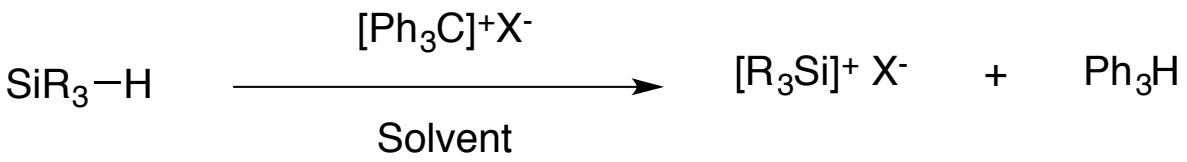
# Arylation of Hydrocarbons Enabled by Organosilicon Reagents and Weakly Coordinating Anions

B. Shoa, A.L. Bagdasarian, S. Popov, H.M. Nelson *Science.* **2017***, 355,*1403-1407.

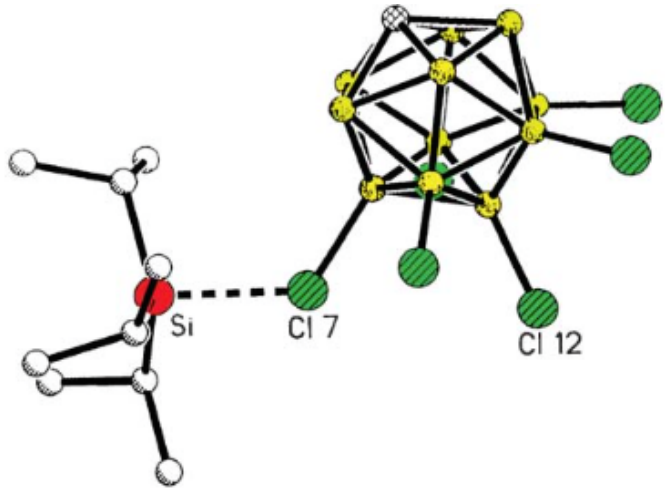
04/15/17

Mike Frasso

# Generation of $R_3Si^+$




- $X^-$ : Halocarbaboranes, $(F_5C_6)_4B^-$
  - Chlorocarbaboranes least coordinating

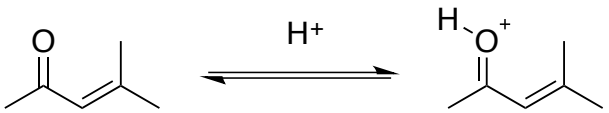



*J. Am. Chem. Soc.* **1996**, *118*, 2922-2298
*Chem. Com.* **2005**, 1669-1677

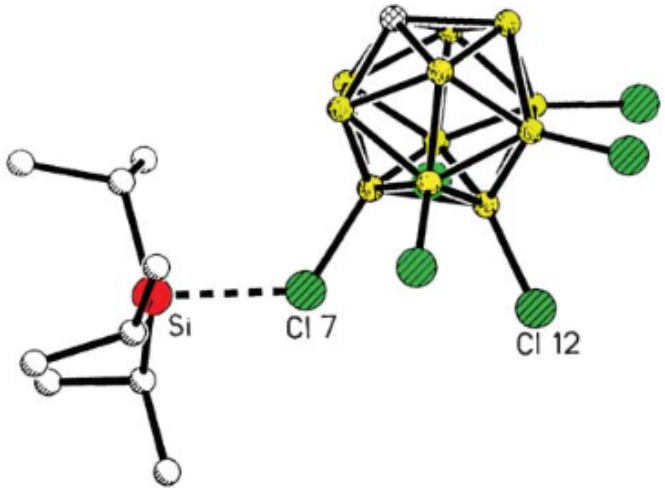
# Generation of $R_3Si^+$

$$SiR_3{-}H \xrightarrow[\text{Solvent}]{[Ph_3C]^+X^-} [R_3Si]^+ X^- + Ph_3H$$

- $X^-$ : Halocarbaboranes, $(F_5C_6)_4B^-$
  - Chlorocarbaborane least coordinating
  - Corresponding carbaborane acid strength: mesityl oxide method; compare $\alpha$, $\beta$ $^{13}C$ shifts

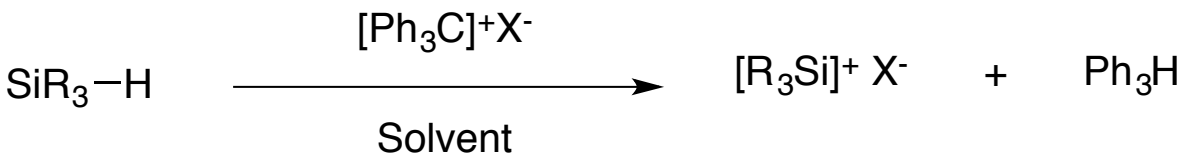



| $H^+$ | $\Delta\delta^{13}C$ |
|---|---|
| None | 32.4 |
| Sulfuric acid | 64.3 |
| Triflic acid | 72.9 |
| Fluorosulfuric acid | 73.8 |
| $H(CHB_{11}Cl_{11})$ | 84.0 |

