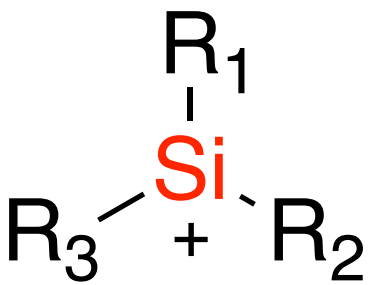
# Silylium Ions

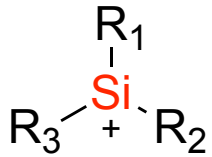


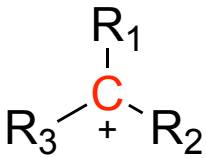

Travis Menard

Group Meeting

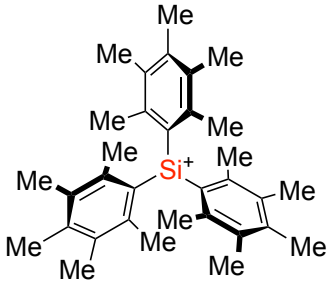
*June 15th, 2021*

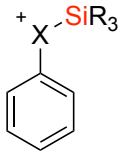
# Silylium Ions

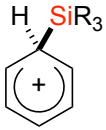


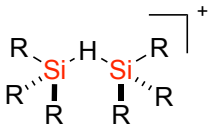



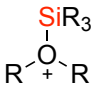

**Cationic silicon containing compounds in which silicon (IV) has a coordination number of three or four, but not five**



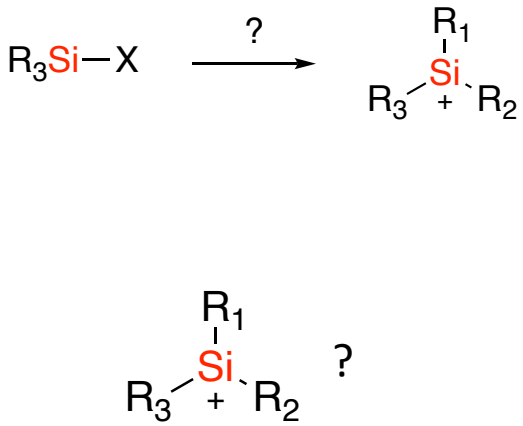



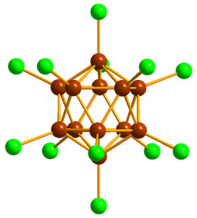



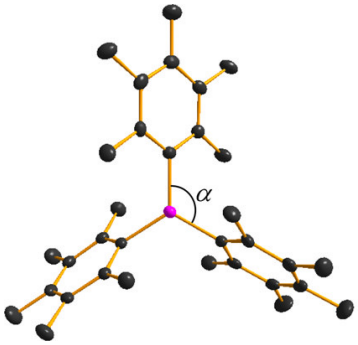

# Outline

## Brief History of Silylium Ions

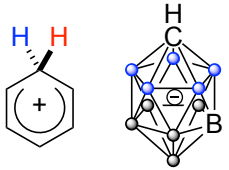


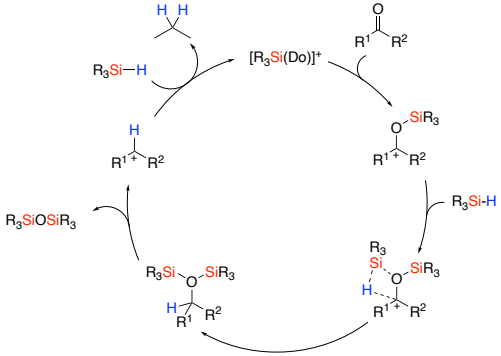

## Preparation and Properties





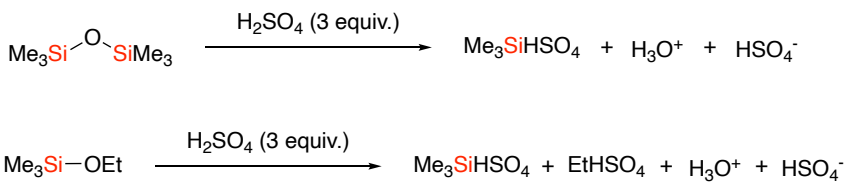

## Applications



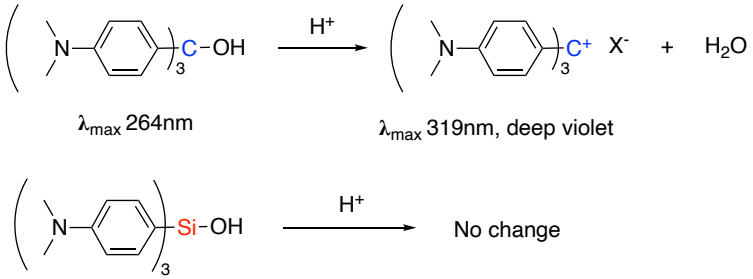



# Silylium Ions – Early Attempts

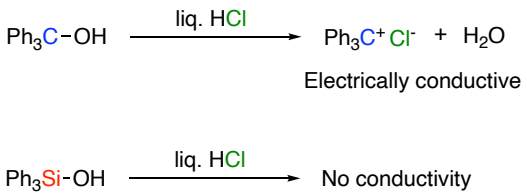
Flowers, Gillespie, and Robinson:



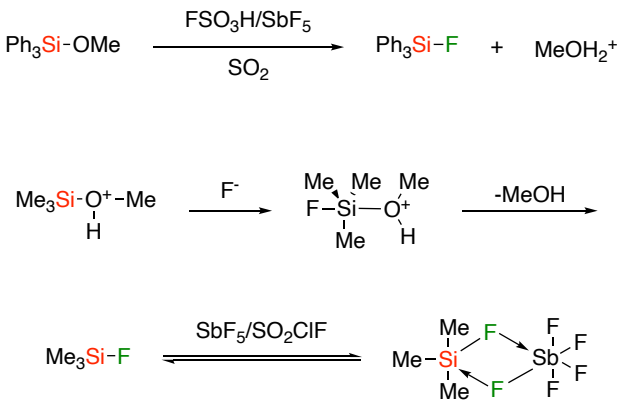

Gilman:




Peach and Waddington:



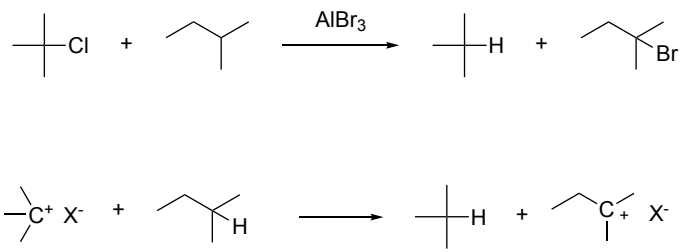

Olah:




R.H. Flowers, R.J. Gillespie and EA. Robinson. Can. J. Chem.. 41 (1963) 2464.; M.E. Peach and T.C. Waddington. J. Chem. Soc; (1961) 1238.; H. Gilman and G.E. Dunn. J. Am. Chem. Soc.. 72 (1950) 2178.; G.A. Olah and Y.K. MO, J. Am. Chem. Soc., 93 (1971) 4942.

# Corey Reaction

Bartlett-Condon-Schneider (BCS) Reaction:




$$(Ph)_3C^+X^- + R_3Si{-}H \longrightarrow (Ph)_3C{-}H + R_3SiH^+X^-$$

Corey and West:

$$(Ph)_3C^+BBr_3^- + R_3Si{-}H \longrightarrow (Ph)_3C{-}H + R_3Si{-}Br + BBr_3$$

$$(Ph)_3C^+Br^- + R_3Si{-}H \longrightarrow (Ph)_3C{-}H + R_3Si{-}Br$$

PERCENTAGE REACTION OF TRIPHENYLSILANE AND TRIETHYLSILANE WITH TRIPHENYLCHLOROMETHANE AND TRIPHENYLBROMOMETHANE IN VARIOUS SOLVENTS

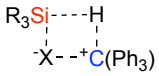
| Reactants | $CH_2Cl_2$, 10 min., 25° | $C_6H_6$, 24 hr., 25° | $CH_3CN$, 18 hr., 25° | $CCl_4$, 18 hr., 76° | THF, 18 hr., 65° |
|---|---|---|---|---|---|
| $Ph_3CBr$, $Ph_3SiH$ | 100 | 100 | 100 | 100 | 0 |
| $Ph_3CBr$, $Et_3SiH$ | 100 | 80 | 100 | 100 | 0 |
| $Ph_3CCl$, $Ph_3SiH$ | 100 | 97[a] | 75 | 100 | 0 |
| $Ph_3CCl$, $Et_3SiH$ | 100 | 70[a] | 45 | 100 | 0 |

[a] HCl was present as a catalyst.

TABLE II

REACTION BETWEEN TRIPHENYLSILANE AND TRIPHENYLBROMOMETHANE IN VARIOUS SOLVENTS

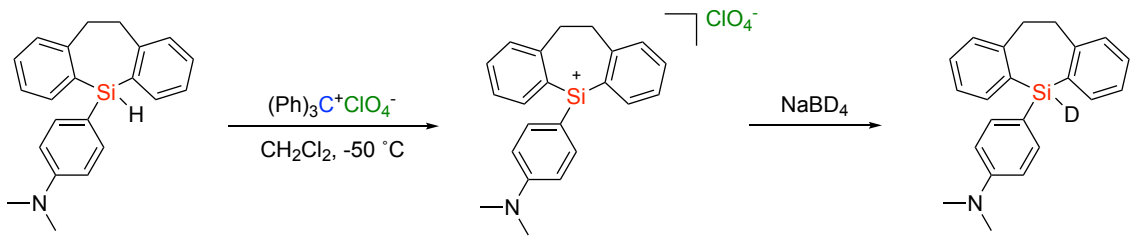
| Solvent | Dielect. const. (t, °C.) | Ref. | Temp., °C. | Time, hr. | Reacs., % |
|---|---|---|---|---|---|
| Cyclohexane | 2.015 (25) | 10 | 25 | 24 | 0 |
| Dioxane | 2.209 (25) | 10 | 25 | 72 | 0 |
| | | | 101 | 9 | 100 |
| Carbon tetrachloride | 2.228 (25) | 10 | 25 | 24 | 0 |
| | | | 76 | 18 | 100 |
| Benzene | 2.274 (25) | 10 | 25 | 12 | 23 |
| | | | 25 | 48 | 60 |
| Tetrachloroethylene | 2.30 (25) | 11 | 25 | 24 | 0 |
| Carbon disulfide | 2.64 (20) | 10 | 25 | 24 | 0 |
| Diethyl ether | 3.97 (25) | 10 | 36 | 18 | 0 |
| Ethyl iodide | 7.82 (20) | 11 | 25 | 0.25 | 100 |
| Tetrahydrofuran | 8.20 (20) | 12 | 67 | 18 | 0 |
| Dichloromethane | 9.08 (20) | 10 | 25 | 0.25 | 100 |
| Dichloroethane | 10.36 (25) | 10 | 25 | .25 | 100 |
| Nitrobenzene | 34.82 (25) | 10 | 25 | .25 | 100 |
| Nitromethane | 35.87 (30) | 11 | 25 | .25 | 100 |




Bartlett, P. D.; Condon, F. E.; Schneider, J. Am. Chem. Soc. 1944, 66, 1531– 1539; J-Y. Corey and R. West, J. Am. Chem. Soc. 85 (1963) 2430

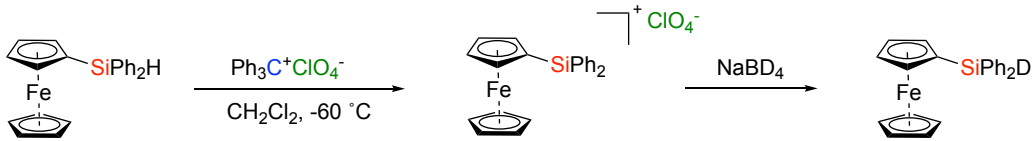
# Stabilized Silylium Ions

Corey and Mislow:



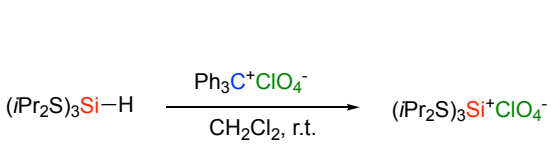

Bright green solution

No conductance in solution




Dark green solution

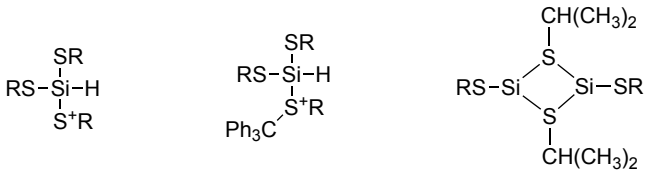
Lambert and Schulz:




