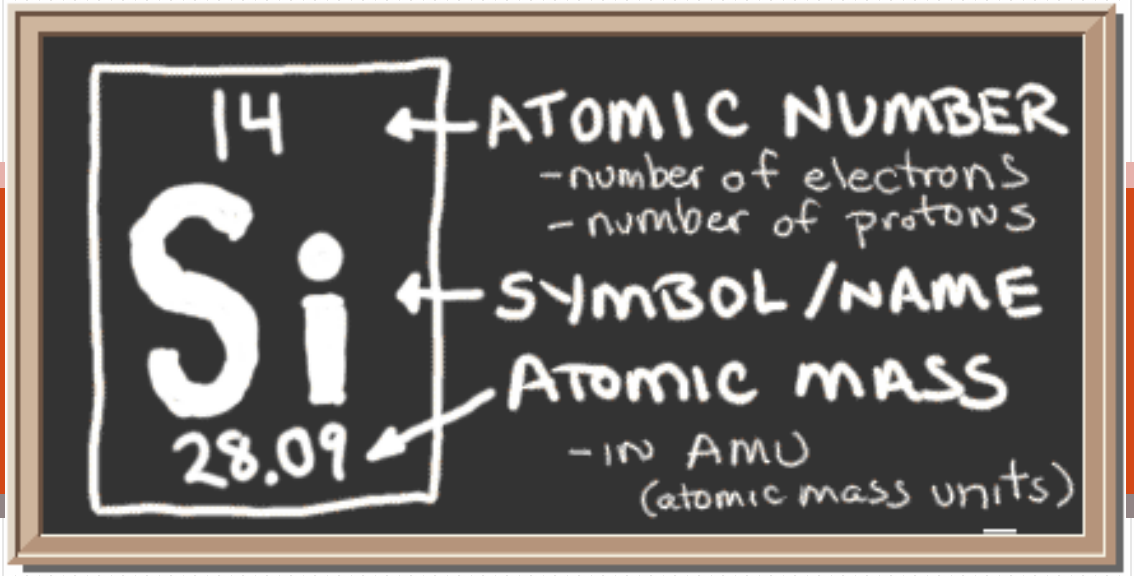
New Silicon Derived Frustrated Lewis Pairs



Supervisor: Pr. Louis Fensterbank
Co-Supervisor: Dr. Gilles Lemiére

sec 54

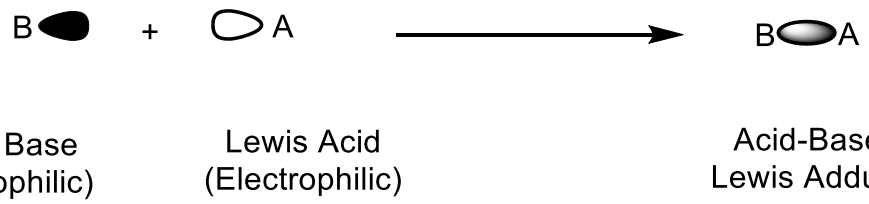
UPMC SORBONNE UNIVERSITÉS

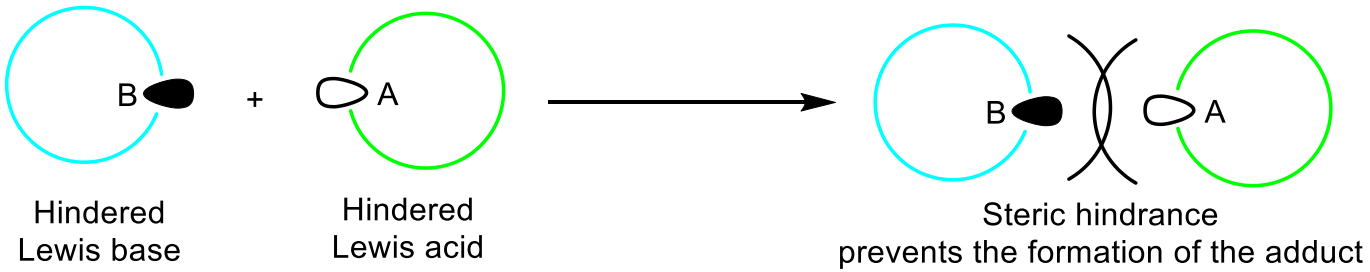
PSL RESEARCH UNIVERSITY PARIS

ED 406
Ecole Doctorale de Chimie Moleculaire
Paris Centre

Frustrated Lewis Pair

- Normal Acid-Base Lewis adduct Vs. Frustrated Lewis Pair (FLP)