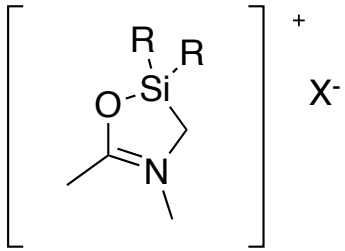


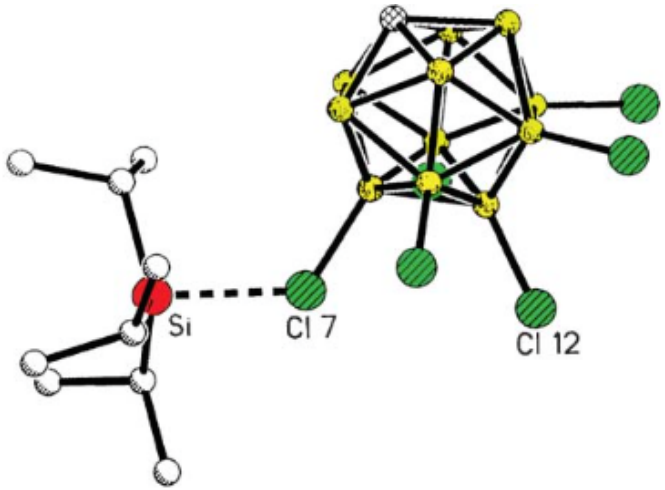

*J. Am. Chem. Soc.* **1996**, *118*, 2922-2298
*Chem. Com.* **2005**, 1669-1677

# Generation of $R_3Si^+$




- $X^-$ : Halocarbaboranes, $(F_5C_6)_4B^-$
  - Chlorocarbaboranes least coordinating
- Solvent: benzene, halobenzenes, stabilized derivatives in $CH_2Cl_2$
  - ex.

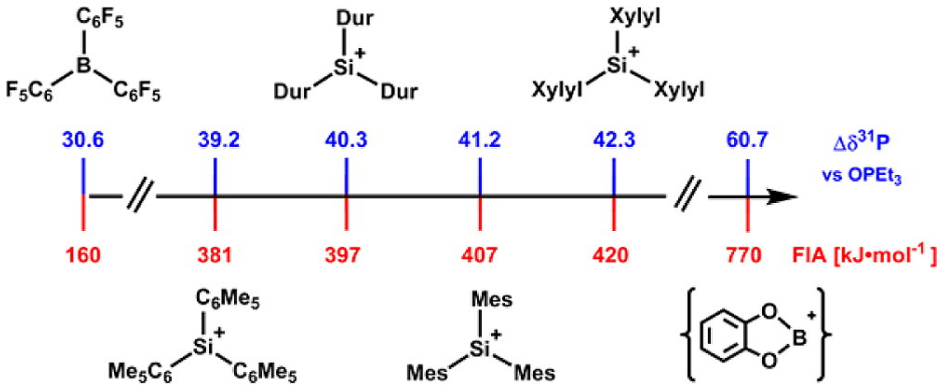


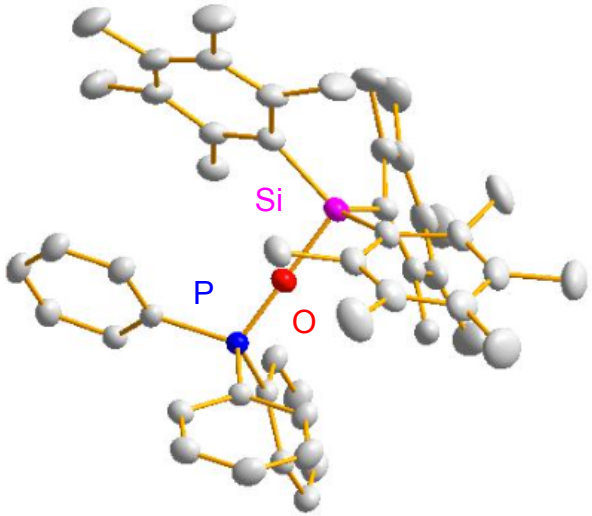




*J. Am. Chem. Soc.* **1996**, *118*, 2922-2298
*Chem. Com.* **2005**, 1669-1677

# Lewis Acidity of $R_3Si^+$

- Determined using Gutmann-Beckett method
- Complex Lewis acid with $OPEt_3$, measure $\Delta\delta^{31}P$
- As $\pi$ conjugation increases, Lewis acidity decreases
  - $\Delta\delta^{31}P$ = 41.2, 44.9 in $(Mes)_3Si^+$ vs $(Tipp)_3Si^+$
  - C-Si bond ~25% longer than C-C bond