110.8 uohm $cm^{-1}$

No EPR signal

1 *i*Pr peak in $^1$HNMR

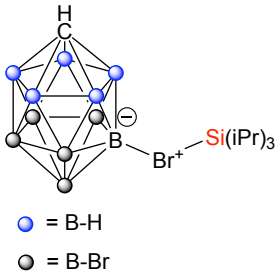


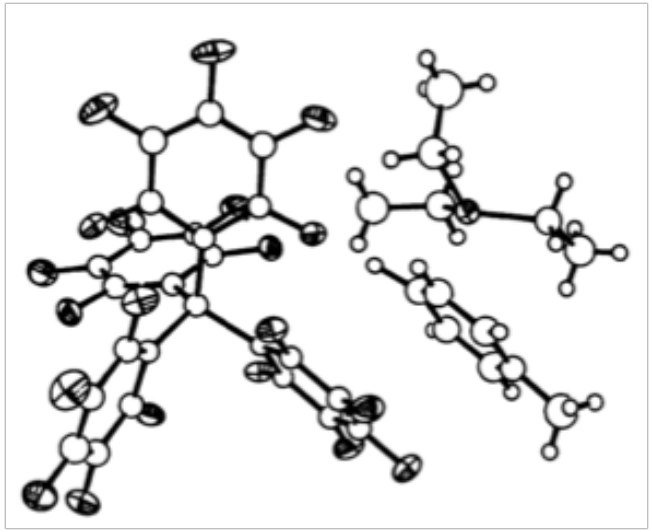

Corey, J. Y. J. Am. Chem. Soc. 1975, 97, 3237-3238; Corey, J. Y.; Gast, D.; Mislow, K. J. Organomet. Chem. 1975, 101, C7-C8;
Lambert, J. B.; Schulz, W. J., Jr. J. Am. Chem. Soc. 1983, 105, 1671-1672

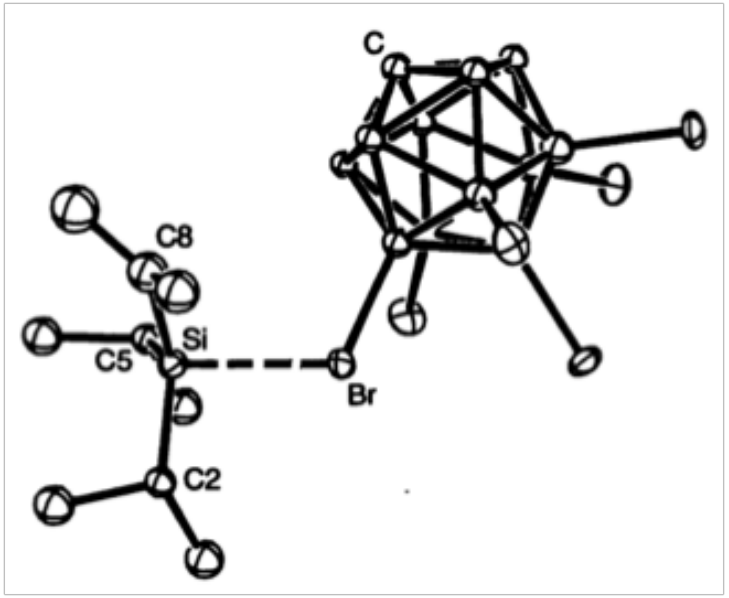
# Highly Non-Coordinating Counteranions

$$Et_3Si{-}H \xrightarrow[CH_2Cl_2,\ r.t.]{[Ph_3C]^+[(C_6F_5)_4B]^-} Et_3Si^+(C_6F_5)_4B^-$$

$$(iPr)_3Si{-}H \xrightarrow[CH_2Cl_2,\ r.t.]{[Ph_3C]^+[(HCB_{11}H_5Br_6)]^-} (iPr)_3Si^+HCB_{11}Br_5^-$$

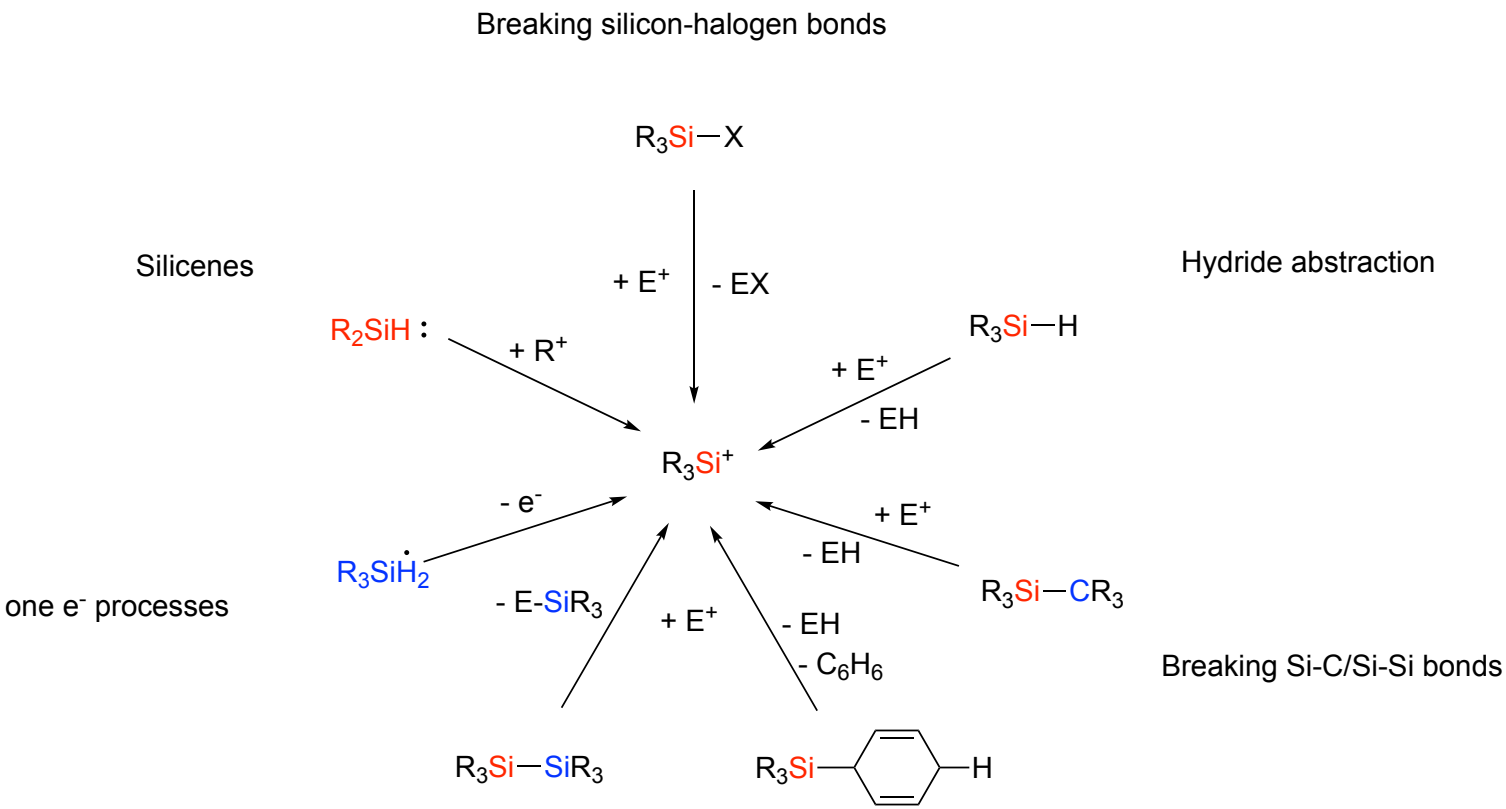




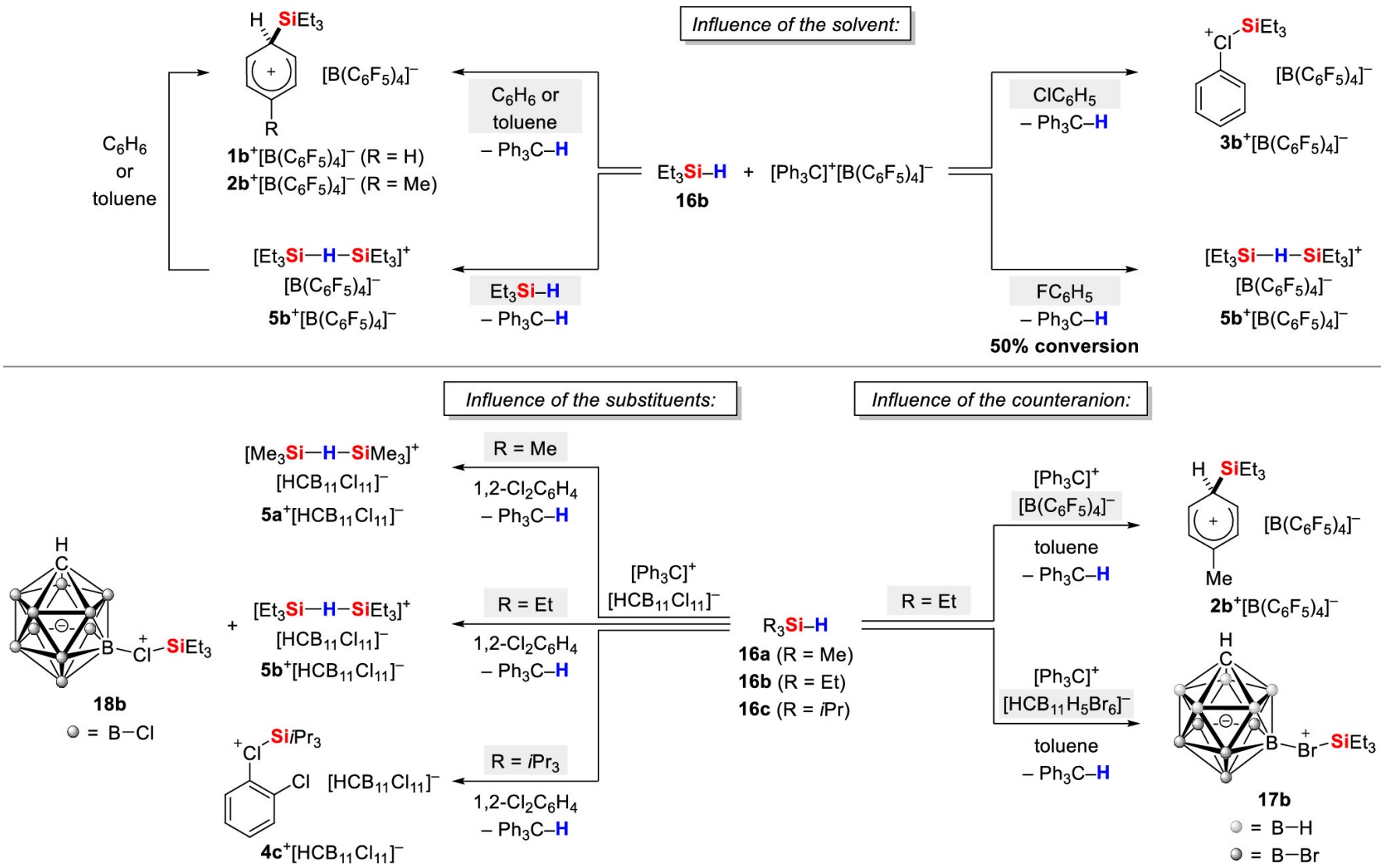

Joseph B. Lambert, Shizhong Zhang, Charlotte L. Stern, John C. Huffman, Science 1993, 1917-1918, Christopher A. Reed, Zuowei Xie, Robert Bau, Alan Benesi, Science, 1993, 402-404