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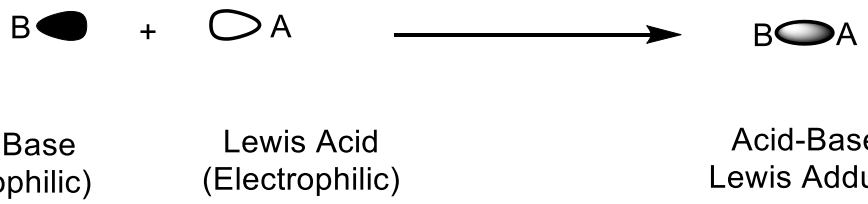
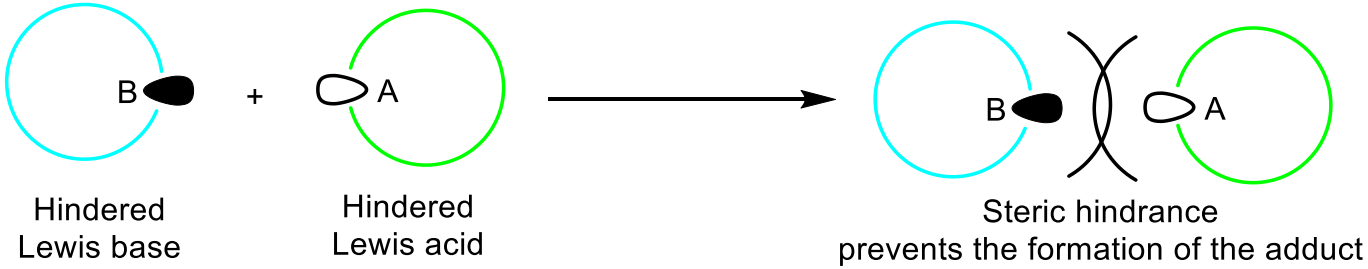
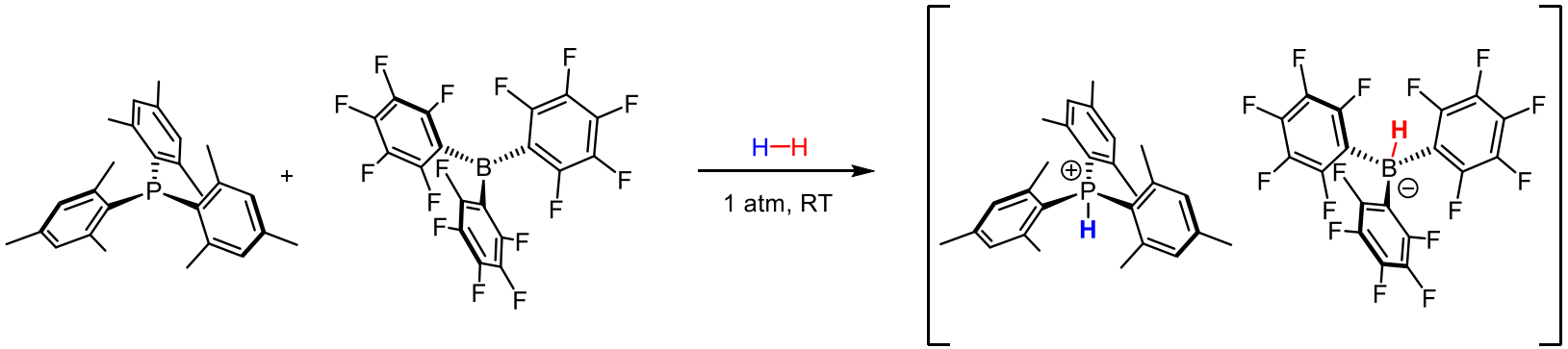


