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The Cyclohexadienyl-Leaving-Group Approach toward Donor-Stabilized Silylium Ions

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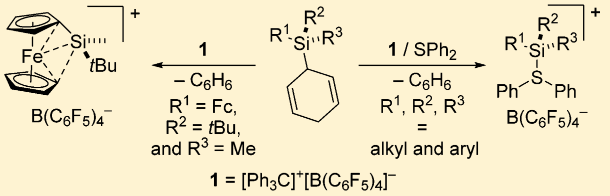
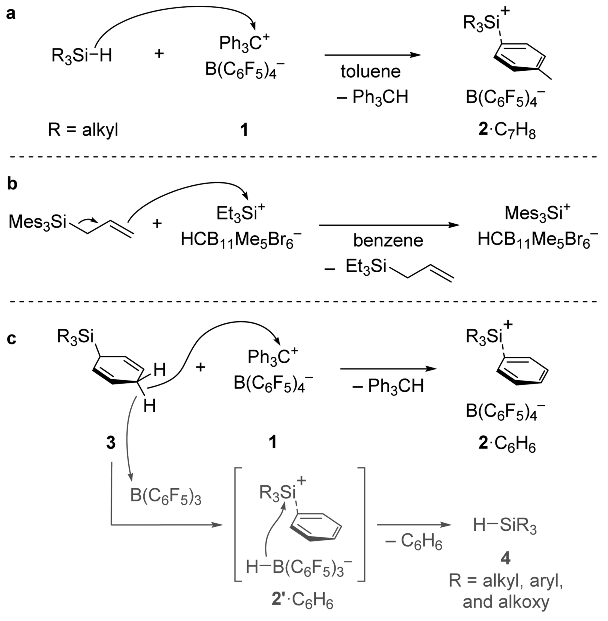
Supporting Information

ABSTRACT: The cyclohexa-2,5-dien-1-yl group is established as a leaving group at silicon as an alternative to the Bartlett–Condon–Schneider silicon-to-carbon hydride transfer and the allyl-leaving-group approach to generate silylium ions. Hydride abstraction from the skipped diene unit employing trityl tetrakis(pentafluorophenyl)borate (**1**, $[Ph_3C]^+[B(C_6F_5)_4]^-$) yields the silicon cation along with benzene. Our investigations reveal that the presence of an internal or external donor group is mandatory to allow for the formation of intra- or intermolecularly stabilized silylium ions. If not, degradation of the precursor is observed as a result of the reaction of the allylic silane units with the released silylium ion. It is also shown that such allylic silanes do form remarkably stable alkyl-substituted carbenium ions when reacted stoichiometrically with benzene-stabilized silylium ions.



The preparation and characterization of positively charged silicon compounds have fueled intense research work over the last three decades.[1] Since the seminal work of Corey demonstrated the viability of the Bartlett–Condon–Schneider silicon-to-carbon hydride transfer to efficiently generate such entities (Scheme 1a),[2,3] several groups have been involved in this fascinating chemistry that eventually culminated in the characterization of a free silylium ion.[4] This achievement had become possible thanks to the development of weakly coordinating carborate counteranions[1c] and the invention of the allyl-leaving-group approach.[5,6] That release mechanism overcomes the limitation of the Bartlett–Condon–Schneider hydride transfer to heterolytically cleave sterically inaccessible Si–H bonds (Scheme 1b).

Scheme 1. Bartlett–Condon–Schneider Silicon-to-Carbon Hydride Transfer (a); Generation of the Trimesitylsilylium Ion by the Allyl-Leaving-Group Approach (b); Planned Cyclohexadienyl-Leaving-Group Approach (c)



