ mol^{-1}. The additional ring strain in cation **4** lowers this value further (by 42 kJ mol^{-1}, compare BDEs of the acyclic **6a** and the cyclic cation **4**). In the case of the more rigid acenaphthyl-based cation **8**, the lowering of the sulfide-stabilization energy by ring strain is even larger (by 71 kJ mol^{-1}, compare BDEs of cation **6** with cation **8**).[10j]



Scheme 2. Hydride transfer reaction that is used to estimate the bond dissociation energy of the Si-S bond in silyl cation **4'**.

A natural bond order (NBO) analysis for cation **4'** reveals a predominant p-character for the σ-Si–S bond (84% p contribution for both atoms). The bond is strongly polarized to the sulfur atom (77% S contribution and 23% Si). The degree of covalency of this bond, as calculated by the Wiberg bond index (WBI), is high (0.64). It is 74% of that predicted for the neutral silylsulfide **5** (0.87) and it is identical to WBI values of related silylsulfonium ions such as **6** and **8** (Figure 3). The results of the NBO analysis classify the Si–S bond as a polar covalent bond, typical for silylsulfonium ions such as **6** and **8**.[10j] The strongly stabilizing amine substituent in cation **4'** weakens the S/Si interaction and as a result the Si–S bond is the weakest in the series of silylsulfonium ions that are shown in Figure 3.

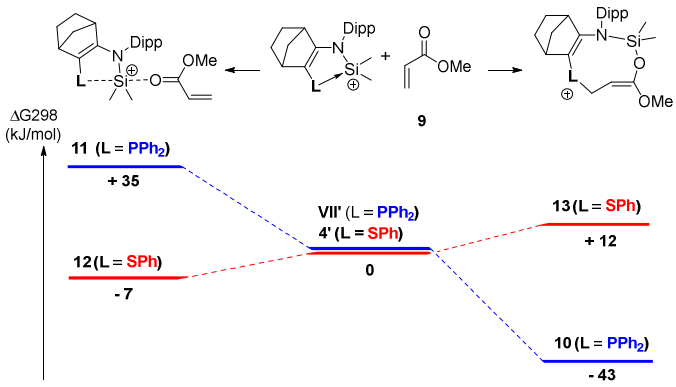
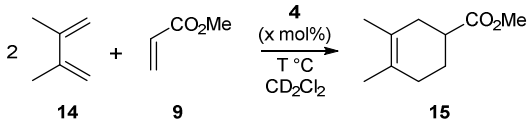


Figure 4. Relative Gibbs free energies (at 298.15 K) computed for the activation of methyl acrylate **9** and insertion leading the formation of 9-membered-heterocycles **10** and **13** using the M06-2X/def-2tzvp level.

In contrast to the phosphine-stabilized silylium ion **VII'** (**VII** without counter-anion), which reacts at room temperature with methyl acrylate **9** to give a 9-membered heterocycle **10** (Figure 4), calculations predict that such an insertion is an unfavorable process for **4'**.[18] Indeed, consistent with the experimental finding,[12] we found that this insertion reaction is thermodynamically favorable for the phosphine-stabilized one **VII'** (ΔG^{298} = -43 kJ mol^{-1}). In contrast, it is endergonic in the case of the silylsulfonium ion **4'** (ΔG^{298} = +12 kJ mol^{-1}, Figure 4). Furthermore, the calculations also predict that, while the formation of donor-acceptor complex **11** by the carbonyl coordination to the silicon center of **VII'** is thermodynamically disfavored (ΔG^{298} = +35 kJ mol^{-1}, Figure 4), the formation of such a complex **12** is a favored process for **4'** (ΔG^{298} = -7 kJ mol^{-1}, Figure 4). This suggests that the sulfide-stabilized silylium ion **4'** preferentially behaves as a simple Lewis acid toward methyl acrylate rather than as a Lewis pair contrary to the case of phosphine-stabilized one **VII'**. Therefore, the silylated sulfonium ion **4'** might be a good candidate to catalyze the Diels-Alder reaction with the activated methyl acrylate.