# Silylium Ions – Synthesis Overview




H. F. T. Klare, L. Albers, L. Süsse, S. Keess, T. Müller, and M. Oestreich, Chem. Rev. 2021, 121, 10, 5889–5985

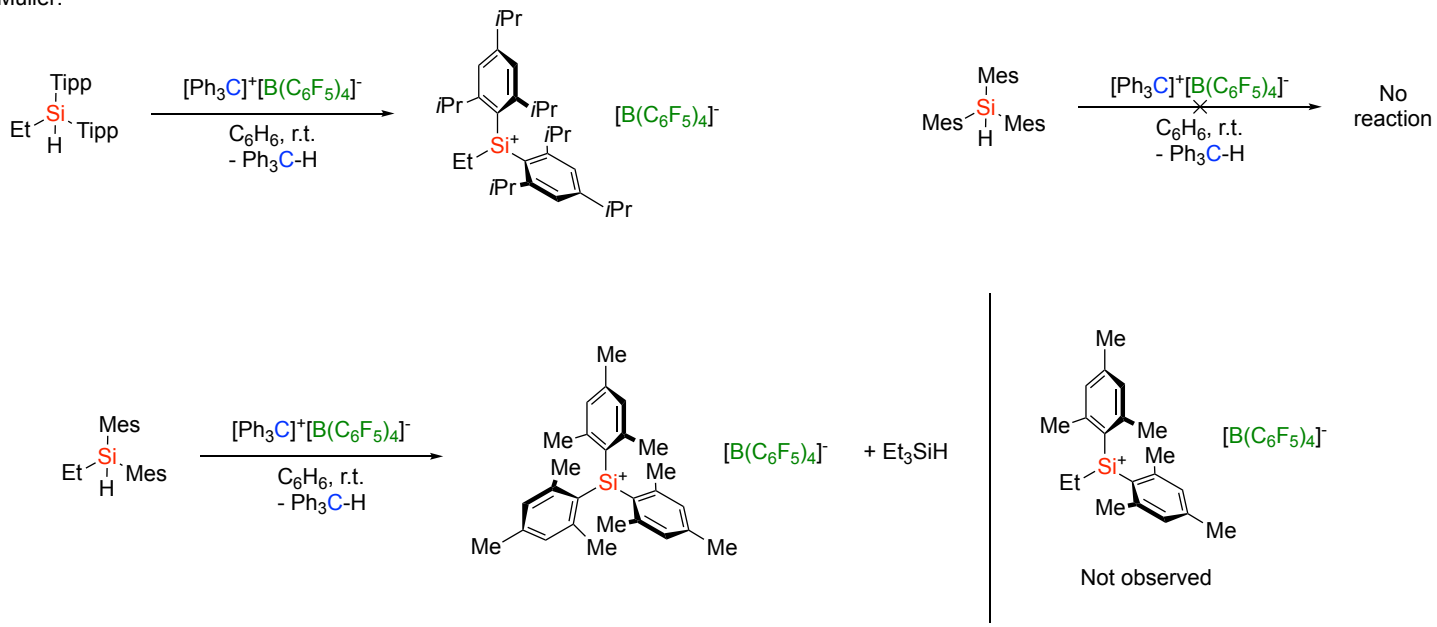
# Structural Considerations



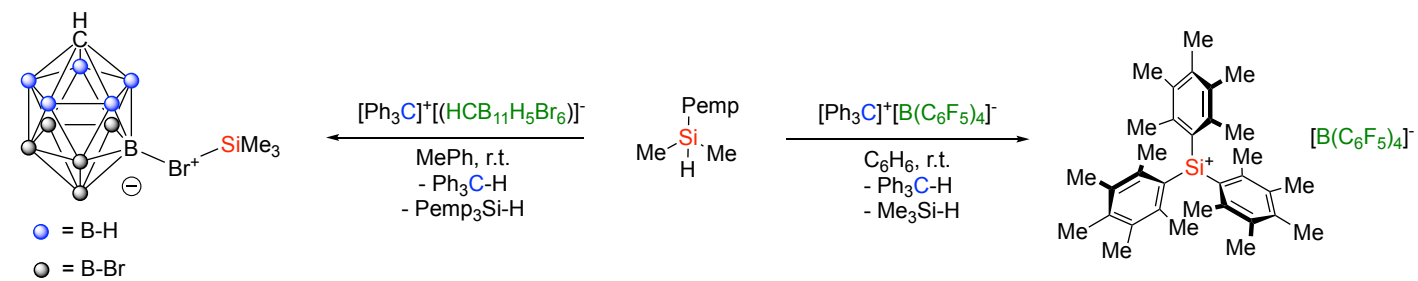

H. F. T. Klare, L. Albers, L. Süsse, S. Keess, T. Müller, and M. Oestreich, Chem. Rev. 2021, 121, 10, 5889–5985

# Substituent Rearrangement

Müller:

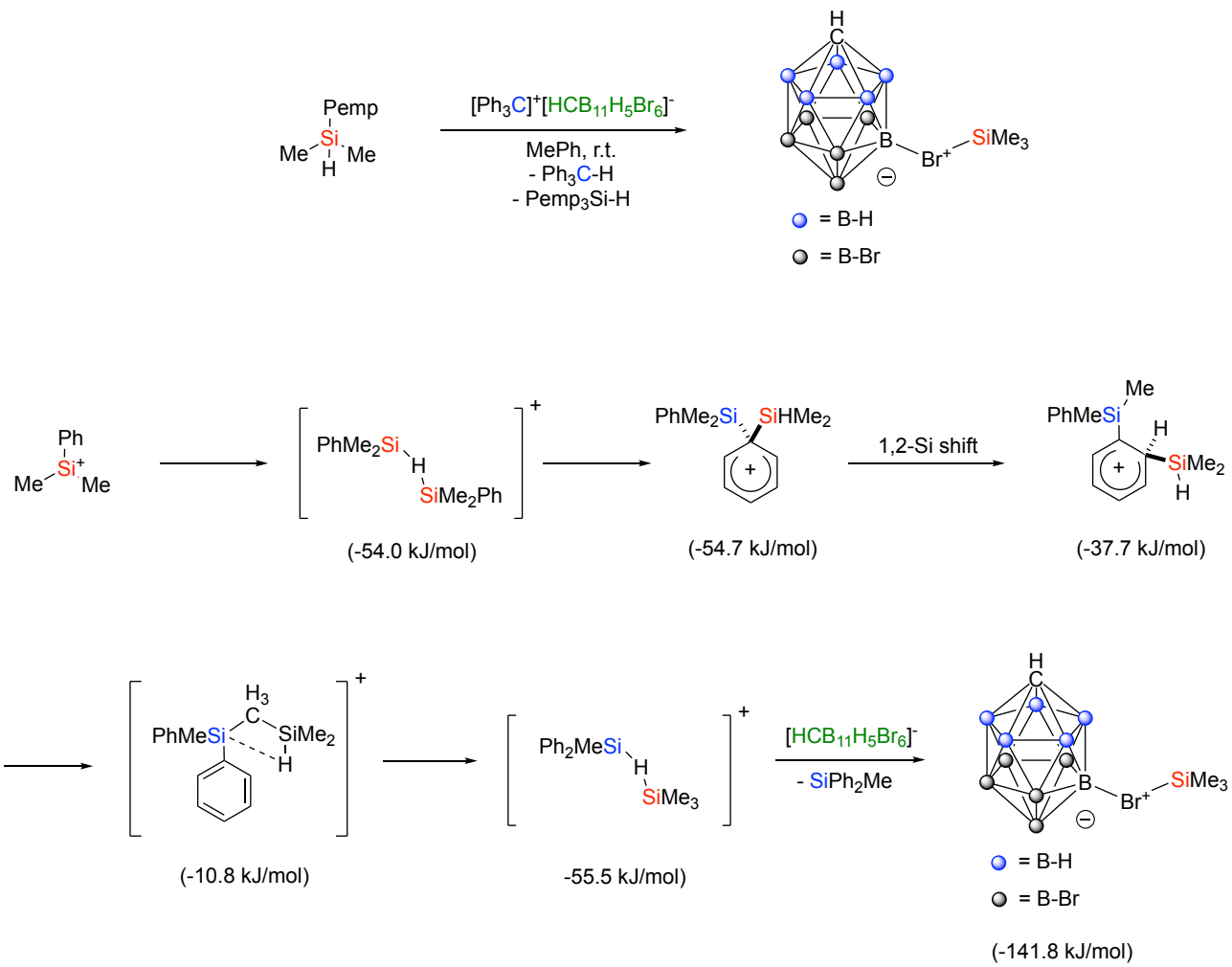



Oestreich:




See citation slide (group 1)

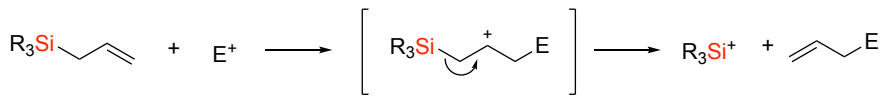
# Substituent Rearrangement



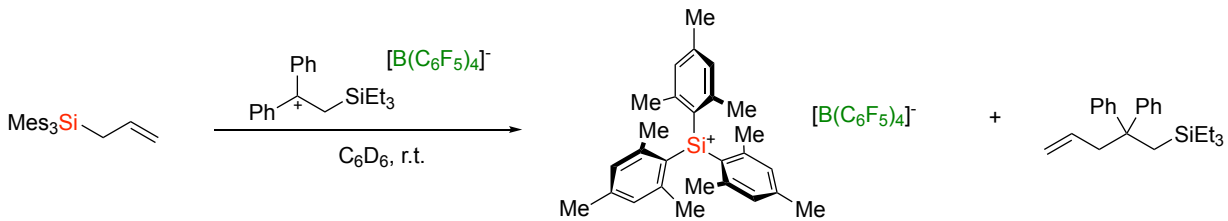

Omann, L.; Pudasaini, B.; Irran, E.; Klare, H. F. T.; Baik, M.-H.; Oestreich, M. Chem. Sci. 2018, 9, 5600−5607

# Silylium Ions – Si-C Bond-Breaking

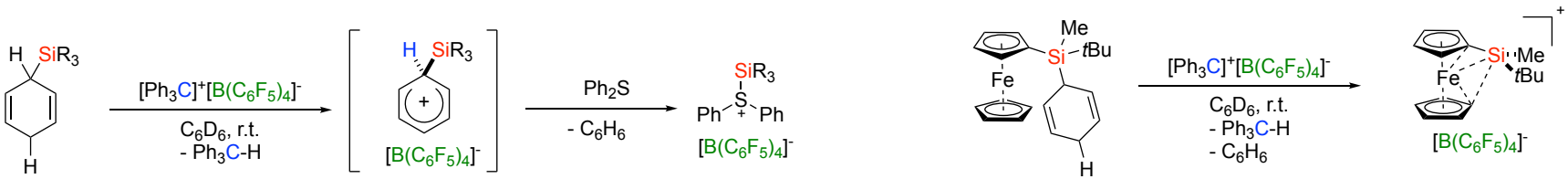
Lambert:




Lambert and Reed:

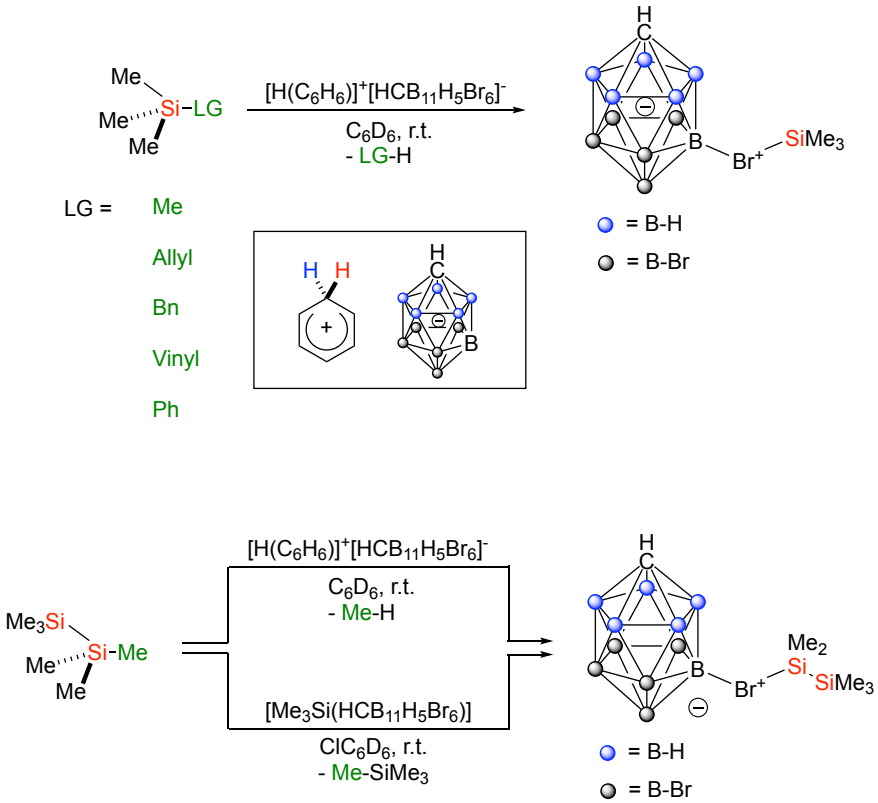


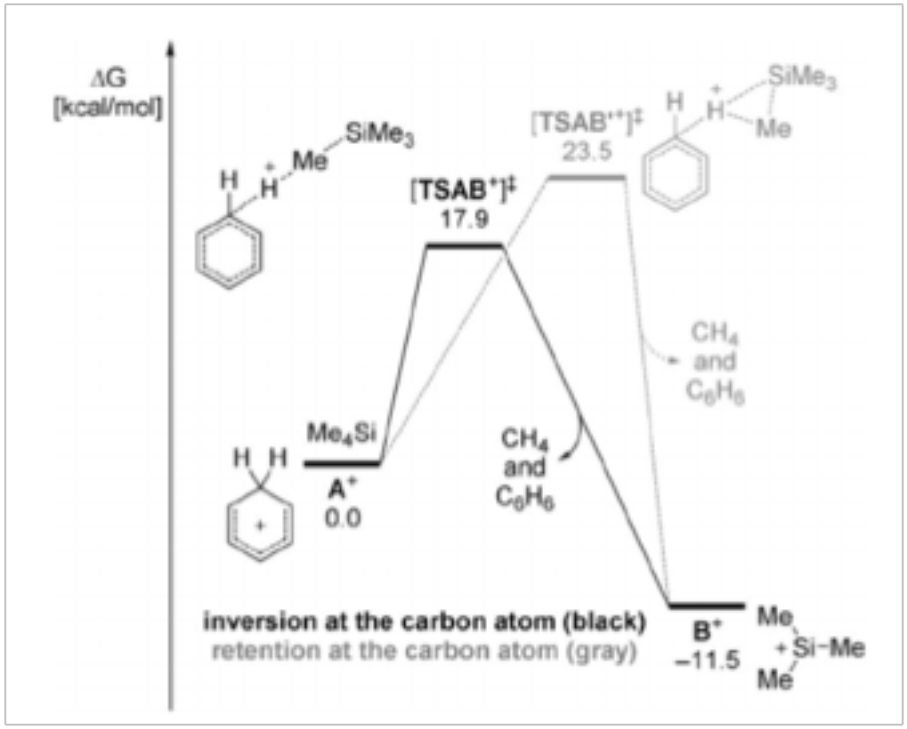

Oestreich:




Lambert, J. B.; Zhao, Y. Angew. Chem., Int. Ed. Engl. 1997, 36, 400−401; Kim, K.-C.; Reed, Lambert, J. B, et al., Science 2002, 297, 825−827; Lambert, J. B, et al., J. Am. Chem. Soc. 1999, 121, 5001−5008; Oestreich, M, et al. Organometallics 2015, 34, 3927−3929

# Silylium Ions – Si-C Bond-Breaking

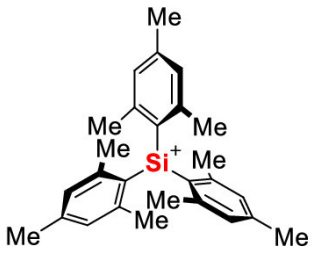



Wu, Q.; Qu, Z.-W.; Omann, L.; Irran, E.; Klare, H. F. T.; Oestreich, M. Angew. Chem., Int. Ed. 2018, 57, 9176–9179; Wu, Q.; Roy, A.; Irran, E.; Qu, Z.-W.; Grimme, S.; Klare, H. F. T.; Oestreich, M.; Angew. Chem., Int. Ed. 2019, 58, 17307–17311

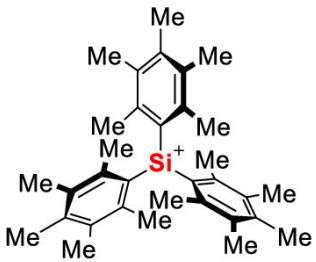
# Silylium Ions – $^{29}$Si Chemical Shifts

♦ **free silylium ions**



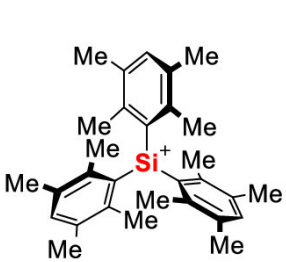
$[B(C_6F_5)_4]^-$

**23a**$^+$ (Refs 78,80)
$\delta$ ($^{29}$Si) 225.5 ppm
($C_6D_6$)



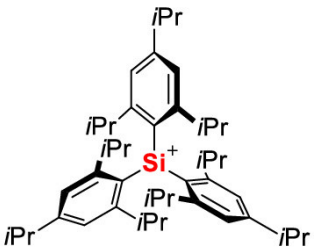
$[B(C_6F_5)_4]^-$

**23b**$^+$ (Refs 81,82)
$\delta$ ($^{29}$Si) 216.2 ppm
($C_6D_6$)



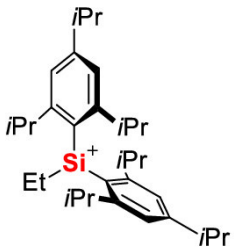
$[B(C_6F_5)_4]^-$

**23c**$^+$ (Ref 79)
$\delta$ ($^{29}$Si) 226.8 ppm
($C_6D_6$)



$[B(C_6F_5)_4]^-$

**23d**$^+$ (Refs 81,82)
$\delta$ ($^{29}$Si) 229.8 ppm
($C_6D_6$)

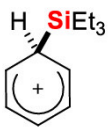


$[B(C_6F_5)_4]^-$

**22a**$^+$ (Refs 81,82)
$\delta$ ($^{29}$Si) 244.7 ppm
($C_6D_6$)

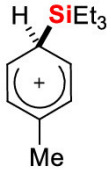
♦ **intermolecular stabilized silylium ions**

solvent-coordinated



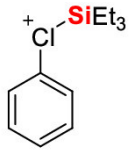
$[B(C_6F_5)_4]^-$

**1b**$^+$ (Refs 30–32)
$\delta$ ($^{29}$Si) 92.3 ppm
($C_6D_6$)



$[B(C_6F_5)_4]^-$

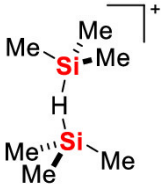
**2b**$^+$ (Refs 30–32)
$\delta$ ($^{29}$Si) 81.8 ppm
($CD_3C_6D_5$)



$[B(C_6F_5)_4]^-$

**3b**$^+$ (Refs 35,37)
$\delta$ ($^{29}$Si) 99.9 ppm
($ClC_6D_5$)

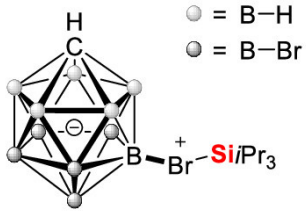
hydrosilane-coordinated



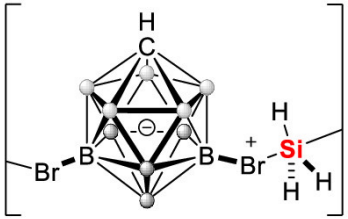
$[HCB_{11}Cl_{11}]^-$

**5a**$^+$ (Ref 34)
$\delta$ ($^{29}$Si) 85.4, 82.2 ppm
(solid-state)

anion-coordinated




**17c** (Refs 43,62,63)
$\delta$ ($^{29}$Si) 109.8 ppm
(solid-state)



**17f** (Ref 118)
$\delta$ ($^{29}$Si) –64.7 ppm
(solid-state)

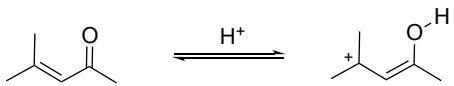
H. F. T. Klare, L. Albers, L. Süsse, S. Keess, T. Müller, and M. Oestreich, Chem. Rev. 2021, 121, 10, 5889–5985

# Brønsted Super-Acids

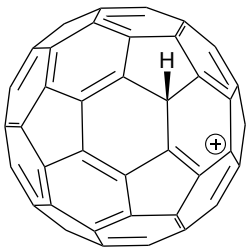
$[Et_3Si\text{-}H\text{-}SiEt_3]$ $[HCB_{11}F_{11}]^-$ —HCl, -196 ˚ to 0 ˚C, - $Et_3SiCl$, - $Et_3SiH$→ $[H(HCB_{11}X_{11})]$

$[Et_3Si(HCB_{11}Cl_{11})]$ —HCl, -196 ˚ to -25 ˚C, - $Et_3SiCl$→ $[H(HCB_{11}Cl_{11})]$

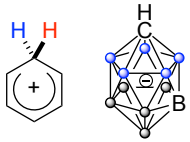
$[(Et_3Si)_2(B_{12}Cl_{12})]$ —HCl (8 equiv.), -196 ˚ to r.t., - 2 $SiCl_4$→ $[H_2(B_{12}Cl_{12})]$

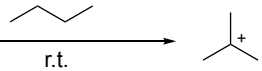


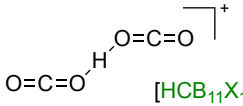

| Acid | $\Delta\delta(^{13}C)$[ppm] | $H_0$ |
|---|---|---|
| $[H(CHB_{11}Cl_{11})]$ | 84.0 | - |
| $[H(CB_{11}H_5Cl_6)]$ | 83.8 | - |
| $[H(CB_{11}H_5Br_6)]$ | 83.8 | - |
| $[H(CB_{11}H_5I_6)]$ | 83.3 | - |
| $FSO_3H$ | 73.8 | -15.1 |
| $CF_3SO_3H$ | 72.9 | -14.1 |
| $H_2SO_4$ | 64.3 | -12.1 |
| none | - | - |



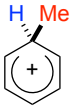

1 equiv.
$[H(CB_{11}H_6Cl_6)]$
Dilute 1,6-$Cl_2C_6H_4$




$[H(HCB_{11}X_{11})]$ —r.t., - $H_2$→  $[HCB_{11}X_{11}]^-$

$[H(HCB_{11}X_{11})]$ —2 $CO_2$, -196 ˚C to r.t.→  $[HCB_{11}X_{11}]^-$



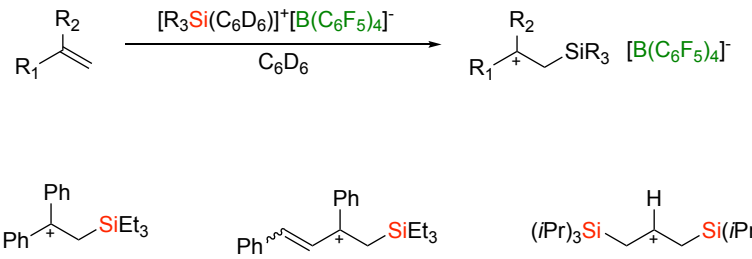
$[Me(HCB_{11}Me_5Br_6)]$ —$C_6H_6$, r.t.→  $[HCB_{11}Me_5Br_6]^-$



$[Me(HCB_{11}Me_5Br_6)]$ —r.t., -$CH_4$→  $[HCB_{11}Me_5Br_6]^-$

See citation slide (group 2)

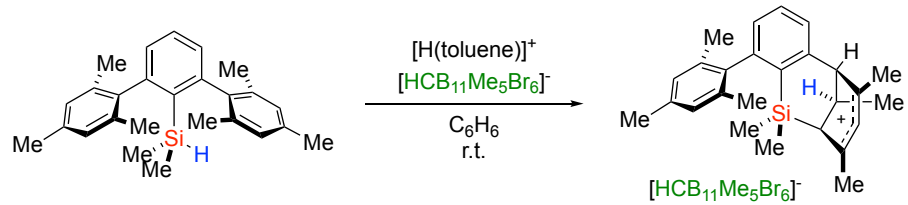
# β-Silyl Carbocations



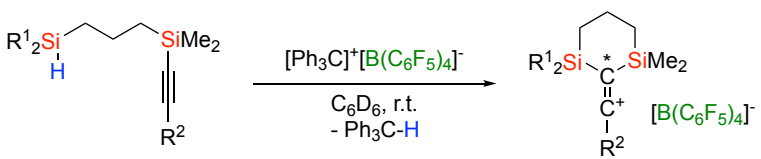

δ($^{13}$C) 225.4 ppm
δ($^{29}$Si) 46.2ppm

δ($^{13}$C) 235.7, 193.7 ppm
δ($^{29}$Si) 34.2, 28.5 ppm

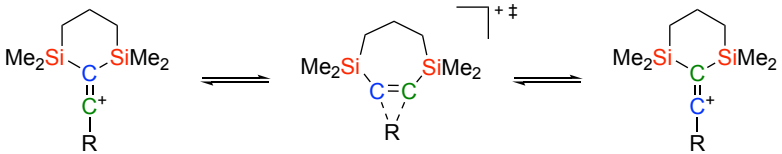
δ($^{13}$C) 229.0 ppm
δ($^{29}$Si) 49.6 ppm




