Abstract:

Synthesis of Bis(silylium) Ions and Their Application to C(sp^2)–F Bond Activation

Co-supervisor 1: Martin Oestreich, Technische Universität Berlin

Co-supervisor 2: Martin Kaupp, Technische Universität Berlin

This project describes a succinct synthetic route to super electrophilic bis(silylium) ions [Si$^+$—spacer—Si$^+$] and especially focuses on their potential catalytic reactivity in the hydrodefluorination of chemically robust C(sp^2)–F bonds. The reaction of selected silane precursors with the Brønsted acid $[C_6H_6{\cdot}H]^+[CHB_{11}H_5Br_6]^-$ is expected to produce hitherto unknown bis(silylium) ions. The extreme electrophilicity of these dications will likely overcome the high activation barrier to the successful heterolytic cleavage of the inert C(sp^2)–F bond. With the aid of DFT calculations performed by the Kaupp group (SFB 1349 *Fluor-Spezifische Wechselwirkungen: Grundlagen und Anwendungen*), a suitable catalytic system will be explored. This project will serve to guide future efforts to synthesize silylium-ion-like species and to develop catalytic functionalization of C–F bonds.

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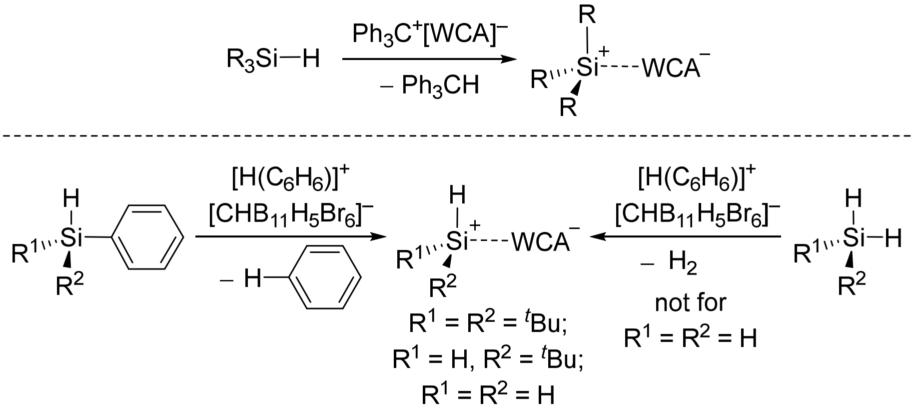
1. Overall goal of the project

The main purpose of the project is to achieve the catalytic hydrodefluorination of chemically robust C(sp^2)–F bonds with the aid of extremely electrophilic silylium ions. For this, elusive bis(silylium) ions [Si$^+$—spacer—Si$^+$] will be designed, prepared, and characterized. Its potential application in catalytic hydrodefluorination of C(sp^2)–F bonds will be experimentally and computationally investigated.

2. State of the art

As a result of their enormous electrophilicity and high fluoride affinity, the use of strong main-group Lewis acids such as silylium ions in the catalytic hydrodefluorination of C(sp^3)–F bonds has been extensively researched in recent years.[1] Relative to C(sp^3)–F bonds, it is very challenging to activate C(sp^2)–F bonds due to the formation of aryl or vinyl cations as high-energy intermdiates.[2] A solution to this problem can be the use of carborane-stabilized silylium ions.[3] However, an intra- or intermolecular C–H activation had always been involved in those hydrodefluorination reactions of C(sp^2)–F bonds.[4] To realize the hydrodefluorination of C(sp^2)–F bonds, new silylium ions must be invented.

The Oestreich Group recently made significant contributions to the synthe-sis of highly reactive silylium ions, especially totally unprecedented hydrogen-substituted silylium ions.[5] Silylium ions are typically accessed by removal of one substituent from a neutral, tetracoordinate silane by the reaction with an electrophilic reagent. The standard protocol is the silicon-to-carbon hydride transfer, in which an electrophilic carbenium ion (R_3C^+) paired with a weakly coordinating anion (WCA) abstracts hydride from a hydrosilane. Dearylative and dehydrogenative protolysis were employed in the synthesis of hydrogen-substituted silylium ions (Scheme 1).