In agreement with theoretical calculations, the addition of methyl acrylate to **4** did not afford the insertion reaction leading to heterocycle **13**, instead, the polymerization of methyl acrylate was observed.[18] Therefore, we have then tested the catalytic activity of **4** for the Diels-Alder reaction between 2,3-dimethylbuta-1,3-diene **14** and methyl acrylate **9** (Table 1). This type of cycloaddition was already chosen by several research groups as a model allowing a direct comparison with the previously reported systems.[5,6]

Table 1. Diels-Alder reaction between 2,3-dimethylbuta-1,3-diene **14** and methyl acrylate **9** catalyzed by **4**.



14 **9** **15**

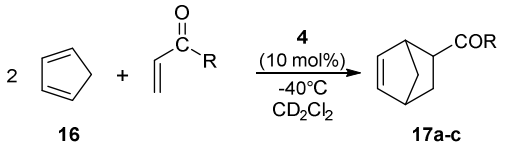
Entry[a]	x mol%	Temp. (°C)	Time (h)	Conv. (%)[b]
1	10	25	0.2	75
2	10	-40	1	> 95
3[c]	10	-40	1	> 95
4	5	-40	1	> 95
5	1	-40	1	55
6	1	-40	3	58
7	10	-80	1	80
8	10	-80	2	85

[a] Reactions were carried out by using 0.09 mmol of methylacrylate **9**, 2,3-dimethylbuta-1,3-diene (2.0 equiv) and 10 mol% of **4** otherwise noted in 0.3 mL of CD_2Cl_2. Reactions were quenched by adding a saturated aqueous solution of $NaHCO_3$. [b] Conversions were determined by ^1H NMR analysis of the crude (following OMe groups from methyl acrylate and cycloadduct). [c] 2,6-di-tert-butylpyridine (25 mol%) was added.

In presence of 10 mol% of catalyst **4** at room temperature, a conversion of 75% is observed in about 10 min leading to the selective formation of cycloadduct **15** (Table 1, Entry 1). The conversion did not evolve further after a longer reaction time, probably due to catalyst degradation. This result is in the range of that obtained by Sawamura and al., using triethylsilylium borate as catalyst (91% conv. at rt with 1 mol% of catalyst in 13 h).[6] By decreasing reaction temperature to –40 °C, complete conversion was achieved in 1 h (Table 1, Entry 2). The possibility of a proton-promoted reaction was ruled out since the same result was obtained in presence of a proton scavenger such as 2,6-di-tert-butylpyridine (25 mol%) (Table 1, Entry 3). The catalyst loading can be reduced to 5 mol% without noticeable change (Table 1, Entry 4). However, with 1 mol% of catalyst, the conversion drops to about 55% after 1 h (Table 1, Entry 5, 58% in 2 h, entry 6). Finally, the reaction can also be performed at –80 °C leading to a conversion of 80-85% (Table 1, Entries 7-8). Extending the scope of the reaction using substituted methyl acrylate (*i.e.* methyl 3-phenylprop-2-enoate or methyl but-2-enoate) did not lead to the formation of the expected cycloadducts. Indeed, similarly to phosphine-stabilized silylium ion **VII**, in those cases, an 1,2-insertion of the carbonyl group into the Si-S bond occurs, preventing the catalytic transformation (see supplementary information). It should be noted that the Diels-Alder cycloaddition was not observed when α,β-unsaturated ketones or aldehydes (*i.e.* but-3-en-2-one or propenal) were used as dienophiles.

Not surprisingly, the Diels-Alder cycloaddition between cyclopentadiene **16** and methyl acrylate **9** can smoothly be performed at –40 °C (Table 2, Entry 1). The desired cycloadduct **17a** was obtained in almost quantitative yield, and in a selective manner. Interestingly, those mild reaction conditions also allow to enlarge the scope of the reaction. Indeed, α,β-unsaturated ketones or aldehydes can also be applied with moderate to good yields (Table 2, Entries 2-3).

Table 2. Diels-Alder reaction between cyclopentadiene **16** and α,β-unsaturated ketones catalyzed by **4**.