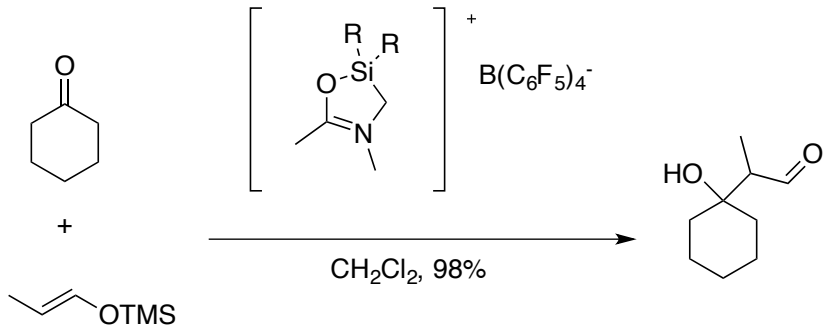


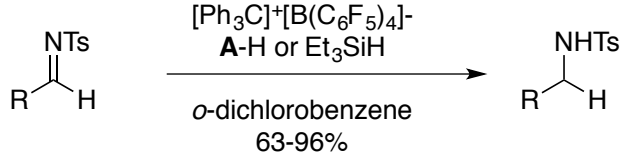



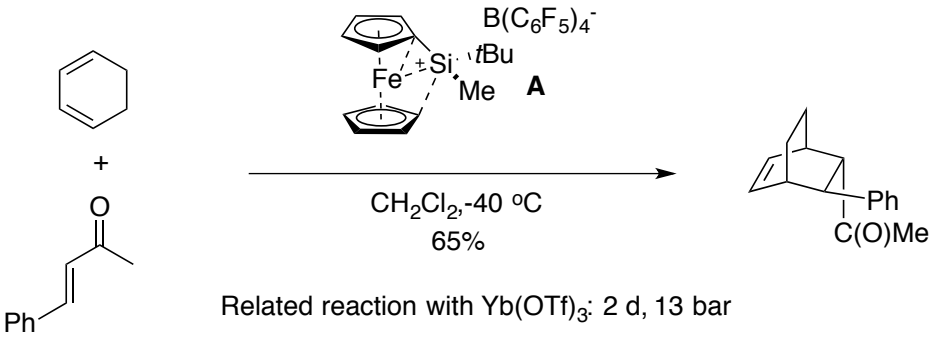

- Duryl = 2,3,5,6-tetramethylphenyl
- Xylyl = 2,6-dimethylphenyl

*Organometallics* **2015**, *34*, 4952-4958

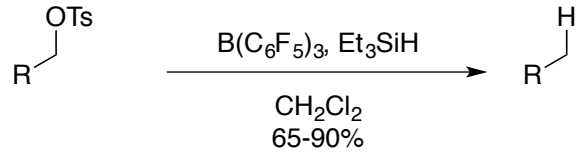
# Previous Use of Silylium Ions



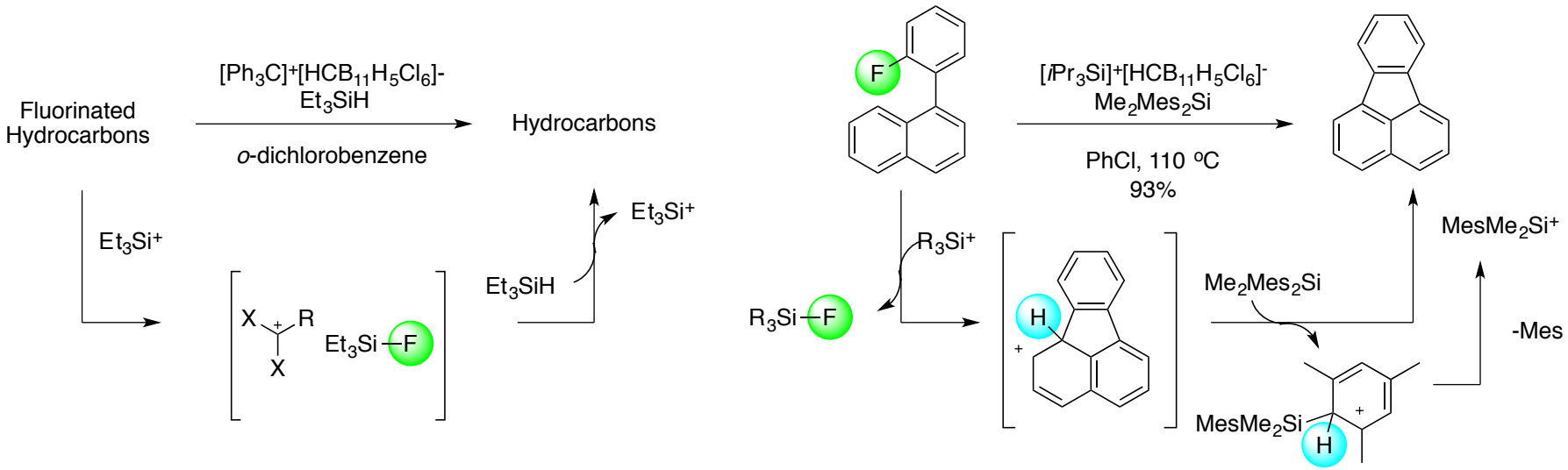

Related reaction with $Yb(OTf)_3$: 2 d, 13 bar




Tolerates Br, $CO_2Me$, ArOR', alkenes, OTBS


*Organometallics* **2013**, *32*, 3575-3582
*J. Am. Chem. Soc.* **2012**, *134*, 4421-4428
*Organometallics* **2013**, *32*, 6643-6646
*Angew. Chem. Int. Ed.* **2017**, *56*, 3389-3391