93% Yield (X-ray)
δ($^{13}$C) 225.2, 196.9 ppm
δ($^{29}$Si) -4.2 ppm



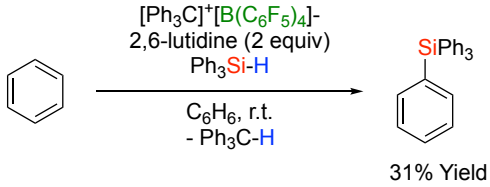

δ($^{13}$C$^{+}$) 178-205 ppm
δ($^{13}$C*) 70-90 ppm
δ($^{29}$Si) 12-29 ppm

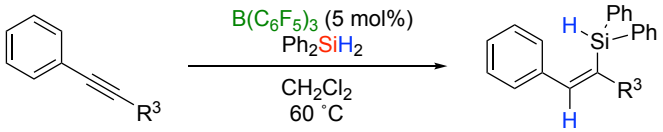


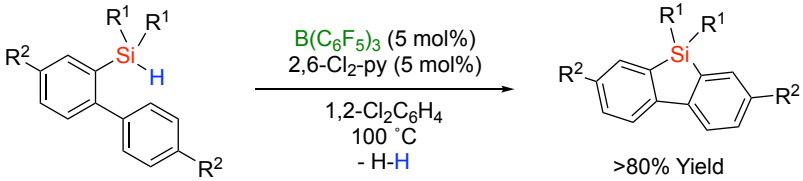

R = $SiMe_3$, $SiMe\mathit{t}Bu_3$, $Si\mathit{i}Pr_3$, $Si(SMe_3)_3$, $GeMe_3$, $Ge\mathit{i}Pr_3$

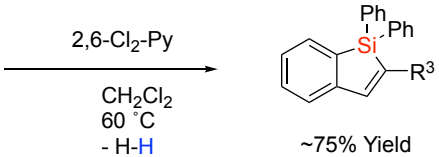
Lambert, J. B.; Zhao, Y. A J. Am. Chem. Soc. 1996, 118, 7867−7868.; Lambert, J. B.; Zhao, Y.; Wu, H. J. Org. Chem. 1999, 64, 2729−2736.; Lambert, J. B.; Liu, C.; Kouliev, T. J. Phys. Org. Chem. 2002, 15, 667−671; Reed, C., et al. Angew. Chem., Int. Ed. 2009, 48, 3787−3790. Müller, T.; Meyer, R.; Lennartz, D.; Siehl, H.-U. Angew. Chem., Int. Ed. 2000, 39, 3074−3077.

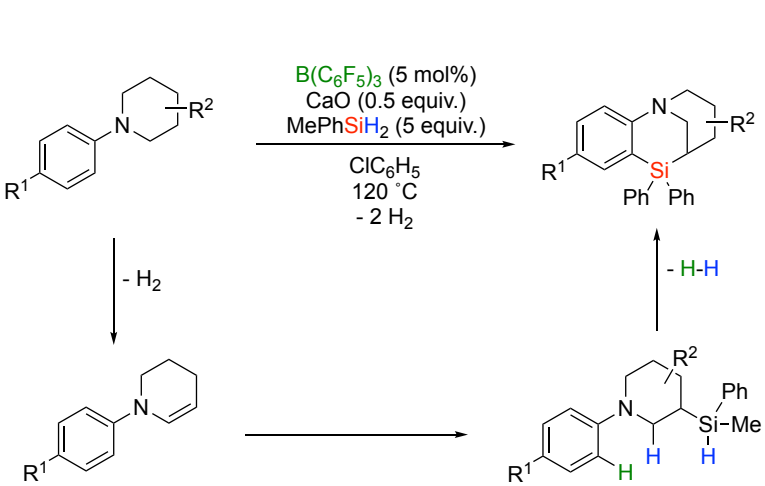
# Sila-Friedel-Crafts

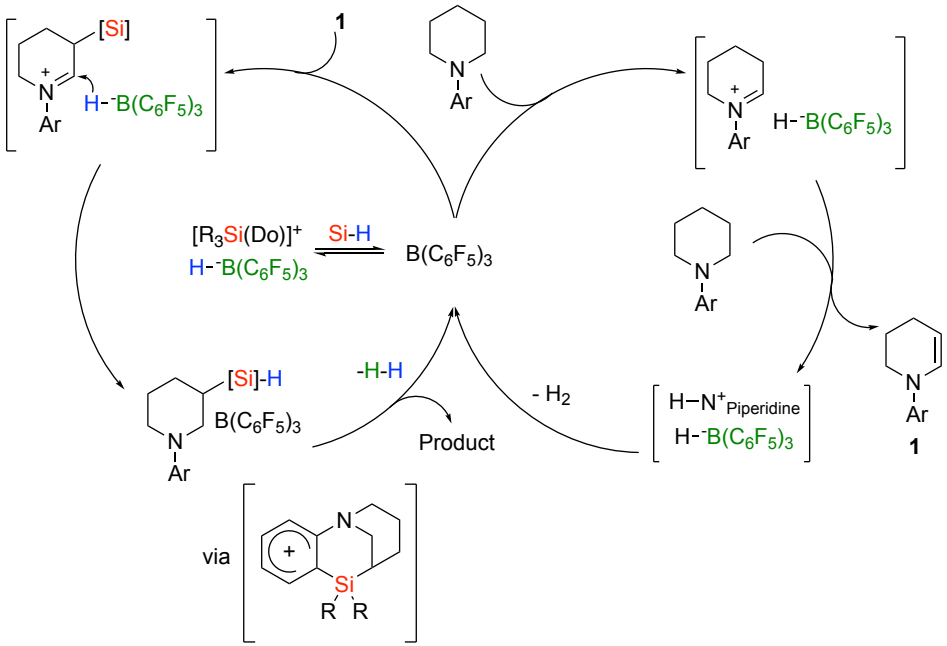


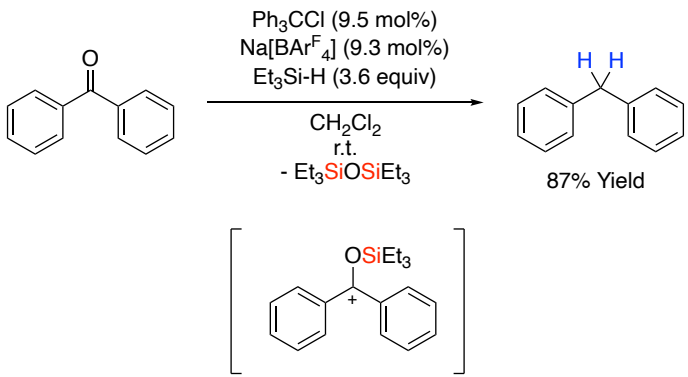



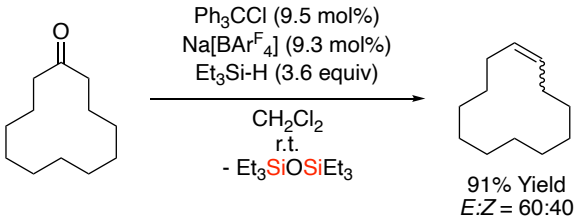



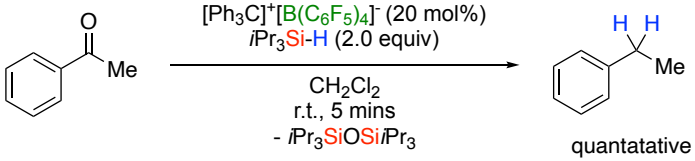

Furukawa, S.; Kobayashi, J.; Kawashima, T. Dalton Trans. 2010, 39, 9329–9336; Curless, L. D.; Ingleson, M. J. Organometallics 2014, 33, 7241–7246; Zhang, J.; Park, S.; Chang, S. J. Am. Chem. Soc. 2018, 140, 13209–13213

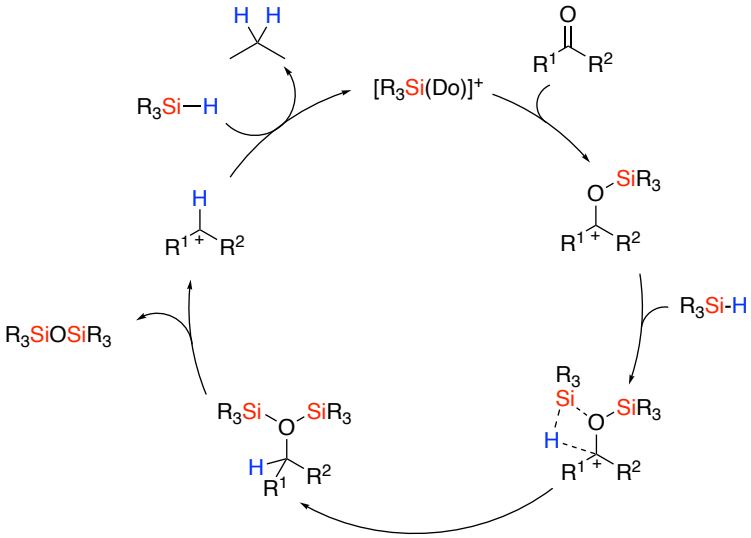
# Silylium Ion Decarboxylation

Kira and Sakurai:



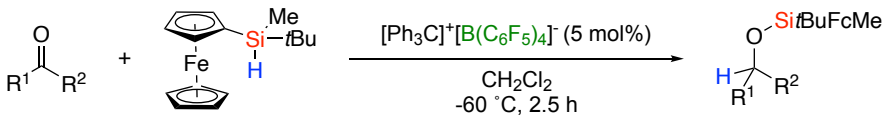



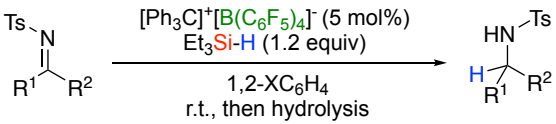



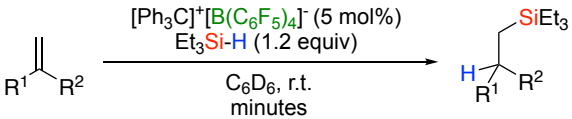



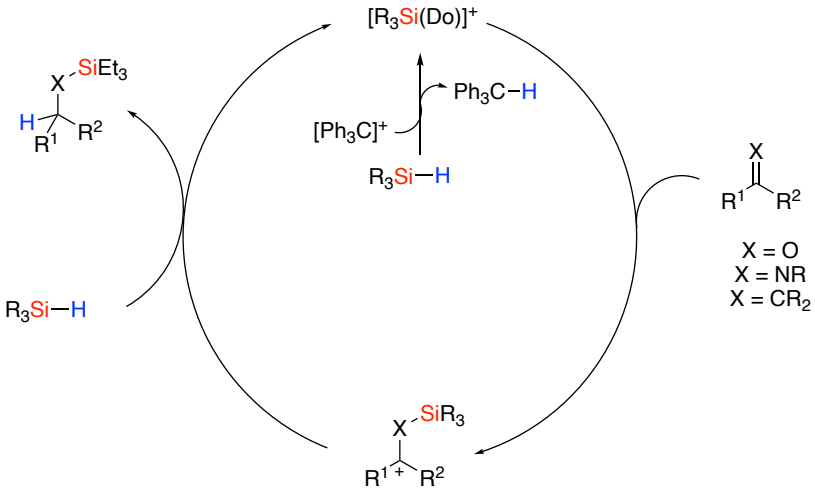

Kira, M.; Hino, T.; Sakurai, H. Chem. Lett. 1992, 21, 555−558; Parks, D. J.; Blackwell, J. M.; Piers, W. E., J. Org. Chem. 2000, 65, 3090−3098;