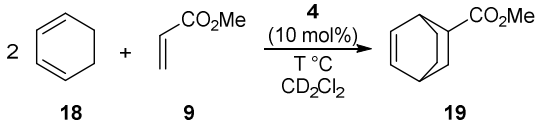


16 **17a-c**

Entry[a]	R	Time (h)	Conv. (%)[b]
1	OMe	1	80
2	Me	1	55
3	H	1	77

[a] Reactions were carried out by using 0.09 mmol of α,β-unsaturated carbonyl, cyclopenta-1,3-diene (2.0 equiv), and 10 mol% of **4** in 0.6 mL of CD_2Cl_2. Reactions are quenched by adding a saturated aqueous solution of $NaHCO_3$. [b] Conversions were determined by ^1H NMR analysis using 1,2-dichloroethane as internal standard.

Table 3. Diels-Alder reaction between cyclohexadiene **18** and methyl acrylate **9** catalyzed by **4**.



18 **9** **19**

Entry[a]	Temp. (°C)	Time (h)	Conv. (%)[b]	**19** / polymer[c]	Yield of **19** (%)[f]
1	25	0.2	75	60/40	45
2	0	1	84	50/50	42
3	-40	1	> 95	42/58	40
4[d]	-40	1	> 95	50/50	48
5[e]	25	0.5	33	100/0	33
6[e]	0	1	46	90/10	41
7[e]	-40	1	89	60/40	52

[a] Reactions were carried out by using 0.09 mmol of methylacrylate **9**, cyclohexa-1,3-diene (2.0 equiv) and 10 mol% of **4** in 0.3 mL of CD_2Cl_2. Reactions were quenched by adding a saturated aqueous solution of $NaHCO_3$. [b] Conversions were determined by ^1H NMR analysis of the crude (following OMe groups from methyl acrylate and cycloadduct). [c] Ratio determined by NMR analysis. [d] 5 eq. of diene were used. [e] Diluted solution of methylacrylate in CD_2Cl_2 (1 mL) was added slowly. [f] Calculated using the data of conversion and ratio (**19**/polymer).

We have then investigated the reaction with less reactive 1,3-cyclohexadiene **18** (Table 3). At room temperature, the conversion attained to approximately 75% in about 10 min to give the corresponding cycloadduct **19**, demonstrating the high catalytic activity of **4** (Table 3, Entry 1). However, unlike the case of 2,3-dimethylbutadiene **14**, a competitive polymerization of methyl acrylate was observed, leading to a 60/40 mixture of cycloadduct **19** and polymethacrylate, respectively. To improve the conversion, the reaction was carried out at lower temperatures (0 and –40 °C), in order to prevent the degradation of the catalyst. Unfortunately, these conditions also favor polymer formation at the expense of the desired cycloadduct (Table 3, Entries 2 and 3). The use of an excess of

diene (5 equiv) lead only to a slightly better selectivity (Table 3, Entry 4). To limit the polymerization process, diluted conditions were then applied (Table 3, Entries 5-7). Indeed, at RT, diluted conditions allowed the completely selective formation of cycloadduct **19** in 30 min, but in this case the conversion only gets 33% (Table 3, Entry 2). Again, like with the initial reaction conditions, lowering the temperature lead to an improvement of the conversion, but lower cycloadduct selectivity (Table 3, Entries 6,7).

It was found that the silylium **4** (10 mol%) also catalyze the reduction of α,α,α,-trifluorotoluene **20** using triethylsilane as the reducing agent. The reaction is rather slow compared to previously reported systems,[10] since only a yield of 68% was obtained after 21 days (Figure 5). The process can be accelerated by performing the reaction at 60 °C (48% after 2 days), however these reaction conditions lead to catalyst degradation and therefore an uncompleted transformation. Similar results were observed with fluoroheptane at room temperature (30% conv. in 3 days with 10 mol% of **4**).

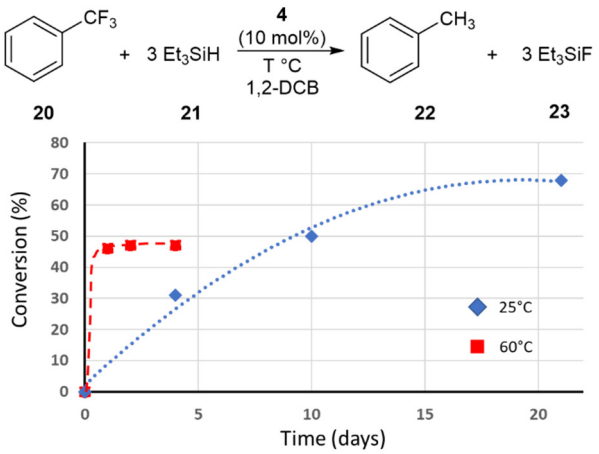


Figure 5. Hydrodefluorination of trifluorotoluene **20** with triethylsilane catalyzed by **4**.