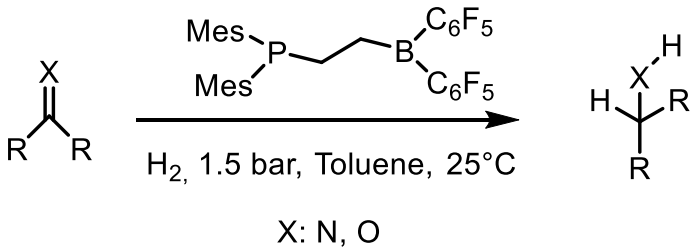


- The activation of small molecules (like hydrogen) is a great field of interest. Frustrated Lewis Pairs are good candidates to perform this kind of reactions.[1]



[1]M. Ullrich, A. J. Lough, D. W. Stephan, *J. Am. Chem. Soc.*, **2009**, *131*, 52-53

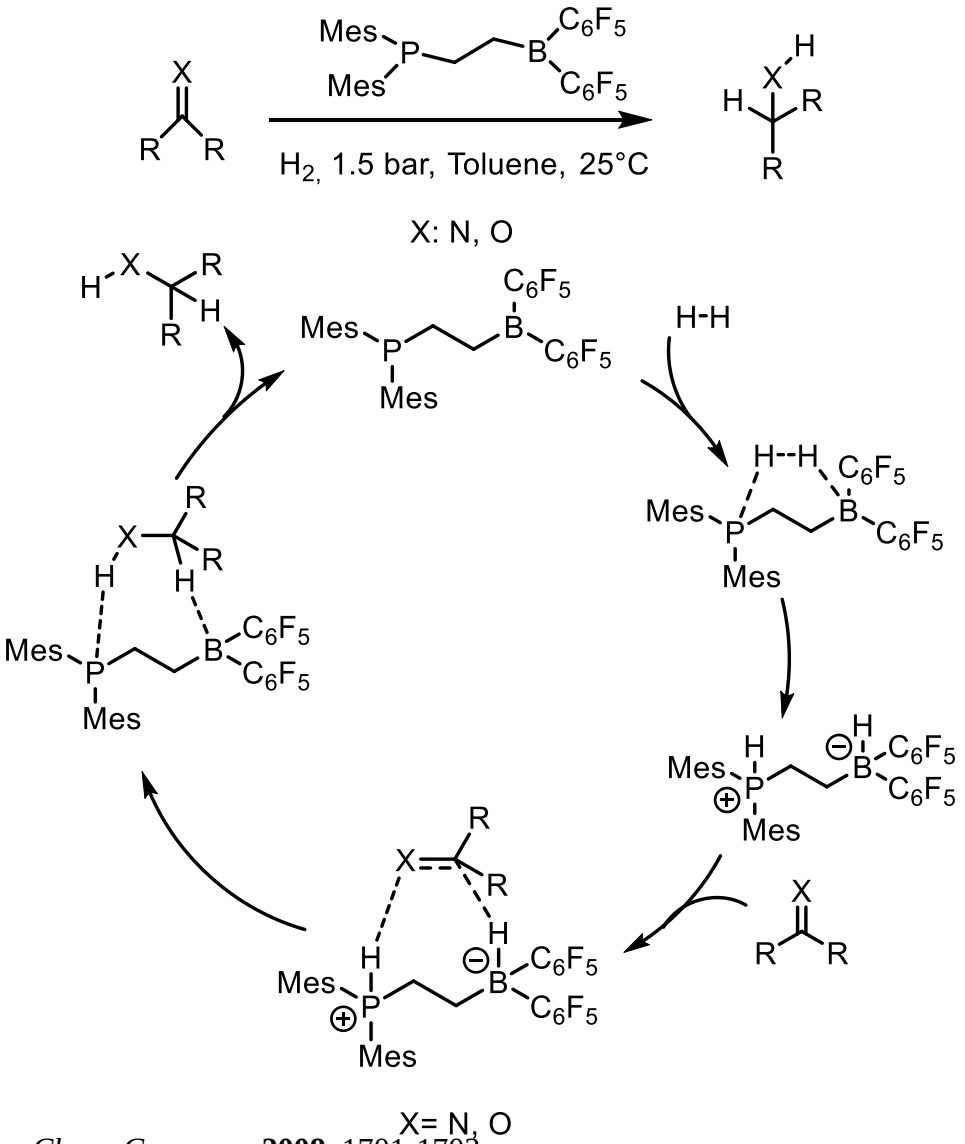
FLP As Catalyst



P. A. Chase, T. Jurca, D. W. Stephan, *Chem. Commun.*, **2008**, 1701-1703

FLP As Catalyst