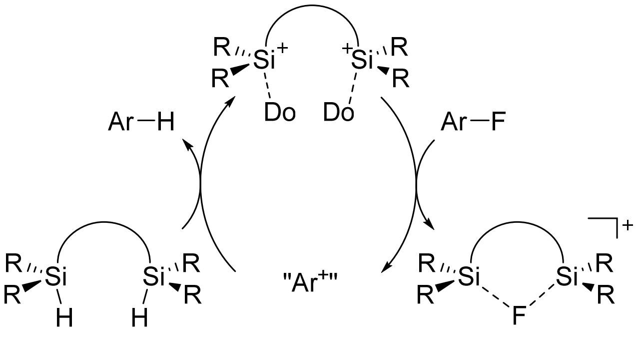
Scheme 1. Synthesis of tertiary and hydrogen-substituted silylium ions

3. Specific aims and how they may be reached:

Objectives: The new bis(silylium) ions [Si$^+$—spacer—Si$^+$] paired with Reed's carborane anion $[CHB_{11}H_5Br_6]^-$ will be first synthesized and characterized. This will be followed by experimental and computational investigation of their reactivity toward C(sp^2)–F bonds, eventually resulting in catalytic hydrodefunctionalization.

Experimental strategies: Based on the previous studies, the Oestreich group has become interested in synthesizing silicon-based dications. After the preparation of the requisite disilane precursors, the benzenium ion paired with Reed's carborane anion $[C_6H_6{\cdot}H]^+[CHB_{11}H_5Br_6]^-$ will be used for the cleavage of Si–C(sp^3) bonds to generate the corresponding dications.[6] Then, a suitable catalytic system for hydrodefluorination of C(sp^2)–F bonds can be designed with the help of computational and experi-mental studies, in which the stoichiometry and kinetics can be monitored by NMR spectroscopy and MS spectrometry.

Work packages: Due to the high Lewis acidity of the targeted silicon-based dications, the first goal is their synthesis and characterization. The generation of the dication from the corresponding alkylated disilane precursor will be warranted by the use of $[C_6H_6{\cdot}H]^+[CHB_{11}H_5Br_6]^-$. After full spectroscopic and structural characterization, the catalytic reactivity of the dication in hydrodefluorination of C(sp^2)–F bonds will be tested. The preformed dication will abstract the fluoride anion from the aryl fluoride substrate. The extremely high electrophilicity of the bis(silylium) ion may help to overcome the activation barrier of fluoride abstraction. Subsequent hydride transfer from the bis(hydrosilane) reagent to the transiently formed aryl cation affords the arene and regenerates the catalyst (Scheme 2). The catalytic reactivity of the silicon-based dication may be tunable by employing various spacers and substituents with different steric and electronic properties. The design of new disilyl dication can be carried out with support from the Kaupp group. By applying DFT calculations, the fluoride ion affinity can be calculated, and the progress of the reactions can be monitored by ^{19}F and ^{29}Si NMR spectroscopy.



Scheme 2. Proposed mechanism of the C(sp^2)–F bond activation promoted by bis(silylium) ions

Statement on facilities: The Oestreich group is equipped with the state-of-the-art facilities for experimental research and analysis of new silylium ions, including NMR machines, an X-ray diffractometer as well as GLC analysis systems. The Kaupp group provides state-of-the-art computational methodology, including experience with DFT methods and advanced solvent models.

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[1] For a review, see: T. Stahl, H. F. T. Klare, M. Oestreich, *ACS Catal.* **2013**, *3*, 1578–1587.

[2] For a perspective, see: H. F. T. Klare, *ACS Catal.* **2017**, *7*, 6999–7002.

[3] S. Duttwyler, F. S. Tham, K. K. Baldridge, J. S. Siegel. *Angew. Chem. Int. Ed.* **2010**, *49*, 7519–7522.

[4] a) O. Allemann, S. Duttwyler, P. Romanato, K. K. Baldridge, J. S. Siegel, *Science* **2011**, *332*, 574–577; b) B. Shao, A. L. Bagdasarian, S. Popov, H. M. Nelson, *Science* **2017**, *355*, 1403–1407.

[5] a) Q. Wu, E. Irran, R. Müller, M. Kaupp, H. F. T. Klare, M. Oestreich, *Science* **2019**, *365*, 168–172; for a review, see: b) J. C. L. Walker, H. F. T. Klare, M. Oestreich, *Nat. Rev. Chem.* **2020**, *4*, 54–62.

[6] Q. Wu, Z. W. Qu, L. Omann, E. Irran, H. F. T. Klare, M. Oestreich, *Angew. Chem. Int. Ed.* **2018**, *57*, 9176–9179.