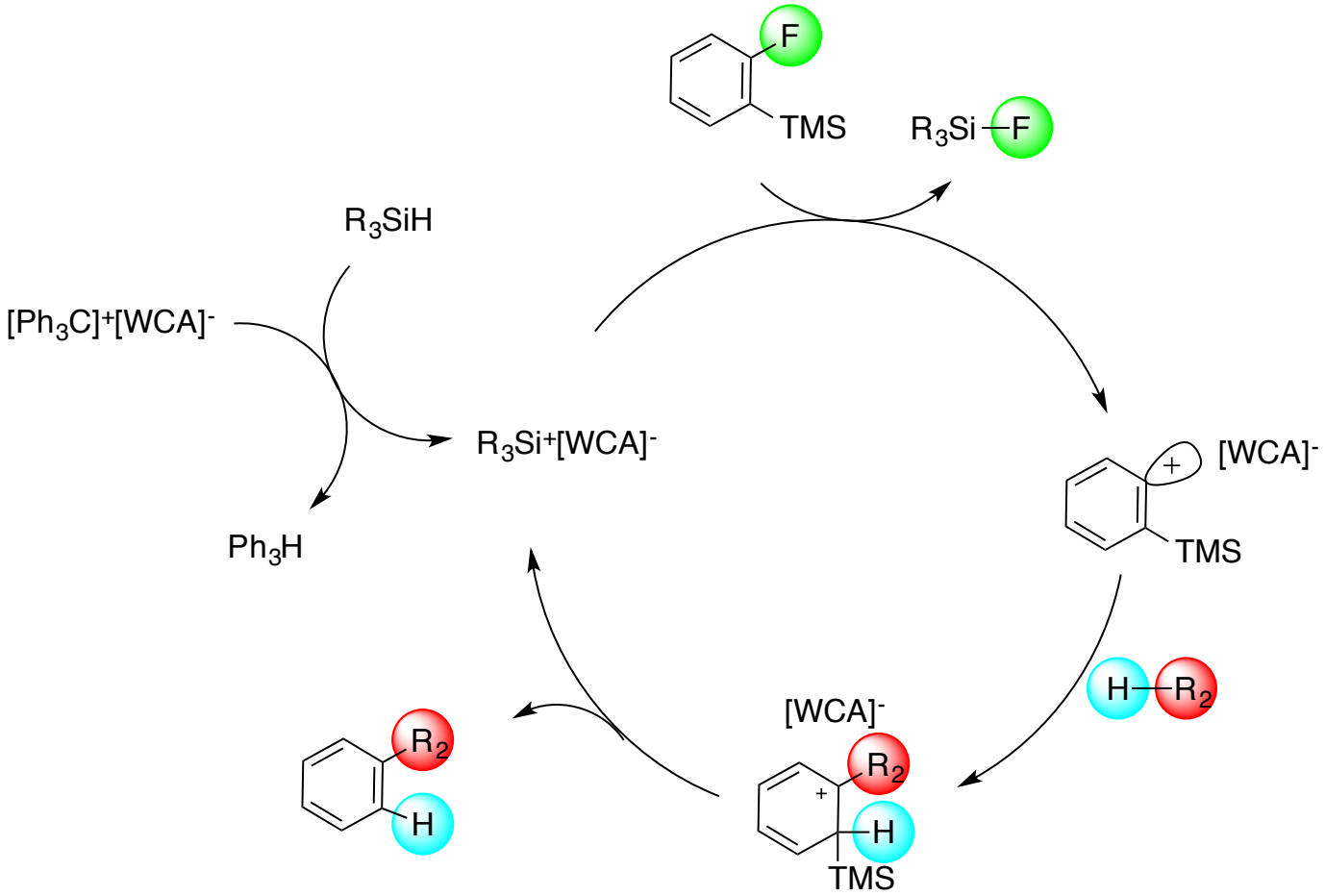
# Inspiration for Current Work




- Si-F bond is favored by 190 and 120 kJ/mol respectively
- Conditions on left later adapted for other halocarbon reductions

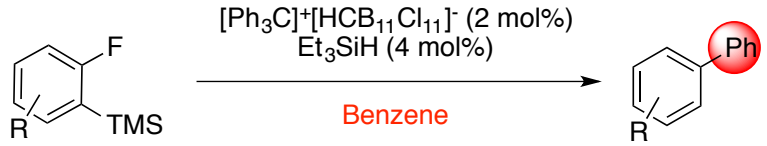
*Science* **2008**, *321*, 1188-1190
*Science* **2011**, *332*, 574-577

# Proposed Mechanism




*Science* **2017**, *355,* 1403-1407.

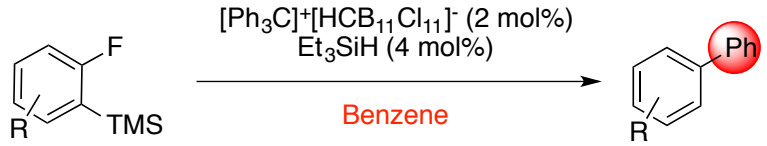
# C-F Arylation: Screen of Conditions

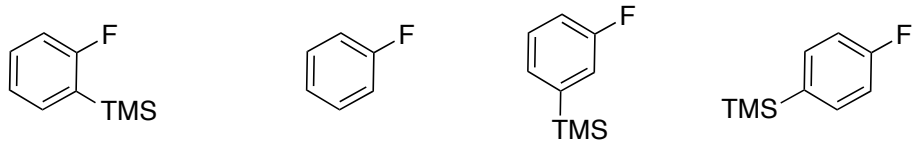



| Anion | % Cat. Loading | Conc. (M) | Temp (ºC) | Yield (%) |
|---|---|---|---|---|
| $[HCB_{11}H_5Cl_6]$ | 5 | 0.1 | 70 | 41 |
| $[HCB_{11}H_5Br_6]$ | 5 | 0.1 | 70 | 0 |
| $[HCB_{11}Me_5Cl_6]$ | 5 | 0.1 | 70 | 0 |
| $[HCB_{11}Cl_{11}]$ | 1 | 0.02 | 30 | 55 |
| $[HCB_{11}Cl_{11}]$ | 2 | 0.1 | 30 | 49 |
| $[HCB_{11}Br_{11}]$ | 5 | 0.1 | 30 | 39 |
| $[(C_6F_5)_4B]$ | 5 | 0.1 | 30 | 27 |

*Science* **2017**, *355,* 1403-1407.