Experimental

General Procedures. All manipulations were performed under an inert atmosphere of argon by using standard Schlenk techniques or high-pressure NMR tube techniques. Dry and oxygen-free solvents were used. ^{1}H, ^{11}B, ^{13}C, ^{19}F and ^{29}Si NMR spectra were recorded on Brucker Avance II 300 MHz, Avance III HD 400 MHz and Avance I and II 500 MHz spectrometers. Chemical shifts are expressed in parts per million with residual solvent signals as internal reference (^{1}H, ^{29}Si and $^{13}C\{^{1}H\}$). ^{19}F chemical shifts were reported in ppm relative to $CFCl_3$. The following abbreviations and their combinations are used: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. ^{1}H and ^{13}C resonance signals were attributed by means of 2D COSY, HSQC and HMBC experiments. All commercially available reagents were used after drying and/or distillation in proper conditions.

Synthesis of 2: To a solution of imine **1**[19] (2.04 g, 7.6 mmol) in THF (25 mL) was added dropwise at –80 °C a solution of *n*-butyllithium 1.6 M in hexane (4.75 mL, 7.6 mmol) and stirred for 1 h. The crude was warmed at room temperature and stirred for 1h, then cooled at –80 °C and diphenyldisulfide (1.65 g, 7.6 mmol) was added dropwise. The resulting solution was warmed to room temperature then stirred for 1h. The solvent was removed under vacuum. The product was extracted with pentane (3 x 25 mL). The solvent was removed under vacuum then crude was washed twice by acetonitrile to give iminosulfide **2** as a white powder (2.30 g, 80% yield). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.61-7.52 (m, 2H, *o/m* of C*H*$_{Ph}$), 7.43-7.32 (m, 2H, *o/m* of C*H*$_{Ph}$), 7.32-7.22 (m, 1H, *p* of C*H*$_{Ph}$), 7.21-7.04 (m, 3H, C*H*$_{dipp}$), 4.00 (d, $^{3}J_{HH}$ = 3.0 Hz, 1H, C*H*-S), 2.98 (sept, $^{3}J_{HH}$ = 6.8 Hz, 1H, C*H*$_{iPr}$), 2.92 (sept, 1H, $^{3}J_{HH}$ = 6.9 Hz, C*H*$_{iPr}$), 2.63 (m, 1H, C*H*$_{bridgehead}$), 2.55 (m, 1H, C*H*$_{bridgehead}$), 2.22-2.11 (m, 1H, C*H*$_2$), 1.99-1.72 (m, 1H, C*H*$_2$), 1.72-1.38 (m, 4H, C*H*$_2$), 1.33 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, C*H*$_{3iPr}$), 1.31 (d, $^{3}J_{HH}$ = 6.9 Hz, 3H, C*H*$_{3iPr}$), 1.24 (d, $^{3}J_{HH}$ = 6.7 Hz, 3H, C*H*$_{3iPr}$), 1.22 (d, $^{3}J_{HH}$ = 6.7 Hz, 3H, C*H*$_{3iPr}$). ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 178.5 (s, N-*C*), 146.8 (s, N-*C*$_{dipp}$), 136.8 (s, *C*$_{Dipp}$), 136.6 (s, *C*$_{Ph}$), 136.5 (s, *C*$_{dipp}$), 130.9 (s, *o/m* of *C*H$_{Ph}$), 129.4 (s, *o/m* of *C*H$_{Ph}$), 126.9 (s, *p* of *C*H$_{Ph}$), 124.0 (s, *C*H$_{dipp}$), 123.3 (s, *C*H$_{dipp}$), 123.2 (s, *C*H$_{dipp}$), 56.1 (s, *C*H-S), 42.7 (s, *C*H$_{bridgehead}$), 42.0 (s, *C*H$_{bridgehead}$), 36.1 (s, *C*H$_2$), 28.4 (s, *C*H$_{iPr}$), 28.3 (s, *C*H$_{iPr}$), 27.8 (s, *C*H$_2$), 24.9 (s, *C*H$_2$), 24.5 (s, *C*H$_{3iPr}$), 24.0 (s, *C*H$_{3iPr}$), 22.9 (s, *C*H$_{3iPr}$), 22.9 (s, *C*H$_{3iPr}$). M.p.= 79.4 °C.