Proposed mechanism



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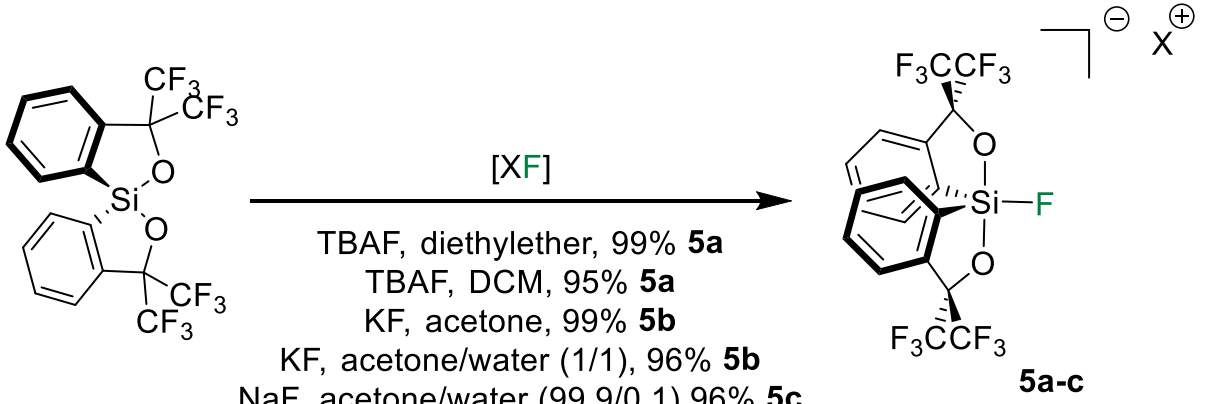
Spirosilane as a Lewis Acid

In our laboratory we are familiar with the use of different spirosilane, such as the Martin's Spirosilane.[2]



Martin's Spirosilane

[1]H. Lenormand, J.-P. Goddard, L. Fensterbank, *Org. Lett.*, **2013**, *15*, 748-751
[2]E. F. Perozzi, J. C. Martin, *J. Am. Chem. Soc*, **1979**, *101*, 1591-1953