# C-F Arylation: β-Si Required?



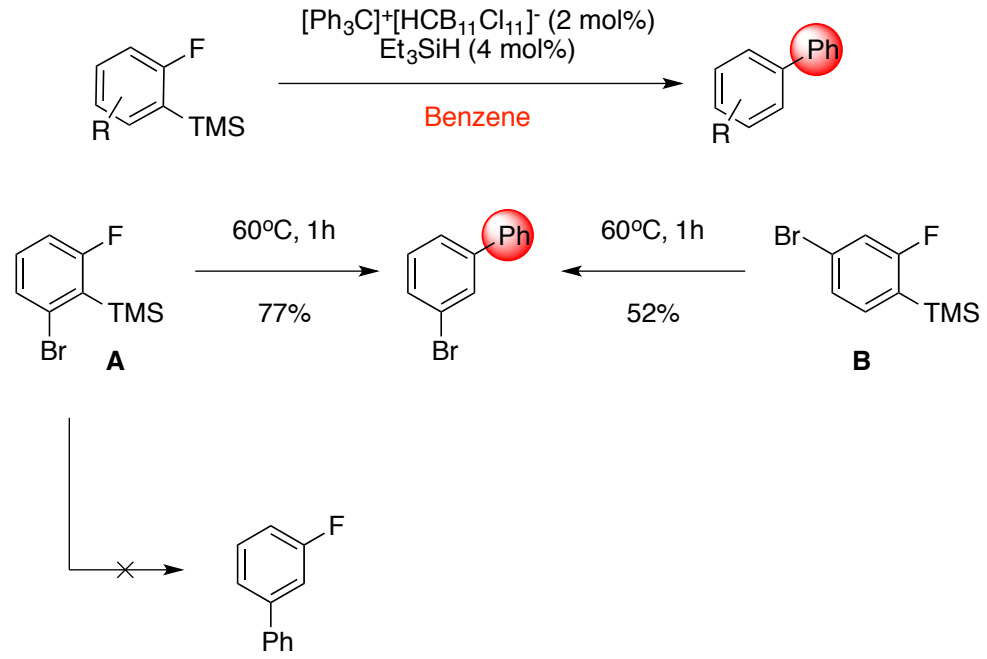




55% desired product | Trace product | No product | No product

- Si required *ortho* to F
- Byproducts are mostly aryl fluorides from protodesilation
  - Difficulty with byproduct characterization mentioned explicitly

*Science* **2017**, *355,* 1403-1407.

# Separation of Fluorophilicity & β-Si Effect




- If β-Si effect more important, a mixture of products should be observed with **A**

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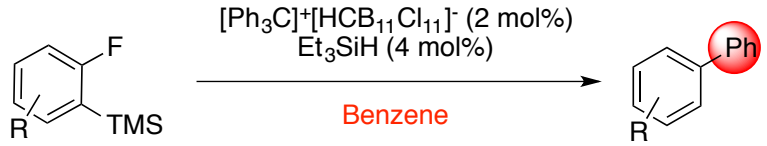
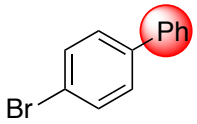
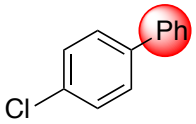
# C-F Arylation: Substrate Scope

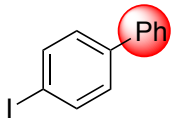


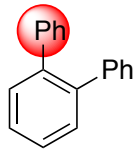

60°C, 1 h
56%



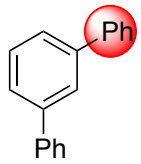

70°C, 9 h
47%



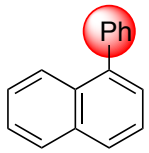

60°C, 1 h
71%



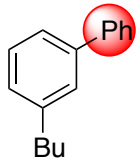

70°C, 36 h
45%



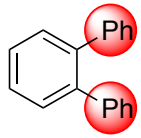

30°C, 1 h
63%



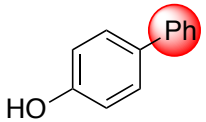

30°C, 1 h
49%



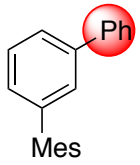

30°C, 0.2 h
99%




60°C, 36 h
36%



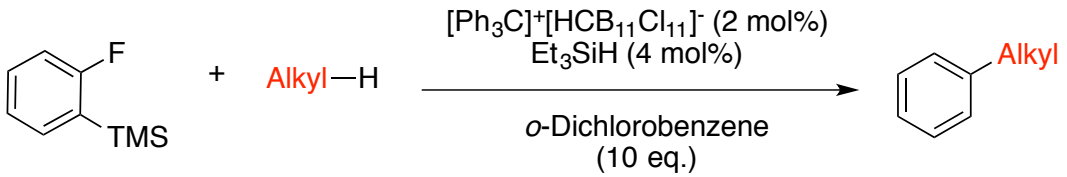

60°C, 48 h
29%
Loss of TBS

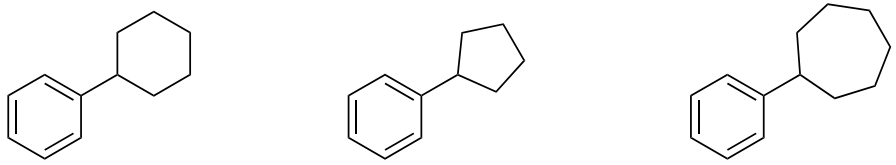



30°C, 1 h
47%

*Science* **2017**, *355,* 1403-1407.