For the past few years, we have been involved in the use of strong main-group Lewis acids in catalysis, e.g., silylium ions as catalysts for challenging Diels–Alder reactions[7] as well as C_6F_5-containing boranes in catalytic Si–H bond activation.[8] In the arena of these electron-deficient boron Lewis acids, we recently devised the ionic degradation of cyclohexa-2,5-dien-1-yl-substituted silanes to hydrosilanes and an arene molecule catalyzed by tris(pentafluorophenyl)borane, $B(C_6F_5)_3$.[9] This process was quantum chemically investigated by Sakata and Fujimoto shortly thereafter[10] and is proposed to pass through carbon-to-boron hydride transfer from the methylene group "opposite" the silicon-bearing carbon atom, i.e., from the less hindered face, of the cyclohexa-1,4-diene core (**3** → $\mathbf{2'}\cdot C_6H_6$, Scheme 1c, gray pathway). The thus-generated Wheland complex,[11] i.e., the arene-stabilized silylium ion, $\mathbf{2'}\cdot C_6H_6$, then collapses to afford hydrosilane **4** by reaction with the borohydride counteranion ($\mathbf{2'}\cdot C_6H_6$ → **4**). Given our background in silylium chemistry,[7,12] we asked ourselves whether the borane in this approach could be replaced with trityl tetrakis(pentafluorophenyl)borate (**1**, $[Ph_3C]^+[B(C_6F_5)_4]^-$)[13] as the hydride acceptor. The plan was to intercept the hydrosilane release at the stage of the arene-stabilized silylium ion **2** (Scheme 1c, black pathway), hence offering a complementary approach to that developed by Lambert.[5]

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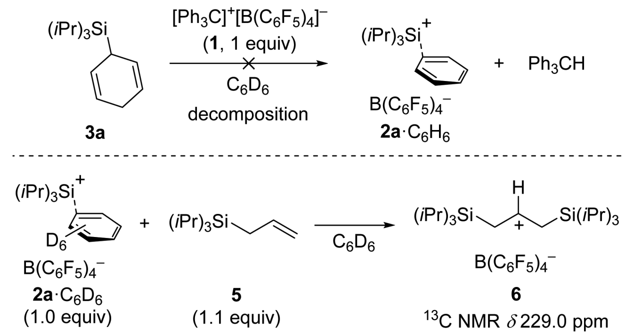
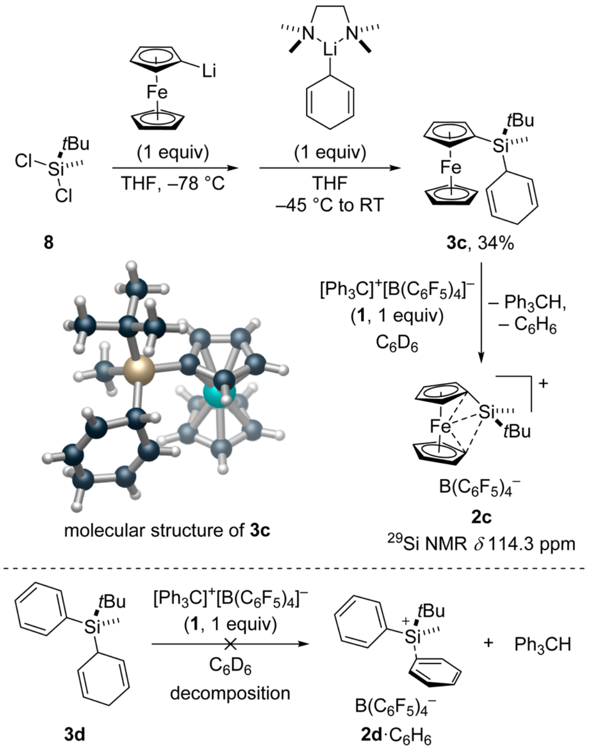
Our study commenced with subjecting a C_6D_6 solution of cylohexa-2,5-dien-1-yltriisopropylsilane (**3a**) to a suspension of trityl salt **1** in the same solvent. After decanting, the resulting clathrate was analyzed by the means of NMR spectroscopy and appeared to contain only unreacted **1**. Conversely, the analysis of the supernatant showed complete decomposition/oligomerization of **3a** to an intractable mixture (Scheme 2, top). We speculated that the formation of small amounts of the desired arenium ion **2a**·C_6H_6 are enough to initiate the decomposition of **3a**, likely involving the allylic silane units. To further verify this hypothesis, we had a look at the stability of allyltriisopropylsilane (**5**) in the presence of $[(i\text{Pr})_3\text{Si}(C_6D_6)]^+[B(C_6F_5)_4]^-$ (**2a**·C_6D_6)[13] (Scheme 2, bottom). We observed the clean formation of the thermally stable secondary carbenium ion $[\text{HC}\{\text{CH}_2\text{Si}(i\text{Pr})_3\}_2]^+[B(C_6F_5)_4]^-$ (**6**). We attribute its remarkable stability at room temperature to the double hyperconjugative β-silicon effect exerted by the two $C(sp^3)-Si$ σ-bonds.[14] Alkyl-substituted carbenium ions of this type are rather rare in the literature and generally not observed at ambient temperature.[15,16] This result parallels a report by Bochmann and co-workers where isolable $[\text{HC}\{\text{CH}(\text{SiMe}_3)(\text{SnMe}_3)\}_2]^+[Zr_2Cl_9]^-$ was generated by the reaction of $[\text{Me}_3\text{Sn}]^+[Zr_2Cl_9]^-$ and (3-(trimethylstannyl)prop-1-ene-1,3-diyl)bis(trimethylsilane).[17] The addition of excess allylic silane **5** to **6** led to the disappearance of **6** and consumption of **5** (not shown). It is therefore reasonable to assume that silylium ion precursor **3a** suffers the same fate when treated with trityl salt **1**. It is also worthy of mention that we were not able to generate any stable intermediate from the reaction of **3a** and an equimolar amount of $[(i\text{Pr})_3\text{Si}(C_6D_6)]^+[B(C_6F_5)_4]^-$ (**2a**·C_6D_6).