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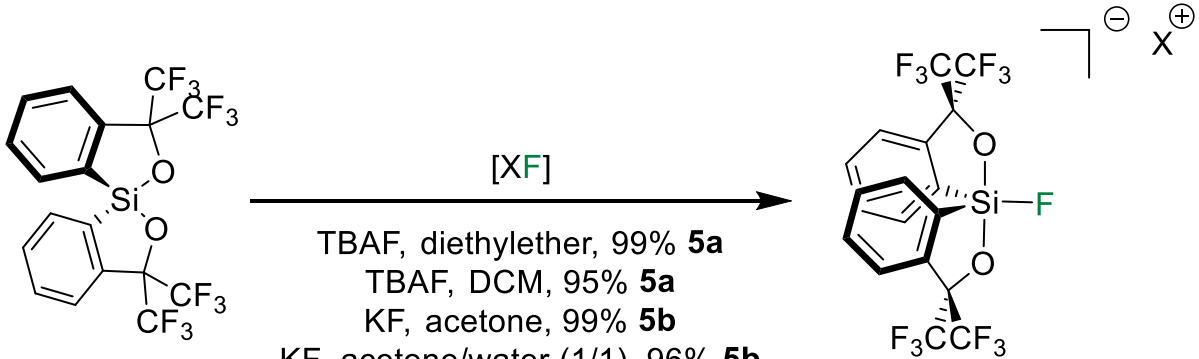
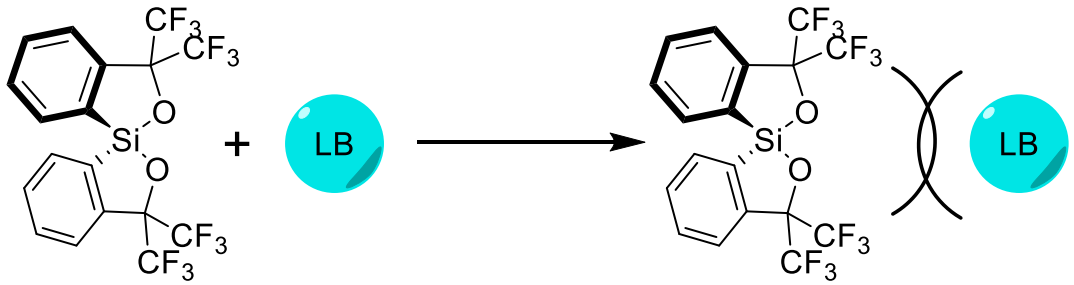


Martin's Spirosilane

Martin's spirosilane possesses a good Lewis acidity and a good steric hindrance

The Idea:



FLP

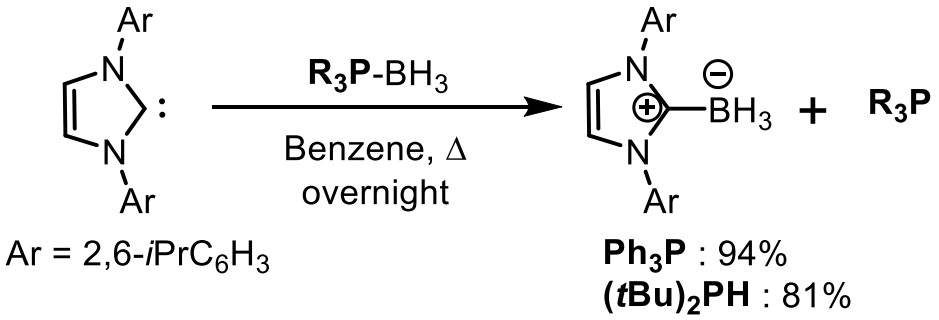
Possible use in catalysis?

In literature no example of FLP made with non halogenated tetravalent silicon as Lewis Acid

[1]H. Lenormand, J.-P. Goddard, L. Fensterbank, *Org. Lett.*, **2013**, *15*, 748-751
[2]E. F. Perozzi, J. C. Martin, *J. Am. Chem. Soc*, **1979**, *101*, 1591-1953

NHC Carbene as a Lewis Base

We also work with the NHC carbene[1], in particular with NHC-Borane[2,3].



[1]A. J. Arduengo, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.*, **1991**, *113*, 361

[2]S.-H. Ueng, A. Solovyev, X. Yuan, S. J. Geib, L. Fensterbank, E. Lacote, M. Malacria, M. Newcomb, J. C. Walton, D. P. Curran, *J. Am. Chem. Soc.*, **2009**, *131*, 11256–11262

[3]M. M. Brahmi, J. Monot, M. D.-E. Murr, D. P. Curran, L. Fensterbank, E. Lacote, M. Malacria, *J. Org. Chem.*, **2010**, *75*, 6983–6985