# Arylation of Alkyl C-H Bonds



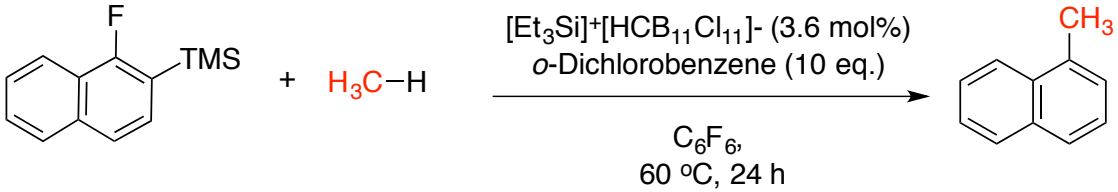
60°C, 2 h
41%

60°C, 1 h
54%

100°C, 9 h
40%

60°C, 8 h
40%
5:2:1 α:β:γ

60°C, 8 h
42%
10:3:1 α:β:γ

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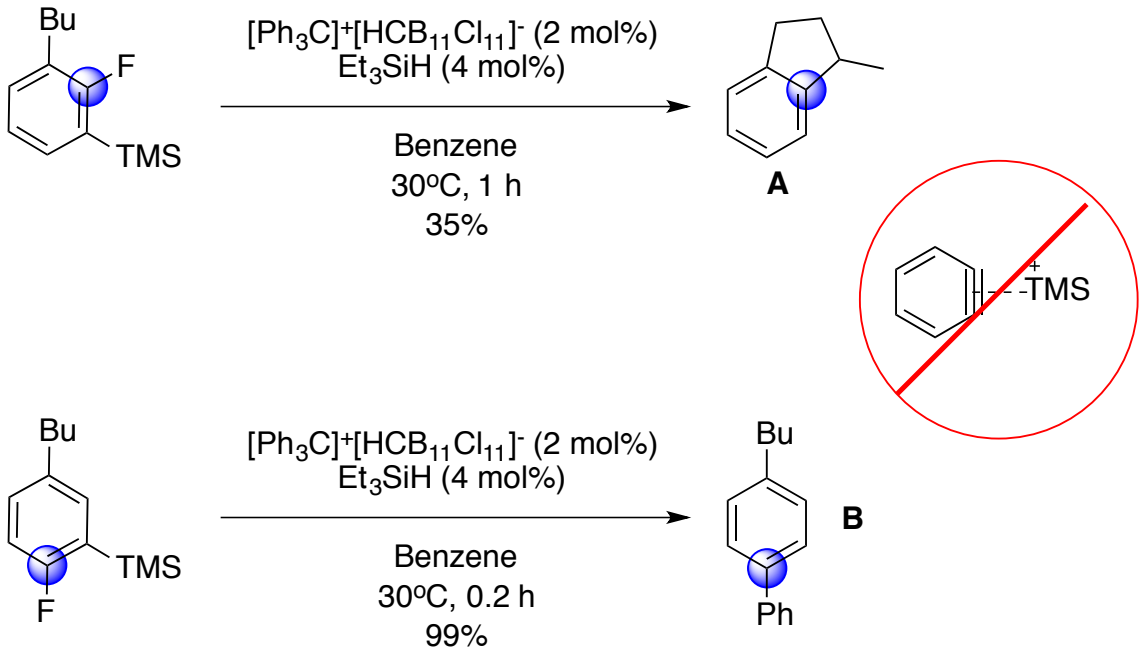
# Aryne Mechanism Operative?




- If aryne formed, both **A** and **B** should
- None of **B** found in first line's reaction mixture

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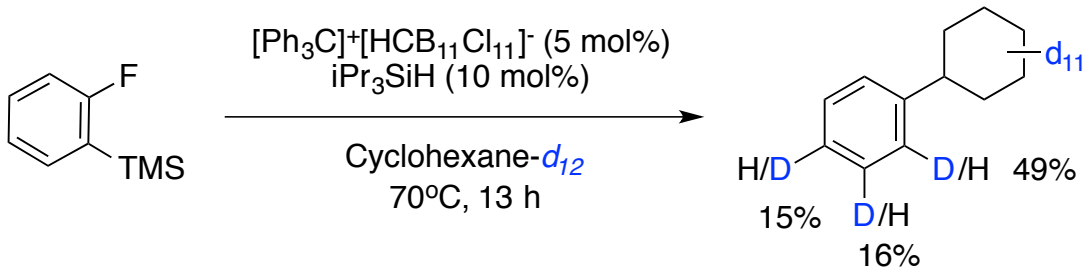
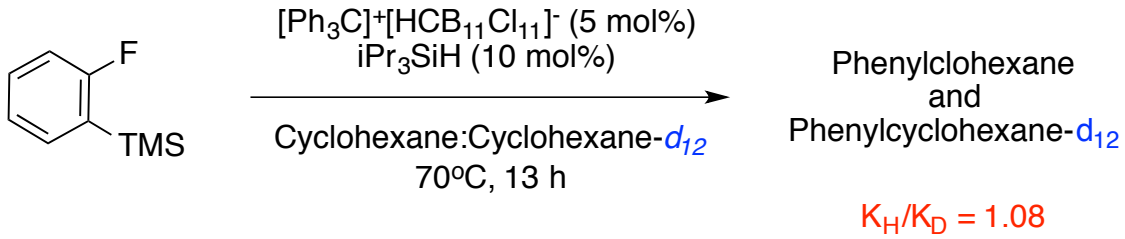
# Deuteration Studies