# Hydrosilation of Dobule Bonds



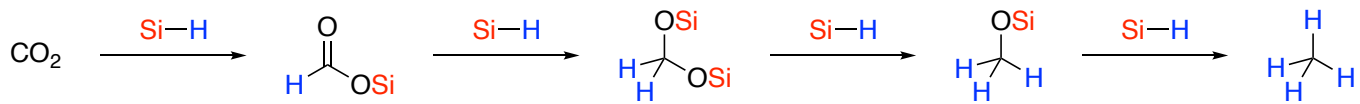



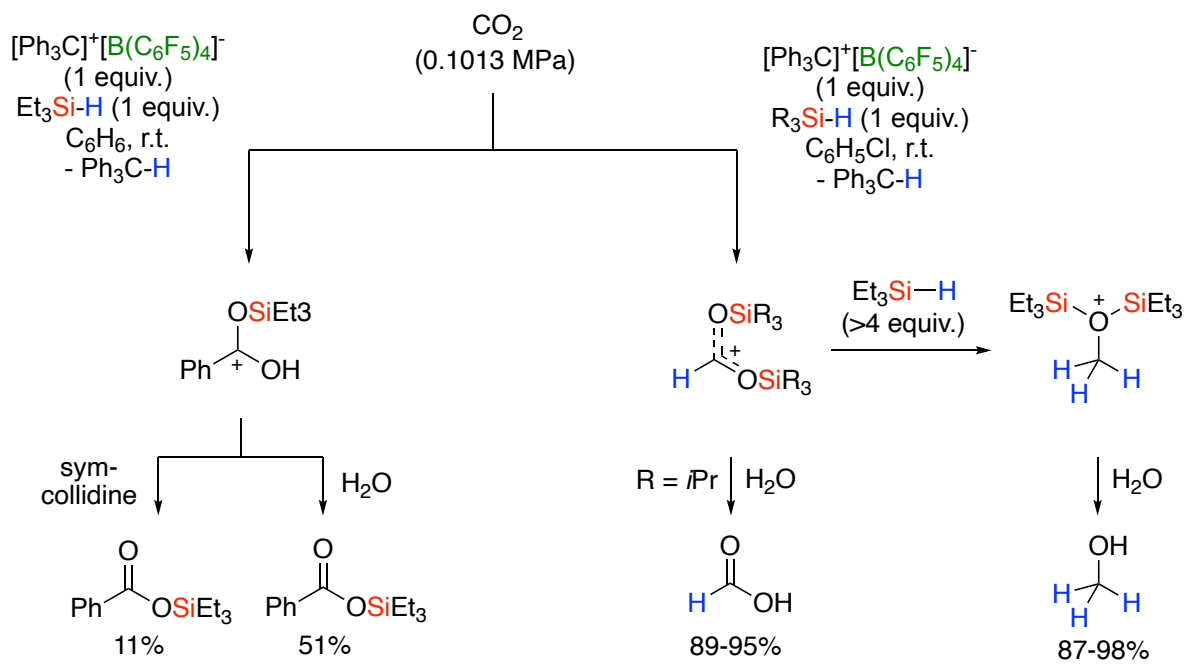




Müther, K.; Oestreich, M., Chem. Commun. 2011, 47, 334−336.; Müther, K.; Mohr, J.; Oestreich, M. Organometallics 2013, 32, 6643−6646;

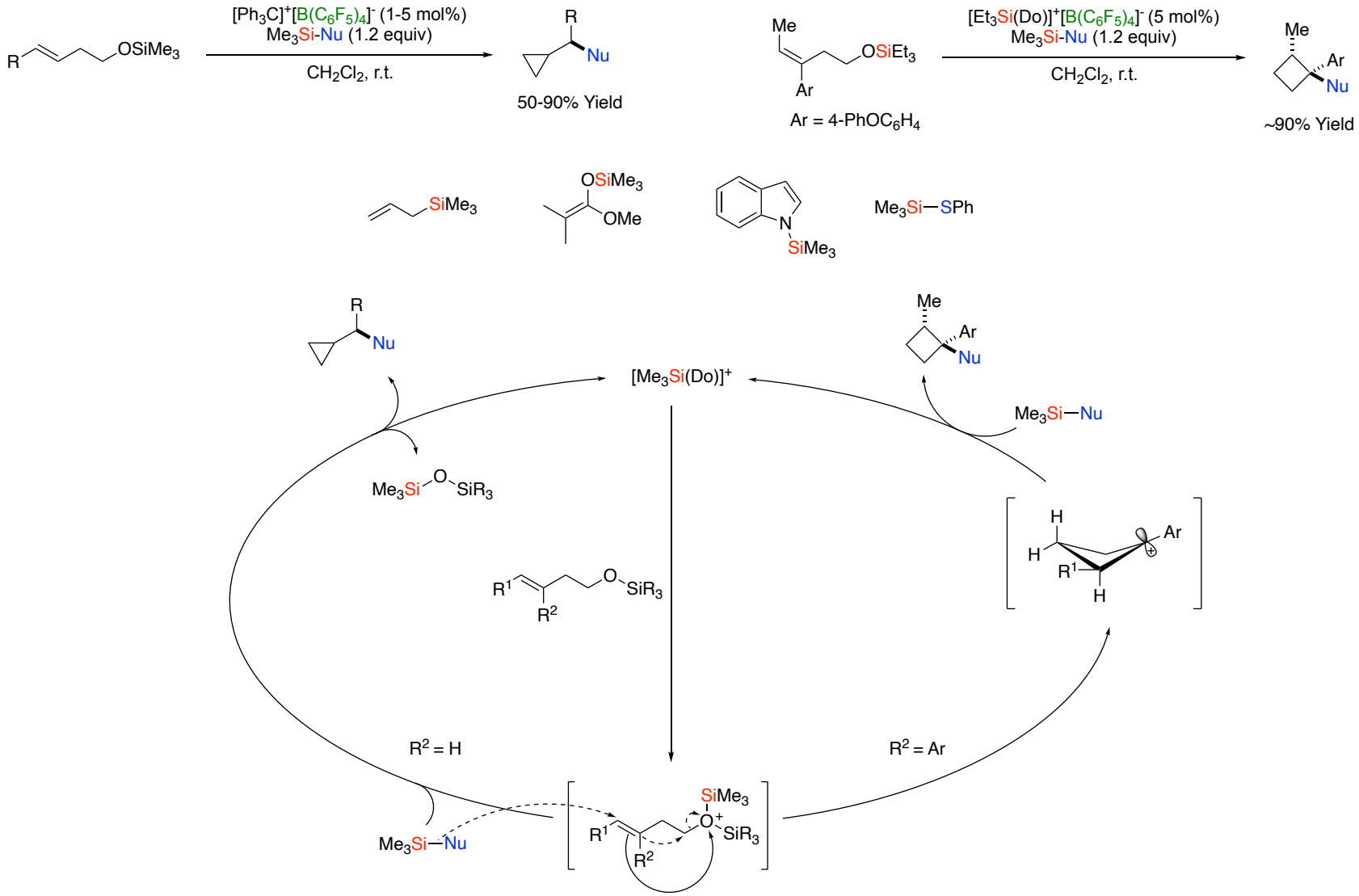
# Reduction of $CO_2$



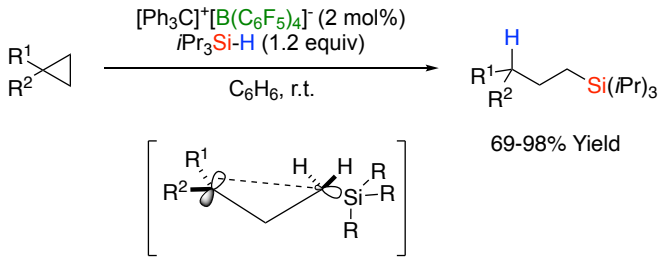

Schäfer, A.; Saak, W.; Haase, D.; Müller, T., Angew. Chem., Int. Ed. 2012, 51, 2981–2984.

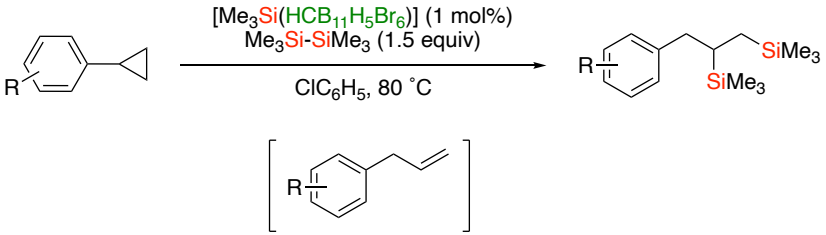
# Strain Introducing Reactions

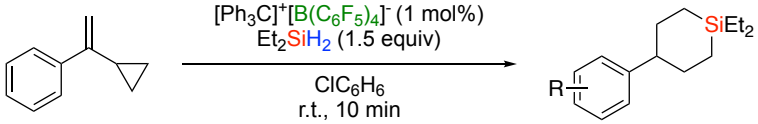


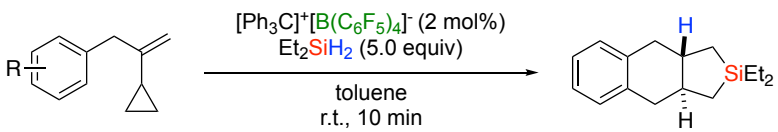

Zhang, J.; Hazra, C. K.; Park, S.; Chang, S., Asian J. Org. Chem. 2019, 8, 1637−1640

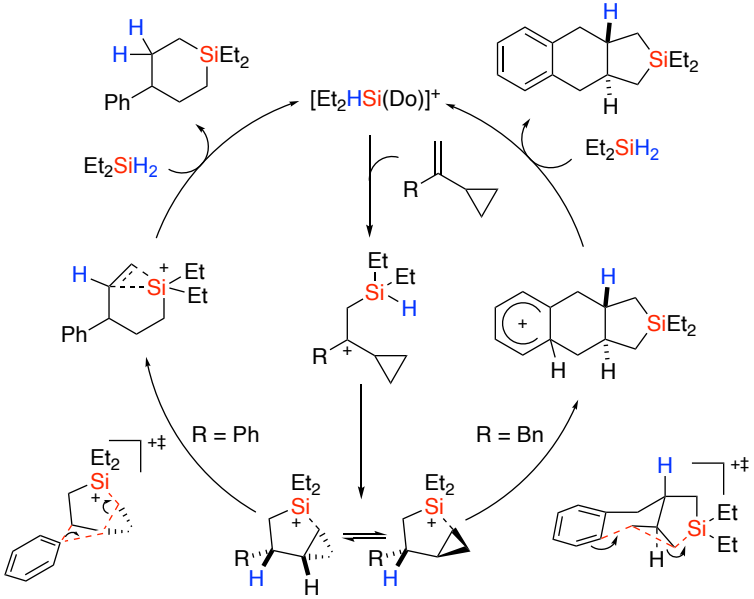
# Ring Cleavage Reactions



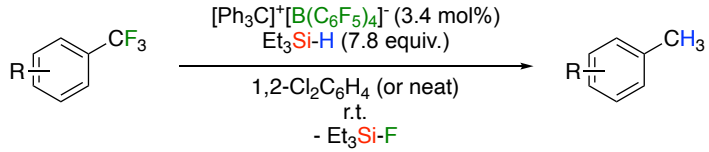



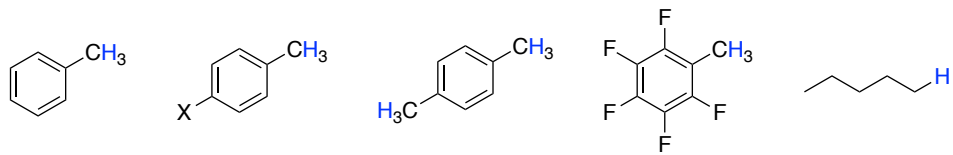



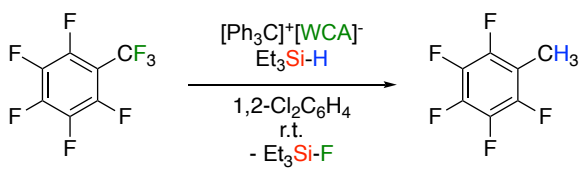

Oestreich, M., et al., Org. Lett. 2020, 22, 1213−1216; Oestreich, M., et al, Angew. Chem., Int. Ed. 2020, 59, 12186−12191; He, T.; Oestreich, M., et al, Chem. Sci. 2021, 12, 569−575