Scheme 2. Attempted Generation of the Triisopropylsilylium Ion by the Cyclohexadienyl-Leaving-Group Approach (Top) and Generation of a Stable Secondary Alkyl Carbenium Ion (Bottom)



We next inferred that better stabilization of the silylium ion will prevent it from reacting with the allylic silane units of the cyclohexa-1,4-diene core. We initially considered kinetic stabilization and targeted cyclohexa-2,5-dien-1-yltrimesitylsilane (**3b**). We were however unable to make the TMEDA complex of cyclohexa-2,5-dien-1-yllithium react with chlorotrimesitylsilane (**7**). Instead of **3b**, we obtained trimesitylsilane (**4b**) as a result of chloride substitution in **7** with in-situ-generated lithium hydride (see Scheme S1 in the Supporting Information).[18] Hence, we decided to switch to donor-stabilized systems, of which many are documented in the literature.[1e] Our group established such stabilization through an electron-rich transition-metal fragment.[7a,12] We therefore embarked on the preparation of ferrocenyl-substituted precursor **3c** (Scheme 3, top). Sequential treatment of *tert*-butyldichloro(methyl)silane (**8**) with ferrocenyllithium and the TMEDA complex of cyclohexa-2,5-dien-1-yllithium furnished **3c** as dark red crystals in 34% yield. Its molecular structure is depicted in Scheme 3; its cyclohexa-2,5-dien-1-yl group is not planar but adopts a boat-like conformation folded toward the silicon atom.[19] This time, the addition of a solution of **3c** in C_6D_6 to trityl salt **1** resulted in clean formation of the ferrocene-stabilized silylium ion **2c**[12a] (Scheme 3, top). To confirm the pivotal role of the ferrocene backbone, we subjected the related phenyl-substituted precursor **3d** to the same procedure, but the targeted arenium ion **2d**·C_6H_6 did not form (Scheme 3, bottom).

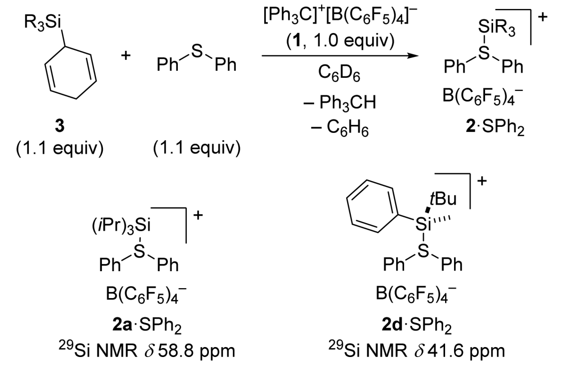
Scheme 3. Formation of a Ferrocene-Stabilized Silylium Ion by the Cyclohexadienyl-Leaving-Group Approach (Top) and Evidence for the Need of Donor Stabilization (Bottom)