- Suggested that hydride shifts in arenium intermediate account for D/H distribution
- KIE: insertion into C-H is not rate determining step

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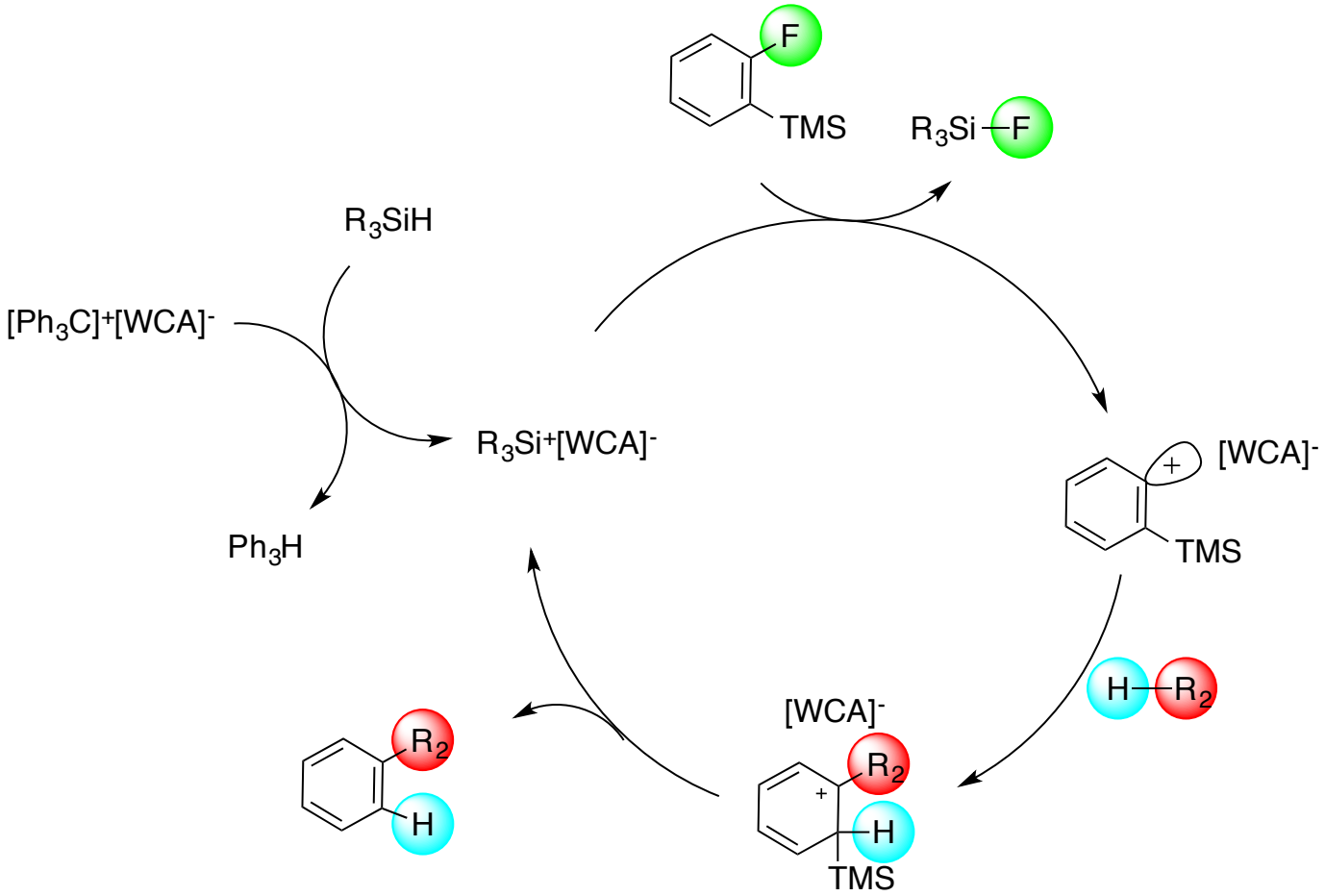
# Proposed Mechanism

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# Conclusion

- First non-transition metal aryl C-F bond activation, subsequent intermolecular functionalization developed
  - Can even functionalize methane
- Criticisms:
  - Method of arriving at reaction conditions somewhat vague
  - Unstabilized silylium ion currently greatly limits functional group compatibility