Synthesis of 3: To a solution of iminosulfide **2** (2.10 g, 5.57 mmol) in THF (25 mL) was added dropwise at –80 °C a solution of *n*-butyllithium 1.6 M in hexane (3.48 mL, 5.57 mmol) and stirred for 1 h. The reaction mixture was warmed up to room temperature and stirred for 1h, then cooled again at –80 °C and freshly distillated chlorodimethylsilane (0.62 mL, 5.57 mmol) was added dropwise. The resulting solution was warmed up to room temperature and stirred for 1h, then the solvent removed under vacuum. Product **3** was extracted with pentane, then the solvent was removed under vacuum. The crude was finally washed by acetonitrile to afford **3** as a white powder (1.62 g, 67% yield). ^{1}H NMR (300 MHz, C_6D_6): δ = 7.35-7.25 (m, 2H, C*H*$_{Ar}$), 7.22-7.12 (m, 1H, C*H*$_{Ar}$), 7.12-7.00 (m, 4H, C*H*$_{Ar}$), 6.95-6.85 (m, 1H, C*H*$_{Ar}$), 4.83 (pseudo sept, $^{3}J_{HH}$ = 3.3 Hz, 1H, Si*H*), 3.38 (sept, $^{3}J_{HH}$ = 6.7 Hz, 1H, C*H*$_{iPr}$), 3.34 (sept, 1H, $^{3}J_{HH}$ = 6.8 Hz, C*H*$_{iPr}$),, 2.88 (s large, 1H, C*H*$_{bridgehead}$), 2.81 (s, 1H, C*H*$_{bridgehead}$), 1.66-1.52 (m, 2H, overlapped C*H*$_2$), 1.52-1.40 (m, 3H, overlapped C*H*$_2$), 1.33 (d, $^{3}J_{HH}$ = 6.9 Hz, 3H, C*H*$_{3iPr}$), 1.25 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, C*H*$_{3iPr}$), 1.19 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, C*H*$_{3iPr}$), 1.15 (d, $^{3}J_{HH}$ = 6.9 Hz, 3H, C*H*$_{3iPr}$), 0.91-0.81 (m, 1H, C*H*$_2$), 0.41 (d, $^{3}J_{HH}$ = 3.1 Hz, Si-*C*H$_3$), 0.26 (d, $^{3}J_{HH}$ = 3.3 Hz, Si-*C*H$_3$). ^{13}C NMR (75 MHz, C_6D_6): δ = 148.0 (s, N-*C*), 140.6 (s, *C*$_{dipp}$), 139.9 (s, *C*$_{dipp}$), 128.9 (s, S-*C*H$_{Ph}$), 127.7 (s, S-*C*$_{Ph}$), 127.2 (s, *C*H$_{Ph}$), 124.8 (s, *C*H$_{Ph}$), 124.4 (s, *C*H$_{dipp}$), 124.3 (s, *C*H$_{dipp}$), 103.5 (s, *C*-S), 47.6 (s, *C*H$_{bridgehead}$), 47.1 (s, *C*H$_{bridgehead}$), 43.8 (s, *C*H$_2$), 28.4 (s, *C*H$_{iPr}$), 27.8 (s, *C*H$_2$), 27.7 (s, *C*H$_{iPr}$), 27.6 (s, *C*H$_2$), 25.2 (s, *C*H$_{iPr}$), 25.0 (s, *C*H$_{iPr}$), 24.8 (s, *C*H$_{iPr}$), 24.7 (s, *C*H$_{iPr}$), 0.9 (s, Si-*C*H$_3$), -1.1 (s, Si-*C*H$_3$). ^{29}Si NMR (60 MHz, C_6D_6): δ = -5.9. M.p.= 93.7 °C.