After the demonstration of the feasibility of the cyclohexadienyl-leaving-group approach, we probed its generality with the aid of an external donor. We had recently been successful with stabilizing silylium ions with sulfides, resulting in chemically rather robust Lewis pairs.[7c,d,20] Revisiting the generation of **2a** from cylohexa-2,5-dien-1-yltriisopropylsilane (**3a**) in the presence of diphenylsulfide was met with success (Scheme 4). Analysis of the clathrate confirmed the formation of $[(i\text{Pr})_3\text{Si}(\text{SPh}_2)]^+[B(C_6F_5)_4]^-$ (**2a**·SPh_2) with a diagnostic ^{29}Si NMR chemical shift of δ 58.8 ppm.[7c,d] We repeated the same experiment with *tert*-butyl(cyclohexa-2,5-dien-1-yl)(methyl)(phenyl)silane (**3d**), and silylium ion **2d** readily formed as its adduct **2d**·SPh_2 with a chemical shift of δ 41.6 ppm. The difference in deshielding of the silicon atoms in **2a**·SPh_2 and **2d**·SPh_2 probably stems from a stronger silicon−sulfur interaction in Lewis adduct **2d**·SPh_2 of sterically less hindered **2d**.

We showed here that cyclohexa-2,5-dien-1-ylsilanes are viable precursors for the generation of silylium ions through carbon-

Scheme 4. Generation of Intermolecularly Sulfur-Stabilized Silylium Ions by the Cyclohexadienyl-Leaving-Group Approach in the Presence of a Sulfide Donor



to-carbon hydride transfer upon treatment with equimolar amounts of trityl salt **1**. However, sufficient stabilization of the released silylium ion by an internal or external donor group must be available to prevent its reaction with the allylic silane units of the unreacted precursor, i.e., the cyclohexa-1,4-diene moiety. Intramolecular stabilization was realized in a ferrocenyl-substituted system, and intermolecular Lewis pair formation was achieved with diphenylsulfide. As part of this work, we also demonstrated that the stoichiometric reaction of an allylic silane and a benzene-stabilized silylium ion yields a remarkably stable alkyl-substituted secondary carbenium ion.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00609.

Synthetic procedures and figures giving NMR spectra of the previously unknown compounds synthesized in this paper (PDF)
CIF file (CIF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Müller, T. In *Structure and Bonding (Berlin)*; Scheschkewitz, D., Ed.; Springer: Berlin, 2014; Vol. *155*, pp 107−162. (b) Müller, T. In *Science of Synthesis: Knowledge Updates 2013/3*; Oestreich, M., Ed.; Thieme: Stuttgart, 2013; pp 1−42. (c) Reed, C. A. *Acc. Chem. Res.* **2010**, *43*, 121−128. (d) Lambert, J. B.; Zhao, Y.; Zhang, S. M. *J. Phys. Org. Chem.* **2001**, *14*, 370−379. (e) Lambert, J. B.; Kania, L.; Zhang, S. *Chem. Rev.* **1995**, *95*, 1191−1201.

(2) (a) Corey, J. Y. *J. Am. Chem. Soc.* **1975**, *97*, 3237−3238. (b) Corey, J. Y.; Gust, D.; Mislow, K. *J. Organomet. Chem.* **1975**, *101*, C7−C8.

(3) Lambert, J. B.; Zhang, S.; Stern, C. L.; Huffman, J. C. *Science* **1993**, *260*, 1917−1918.

(4) Kim, K.-C.; Reed, C. A.; Elliott, D. W.; Mueller, L. J.; Tham, F.; Lin, L.; Lambert, J. B. *Science* **2002**, *297*, 825−827.

(5) Lambert, J. B.; Zhao, Y.; Wu, H.; Tse, W. C.; Kuhlmann, B. *J. Am. Chem. Soc.* **1999**, *121*, 5001−5008.

(6) The technique itself had been reported earlier by Schade and Mayr: Schade, C.; Mayr, H. *Makromol. Chem., Rapid Commun.* **1988**, *9*, 477−482.