# Hydrodefluorination (HDF)

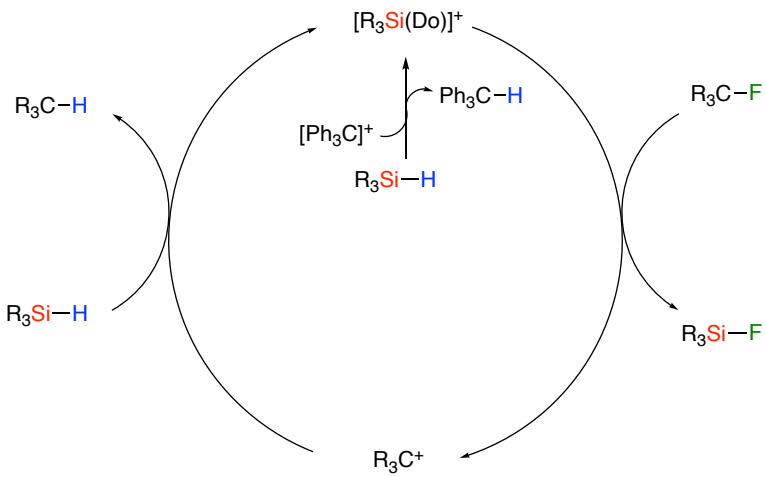


>99% >99% >77% 33% >99%

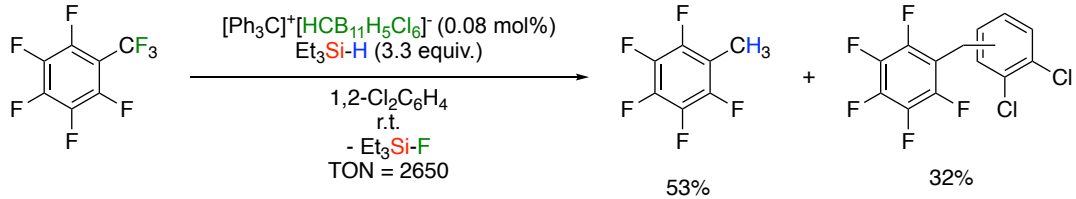


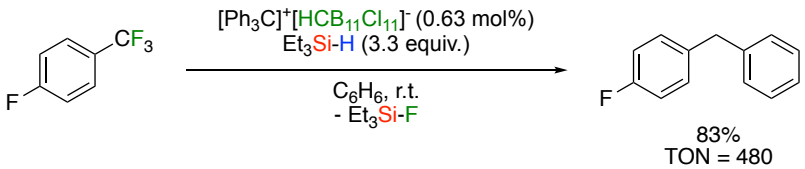

| $[Ph_3C]^+$ $[B(C_6F_4)_4]^-$ (4.7 mol%) decomp. after TON = 19 | $[Ph_3C]^+$ $[HCB_{11}H_5Br_6]^-$ (0.11 mol%) TON = 220 after 1h | $[Ph_3C]^+$ $[HCB_{11}H_5Cl_6]^-$ (0.11 mol%) TON = 880 after 1h | $[Ph_3C]^+$ $[HCB_{11}Cl_{11}]^-$ (0.11 mol%) TON = 370 after 1h | $[Ph_3C]^+$ $[B_{12}Cl_{12}]^{2-}$ (0.16 mol%) TON = 110 after 1h |
|---|---|---|---|---|

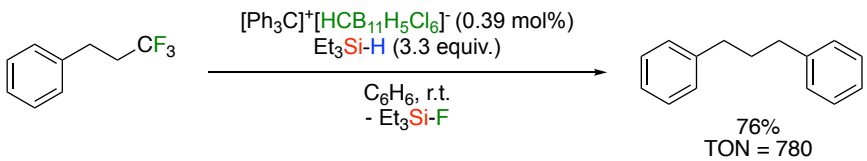


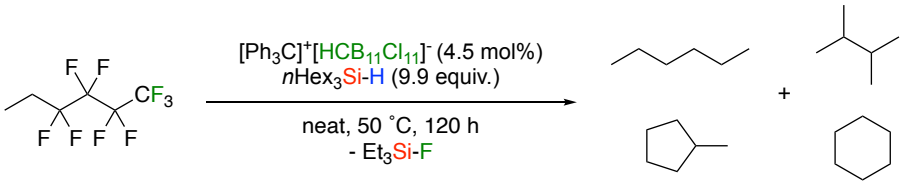

Scott, V. J.; Çelenligil-Çetin, R.; Ozerov, O. V. J. Am. Chem. Soc. 2005, 127, 2852–2853; H. F. T. Klare, L. Albers, L. Süsse, S. Keess, T. Müller, and M. Oestreich, Chem. Rev. 2021, 121, 10, 5889–5985

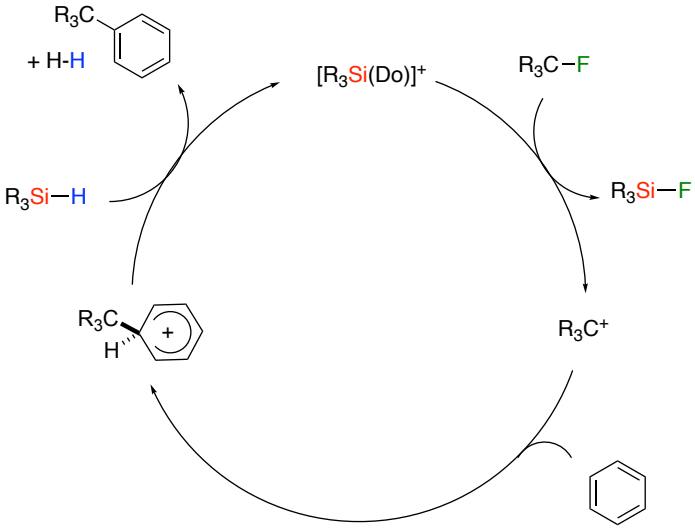
# Hydrodefluorination (HDF)



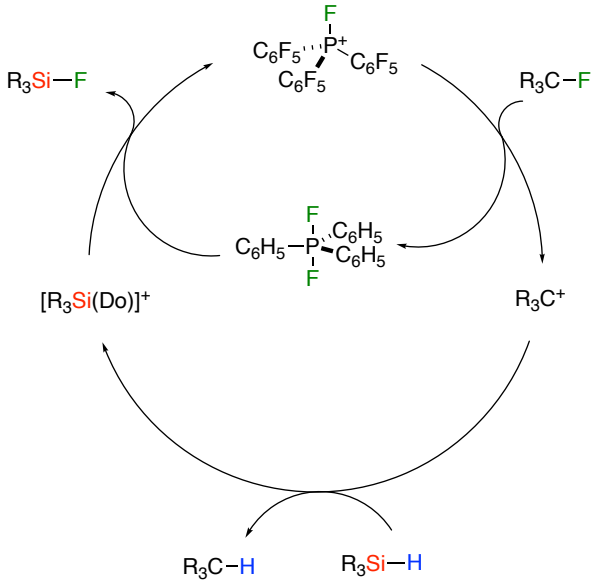



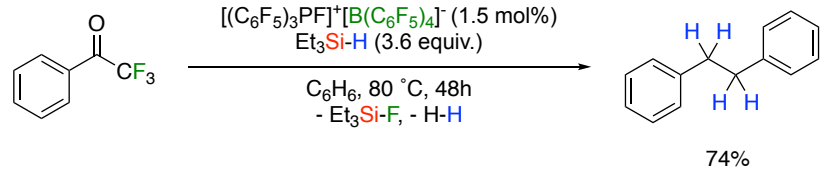



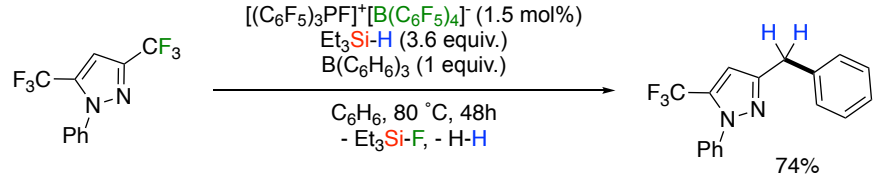



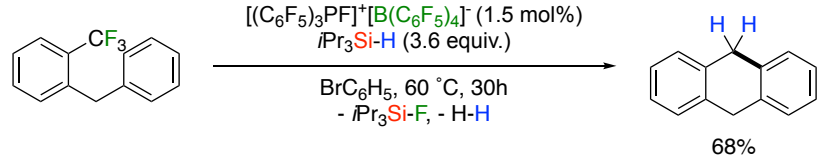

Douvris, C.; Ozerov, O. V. Science 2008, 321, 1188−1190; Douvris, C.; Nagaraja, C. M.; Chen, C.-H.; Foxman, B. M.; Ozerov, O. V. , J. Am. Chem. Soc. 2010, 132, 4946−4953

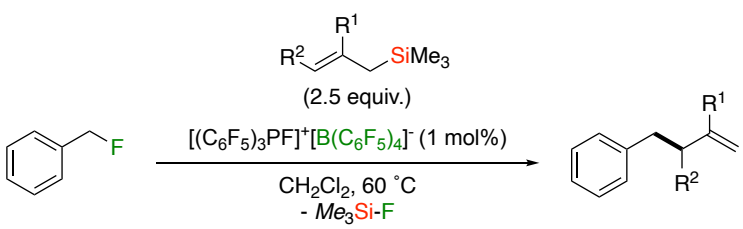
# Merging HDF and Sila-Friedel-Crafts

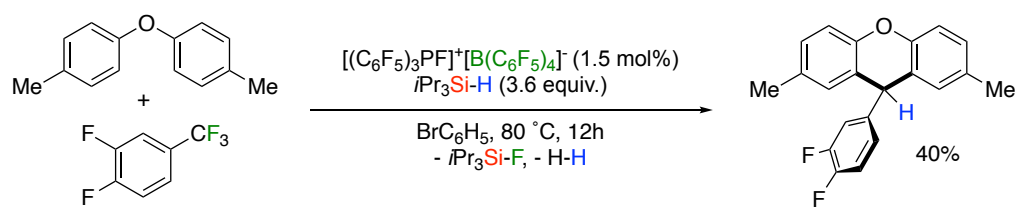
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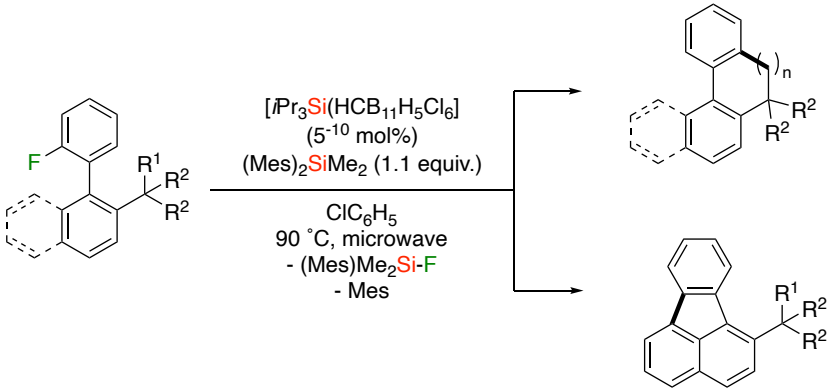
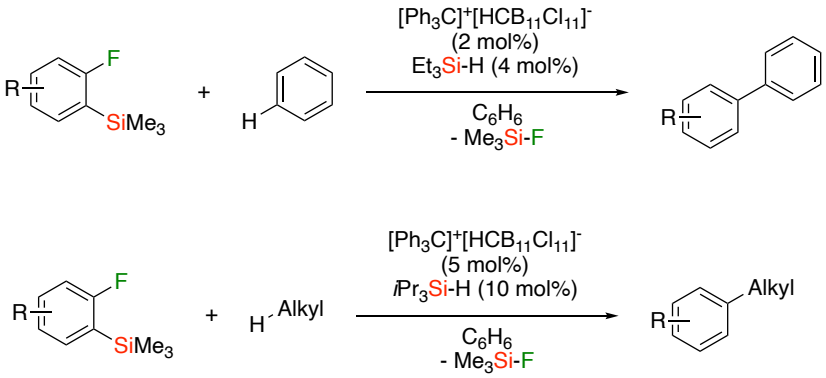
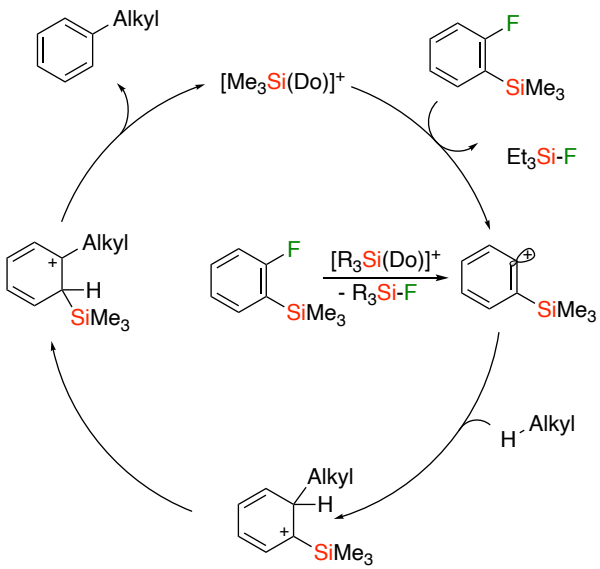
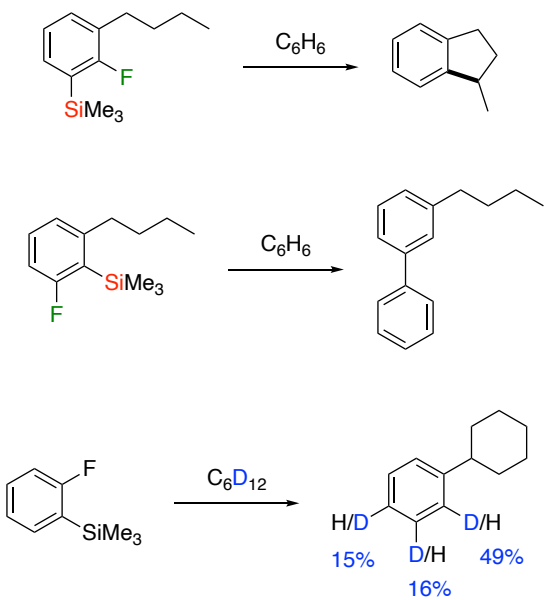
# Coupling of Non-Activated Aryl Fluorides