Synthesis of 4: To a solution of **3** (0.53 g, 1.22 mmol) in benzene (4 mL) was added trityl tetrakis(pentafluorophenyl)borane (1.01 g, 1.10 mmol), then the solution was stirred for 10 min. After formation of two phases, the upper phase was removed and the lower phase washed twice by benzene (1 mL). Lower phase was dried under vacuum to give **4** as a pale brown powder (1.06 g, 78%). Yellow crystals were grown from a saturated chloroform solution. ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 7.72-7.68 (m, 3H, of S-C_6H_5), 7.53-7.48 (m, 2H, of S-C_6H_5), 7.38 (t, $^{3}J_{HH}$ = 7.8 Hz, 1H, CH_{dipp}), 7.28 (dd, $^{3}J_{HH}$ = 7.8 Hz and $^{4}J_{HH}$ = 1.6 Hz, 1H, CH_{dipp}), 7.18 (dd, $^{3}J_{HH}$ = 7.8 Hz and $^{4}J_{HH}$ = 1.6 Hz, 1H, CH_{dipp}), 3.40 (s, 1H, C$H_{bridgehead}$), 2.99 (sept., $^{3}J_{HH}$ = 6.9 Hz, 1H, CH_{iPr}), 2.85 (s, 1H, C$H_{bridgehead}$), 2.54 (sept., $^{3}J_{HH}$ = 6.9 Hz, 1H, CH_{iPr}), 2.13-2.01 (m, 2H, CH_2), 1.97-1.92 (m, 1H, CH_2), 1.61-1.55 (m, 1H, CH_2), 1.52-1.43 (m, 1H, CH_2), 1.39-1.31 (m, 1H, CH_2), 1.25 (d, $^{3}J_{HH}$ = 6.9 Hz, 3H, CH_{3iPr}), 1.21 (d, $^{3}J_{HH}$ = 6.9 Hz, 3H, CH_{3iPr}), 1.13 (d, $^{3}J_{HH}$ = 6.9 Hz, 3H, CH_{3iPr}), 0.98 (s, 3H, Si-CH_3), 0.85 (d, $^{3}J_{HH}$ = 6.9 Hz, 3H, CH_{3iPr}), 0.45 (s, 3H, Si-CH_3). ^{13}C NMR (126 MHz, CD_2Cl_2): δ = 175.9 (s, N-*C*), 148.3 (br d, J_{CF} = 242.3 Hz, Ar*C*-F), 147.9 (s, C_{dipp}), 147.4 (s, C_{dipp}), 138.4 (br d, J_{CF} = 244.2 Hz, Ar*C*-F), 136.3 (br d, J_{CF} = 244.2 Hz, Ar*C*-F), 132.9 (s, *C*H$_{Ph}$), 131.7 (s, *C*H$_{Ph}$), 130.2 (s, *C*H$_{dipp}$), 129.8 N-C_{dipp}), 127.1(s, *C*H$_{Ph}$), 125.6 (s, *C*H$_{dipp}$), 125.6 (s, *C*H$_{dipp}$), 124.2 (s, *i* of C_{Ph}), 91.5 (s, *C*-S), 46.8 (s, *C*H$_2$), 44.1 (s, *C*H$_{bridgehead}$), 43.3 (s, *C*H$_{bridgehead}$), 28.6 (s, *C*H$_{iPr}$), 28.3 (s, *C*H$_2$), 28.2 (s, *C*H$_{iPr}$), 26.1 (s, *C*H$_2$), 25.6 (s, *C*H$_{3iPr}$), 25.1 (s, *C*H$_{3iPr}$), 24.5 (s, *C*H$_{3iPr}$), 22.4 (s, *C*H$_{3iPr}$), 2.1 (s, Si-*C*H$_3$), -3.8 (s, Si-*C*H$_3$). ^{19}F NMR (471 MHz, CD_2Cl_2): δ = -133.0 (br, o of ArC-*F*), -163.6 (t, J_{FF} = 20.4 Hz, *p* of ArC-*F*), -167.4 (t, J_{FF} = 18.1 Hz, *m* of ArC-*F*). ^{11}B NMR (160 MHz, CD_2Cl_2): δ = -16.6 (s, B_{Ar}). ^{29}Si NMR (99 MHz, CD_2Cl_2): δ = 54.3 (s, *Si*Me$_2$). M.p. = 114.1 °C.