(7) (a) Klare, H. F. T.; Bergander, K.; Oestreich, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 9077−9079. (b) Schmidt, R. K.; Müther, K.; Mück-Lichtenfeld, C.; Grimme, S.; Oestreich, M. *J. Am. Chem. Soc.* **2012**, *134*, 4421−4428. (c) Rohde, V. H. G.; Pommerening, P.; Klare, H. F. T.; Oestreich, M. *Organometallics* **2014**, *33*, 3618−3628. (d) Rohde, V. H. G.; Müller, M. F.; Oestreich, M. *Organometallics* **2015**, *34*, 3358−3373.

(8) For a recent review, see: (a) Oestreich, M.; Hermeke, J.; Mohr, J. *Chem. Soc. Rev.* **2015**, *44*, 2202−2220. For mechanistic work, see: (b) Rendler, S.; Oestreich, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 5997−6000. (c) Hermeke, J.; Mewald, M.; Oestreich, M. *J. Am. Chem. Soc.* **2013**, *135*, 17537−17546.

(9) (a) Simonneau, A.; Oestreich, M. *Angew. Chem., Int. Ed.* **2013**, *52*, 11905−11907. (b) Simonneau, A.; Friebel, J.; Oestreich, M. *Eur. J. Org. Chem.* **2014**, 2077−2083. (c) Keess, S.; Simonneau, A.; Oestreich, M. *Organometallics* **2015**, *34*, 790−799.

(10) Sakata, K.; Fujimoto, H. *Organometallics* **2015**, *34*, 236−241.

(11) Arenium ion intermediates are named after Wheland, but their existence had already been noted by Pfeiffer and Wizinger before Wheland's quantum-mechanical analysis: (a) Wheland, G. W. *J. Am. Chem. Soc.* **1942**, *64*, 900−908. (b) Pfeiffer, P.; Wizinger, R. *Liebigs Ann. Chem.* **1928**, *461*, 132−154.

(12) (a) Müther, K.; Fröhlich, R.; Mück-Lichtenfeld, C.; Grimme, S.; Oestreich, M. *J. Am. Chem. Soc.* **2011**, *133*, 12442−12444. (b) Müther, K.; Hrobárik, P.; Hrobáriková, V.; Kaupp, M.; Oestreich, M. *Chem. - Eur. J.* **2013**, *19*, 16579−16594.

(13) Lambert, J. B.; Zhang, S. *J. Chem. Soc., Chem. Commun.* **1993**, 383−384.

(14) Lambert, J. B.; Zhao, Y.; Emblidge, R. W.; Salvador, L. A.; Liu, X.; So, J.-H.; Chelius, E. C. *Acc. Chem. Res.* **1999**, *32*, 183−190.

(15) For seminal reports of carbenium ions/carbocations stabilized through the β-silicon effect, see: (a) Lambert, J. B.; Zhao, Y.; Wu, H. *J. Org. Chem.* **1999**, *64*, 2729−2736. (b) Meyer, R.; Werner, K.; Müller, T. *Chem. - Eur. J.* **2002**, *8*, 1163−1172.

(16) (a) Olah, G. A.; Prakash, G. K. S., Eds. *Carbocation Chemistry*; Wiley: Hoboken, 2004. (b) Vogel, P. *Carbocation Chemistry*; Elsevier: Amsterdam, 1985. (c) Bethell, D.; Gold, V. *Carbonium Ions*; Academic Press: London, 1967. (d) Olah, G. A.; Schleyer, P. v. R., Eds.; *Carbonium Ions*; Wiley: New York, 1968−1976; Vols *I*−*V*.

(17) Schormann, M.; Garratt, S.; Hughes, D. L.; Green, J. C.; Bochmann, M. *J. Am. Chem. Soc.* **2002**, *124*, 11266−11267.

(18) For the formation of lithium hydride from cyclohexa-2,5-dien-1-yllithium, see: Bates, R. B.; Gosselink, D. W.; Kaczynski, J. A. *Tetrahedron Lett.* **1967**, 199−204.

(19) For conformational analyses of cyclohexa-1,4-dienes, see: Bennett, M. J.; Purdham, J. T. *Can. J. Chem.* **1978**, *56*, 1358−1363 and cited references .

(20) Prakash, G. K. S.; Bae, C.; Wang, Q.; Rasul, G.; Olah, G. A. *J. Org. Chem.* **2000**, *65*, 7646−7649.