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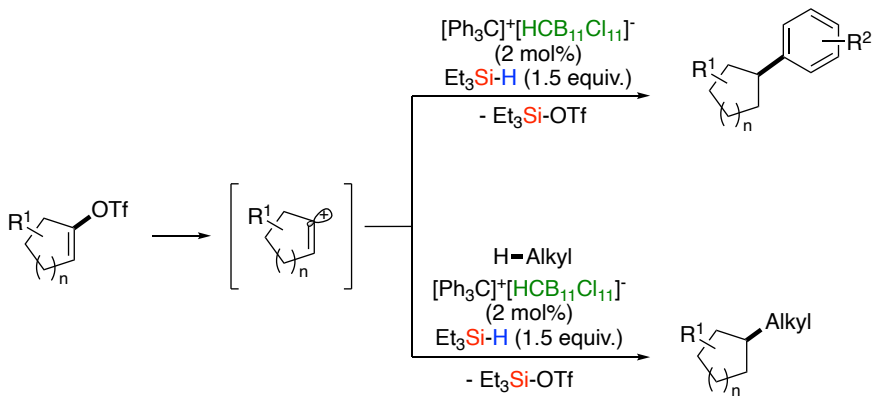
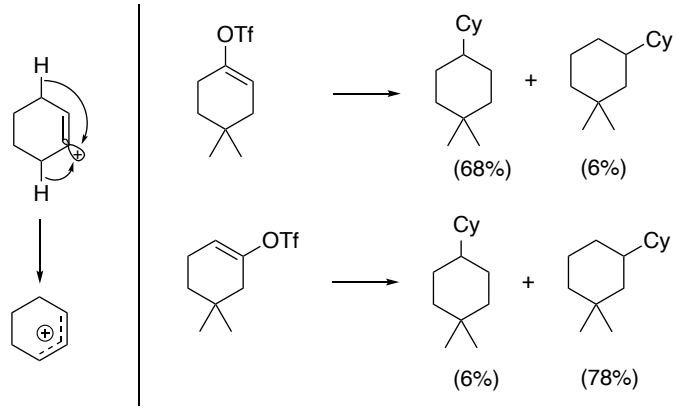
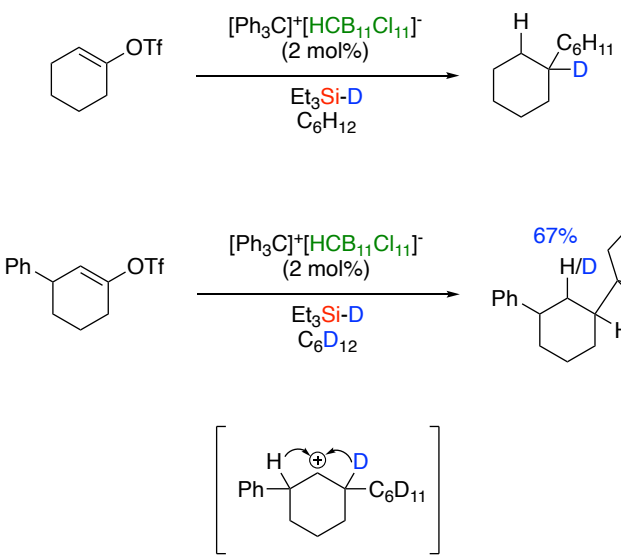
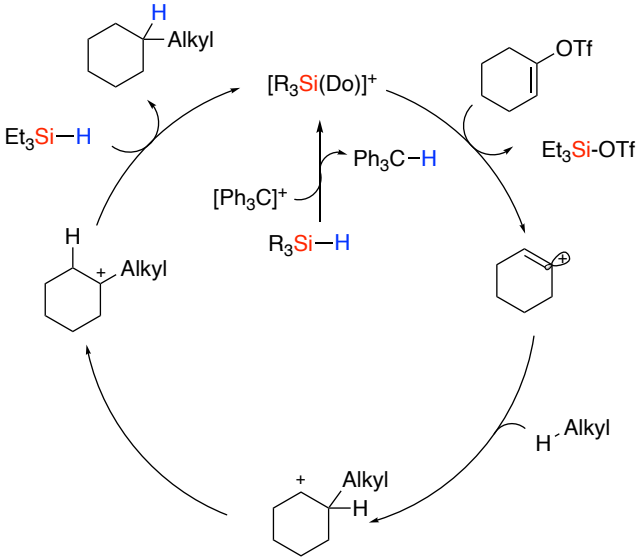
# Vinyl Triflate Couplings

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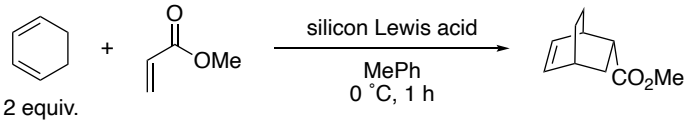
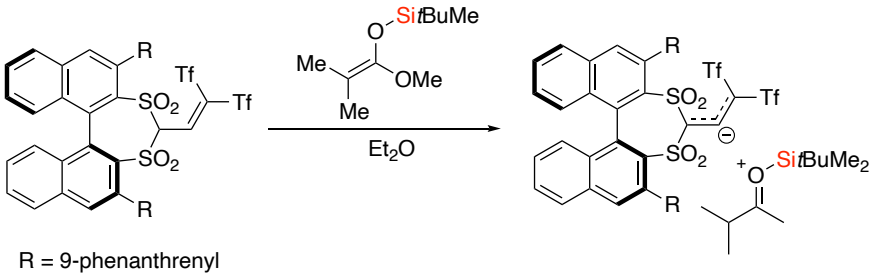
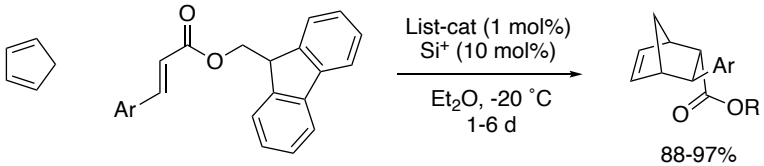
# Silylium Ion Catalyzed Diels-Alder



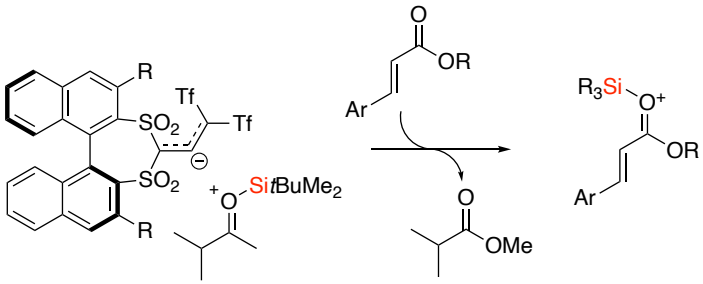

| $Me_3SiOTf$ (10 mol%) | $Me_3SiNTf_2$ (10 mol%) | $[Et_3Si(toluene)]^+[B(C_6F_5)_4]^-$ (1 mol%) |
|---|---|---|
| $\delta(^{29}Si)$ 43.5 ppm (neat) | $\delta(^{29}Si)$ 55.9 ppm (neat) | $\delta(^{29}Si)$ 81.8 ppm (toluene-$d_8$) |
| 0% | 92%, *endo:exo* = 98:2 | 97%, *endo:exo* = 98:2 |

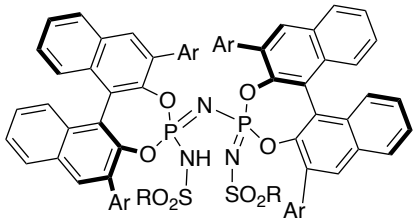



R = 9-phenanthrenyl

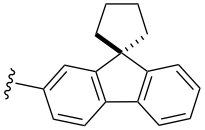



88-97%
d.r. > 95:5
85-94% ee

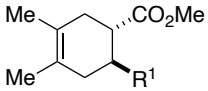



Ar =

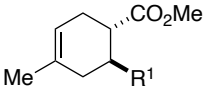


R = $C_6F_{13}$



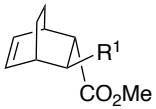

$R^1 = CH_2CH_2Ph$
82%, 84% ee

$R^1$ = Ph
55%, 92% ee




$R^1 = CH_2CH_2Ph$
99%, 94% ee, rs > 98:2

$R^1$ = Ph
71%, 96% ee, rs > 98:2




$R^1 = CH_2CH_2Ph$
99%, 94% ee, d.r. = 93:7

$R^1$ = Ph
< 20% conversion

H. F. T. Klare, L. Albers, L. Süsse, S. Keess, T. Müller, and M. Oestreich, Chem. Rev. 2021, 121, 10, 5889–5985; List, B., et al., Science 2016, 351, 949−952.; List, B., et al., J. Am. Chem. Soc. 2018, 140, 12671−12676

# Additional Reading

CHEMICAL REVIEWS

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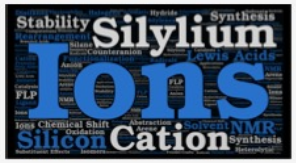
## Silylium Ions: From Elusive Reactive Intermediates to Potent Catalysts

Hendrik F. T. Klare,* Lena Albers, Lars Süsse, Sebastian Keess, Thomas Müller,* and Martin Oestreich*

Cite This: *Chem. Rev.* 2021, 121, 5889–5985 Read Online



**ABSTRACT:** The history of silyl cations has all the makings of a drama but with a happy ending. Being considered reactive intermediates impossible to isolate in the condensed phase for decades, their actual characterization in solution and later in solid state did only fuel the discussion about their existence and initially created a lot of controversy. This perception has completely changed today, and silyl cations and their donor-stabilized congeners are now widely accepted compounds with promising use in synthetic chemistry. This review provides a comprehensive summary of the fundamental facts and principles of the chemistry of silyl cations, including reliable ways of their preparation as well as their physical and chemical properties. The striking features of silyl cations are their enormous electrophilicity and as such reactivity as super Lewis acids as well as fluorophilicity. Known applications rely on silyl cations as reactants, stoichiometric reagents, and promoters where the reaction success is based on their steady regeneration over the course of the reaction. Silyl cations can even be discrete catalysts, thereby opening the next chapter of their way into the toolbox of synthetic methodology.

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**Review**

## THE SILICONIUM ION QUESTION

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(Received January 7th, 1974)

*Chem. Rev.* **1995**, *95*, 1191–1201

## Modern Approaches to Silylium Cations in Condensed Phase

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**Group 2:** Reed, C. A. Acc. Chem. Res. 2010, 43, 121−128; Juhasz, M.; Hoffmann, S.; Stoyanov, E.; Kim, K.-C.; Reed, C. A.; Angew. Chem., Int. Ed. 2004, 43, 5352− 5355.; Nava, M.; Stoyanova, I. V.; Cummings, S.; Stoyanov, E. S.; Reed, C. A. Angew. Chem., Int. Ed. 2014, 53, 1131−1134., Boeré, R. T.; Kacprzak, S.; Keßler, M.; Knapp, C.; Riebau, R.; Riedel, S.; Roemmele, T. L.; Rühle, M.; Scherer, H.; Weber, S. Angew. Chem., Int. Ed. 2011, 50, 549−552.; Cummings, S.; Hratchian, H. P.; Reed, C. A. Angew. Chem., Int. Ed. 2016, 55, 1382−1386.; Kato, T.; Stoyanov, E.; Geier, J.; Grützmacher, H.; Reed, C. A. J. Am. Chem. Soc. 2004, 126, 12451−12457; Kato, T.; Reed, C. A. Angew. Chem., Int. Ed. 2004, 43, 2908−2911