General protocol for Diels-Alder reaction: In a J. Young NMR tube, **4** (10 mol%) was dissolved in CD_2Cl_2 (0.3 mL). The reaction mixture was placed at the desired temperature. Then 2,3-dimethylbuta-1,3-diene **14** or cyclohexadiene **18** (2.0 equiv) and methyl acrylate **9** (0.09 mmol) were added successively. Reactions were quenched after 1h by adding a saturated aqueous solution of $NaHCO_3$. Conversions were determined by ^{1}H NMR analysis of the crude (following OMe groups from methyl acrylate and cycloadduct). The spectroscopic data are in agreement with previously reported literature values.[6,7a] Bicyclo[2.2.2]oct-5-en-2-carboxylic acid methyl ester was obtained in a 99:1 endo:exo ratio (δ = 3.64 for CO_2CH_3 in ^{1}H NMR in $CDCl_3$).[6]

Diluted conditions: In a Schlenk tube, **4** (10 mol%) was dissolved in CD_2Cl_2 (0.3 mL) then cyclohexadiene **18** was added. The reaction mixture was placed at the desired temperature. Then a solution methyl acrylate **9** (0.009 mol) in dichloromethane (1 mL) was added. Reactions were then quenched after 1 h by adding a saturated aqueous solution of $NaHCO_3$.

Diels-Alder reaction with cyclopentadiene: In a J. Young NMR tube, **4** (10 mol%) was dissolved in CD_2Cl_2 (0.3 mL). The reaction mixture was placed at the desired temperature. Then a solution of cyclopentadiene **16** (0.18 mmol), α,β-unsaturated ketones (0.09 mmol) and 1,2-dichloethane (0.09 mmol as internal standard) in dichloromethane (0.3 mL) was added. Reactions were quenched after 1 h by adding a saturated aqueous solution of $NaHCO_3$. The spectroscopic data are in agreement with previously reported literature values.[8a,20] 1-(Bicyclo[2.2.1]hept-5-en-2-yl)ethenone was obtained in a 82:18 endo:exo ratio. Bicyclo[2.2.1]hept-5-en-2-carboxaldehyde was obtained in a 84:16 endo:exo ratio. For methyl norbornene-5-carboxylate, the ^{1}H NMR spectrum is in excellent agreement with the endo-ester (endo:exo > 99:1).

General protocol for hydrodefluorination reaction: In a J. Young NMR tube, **4** (10 mol%) was dissolved in 1,2-dichlorobenzene (0.3 mL). The α,α,α-trifuorotoluene **20** (0.09 mmol), triethylsilane **21** (3.1 equiv) were successively added. Then reaction mixture was placed at desired temperature. Conversions were determined by ^{19}F NMR analysis of the crude (α,α,α-trifuorotoluene **20** /Et_3SiF **23** ratio).

Conclusions

In conclusion, a new type of sulfide-stabilized-silylium ion **4**, based on a norbornene scaffold, was prepared and fully characterized by NMR spectroscopy, X-ray crystallography and DFT calculations. Due to the weak nucleophilic character of sulfide ligand and the strongly stabilizing amino-substituent at silicon, both inducing a weak S→Si interaction, silylium ion complex **4** acts as a Lewis acid, contrary to its phosphine analogue **VII** that behaves as a Lewis pair. As a result, **4** shows a high catalytic activity in the Diels-Alder cycloaddition with poorly reactive dienes at low temperature. Efforts are currently underway to extend the diversity of catalytic applications of **4**.

Author Contributions

Conceptualization: A.B., T.K., T.M., E.M.; Investigation: A.D., G.A.O., R.L.; X-ray structural studies: N.S.-M.; Supervision : T.M., T.K., E.M.; Writing – original draft: A.D., G.A.O., T.M., E.M. ; Writing – review & editing: All authors. All authors have read and agreed to the published version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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