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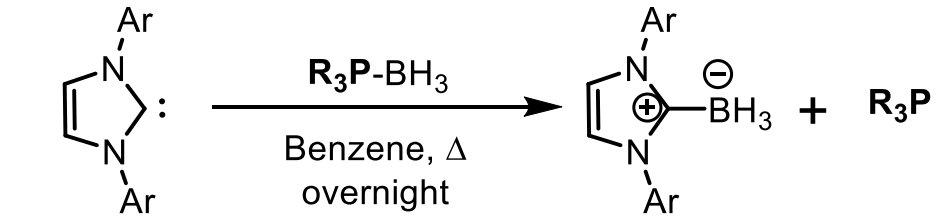
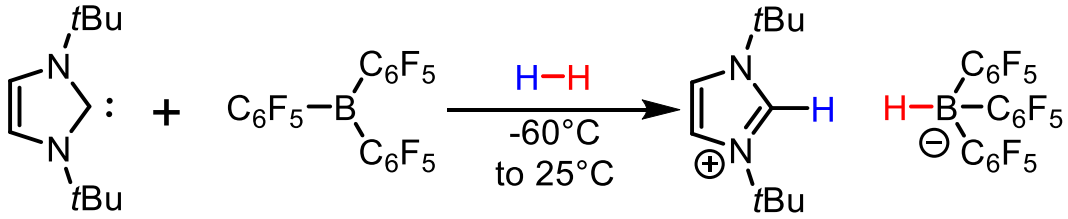


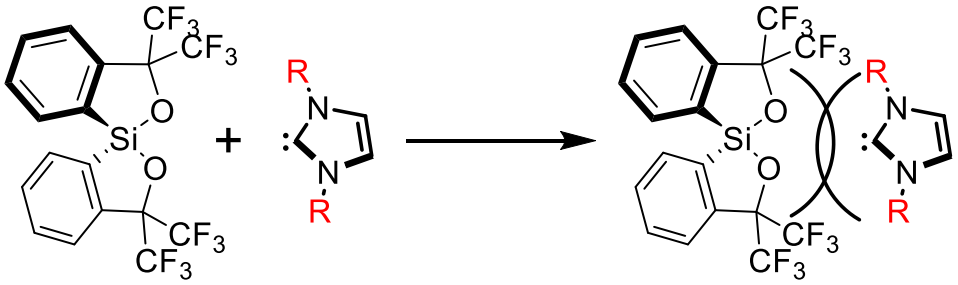
There are examples of NHC-Carbene used in FLP chemistry.[4]
Quite all the examples with NHC-carbene use Borane as Lewis Acid



[1]A. J. Arduengo, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.*, **1991**, *113*, 361
[2]S.-H. Ueng, A. Solovyev, X. Yuan, S. J. Geib, L. Fensterbank, E. Lacote, M. Malacria, M. Newcomb, J. C. Walton, D. P. Curran, *J. Am. Chem. Soc.*, **2009**, *131*, 11256–11262
[3]M. M. Brahmi, J. Monot, M. D.-E. Murr, D. P. Curran, L. Fensterbank, E. Lacote, M. Malacria, *J. Org. Chem.*, **2010**, *75*, 6983–6985
[4]P. A. Chase, D. W. Stephan, *Angew. Chem. Int. Ed.*, **2008**, *47*, 7433 –7437

Thesis scope

The idea is to study the interaction between the Martin's Spirosilane and NHC-carbene and their reactivity.



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"Frustrated"

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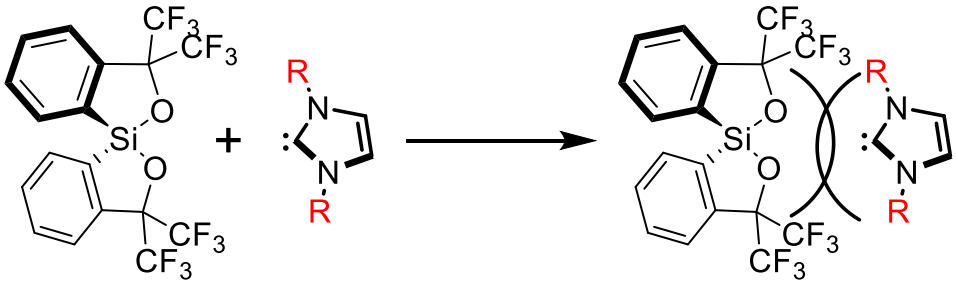
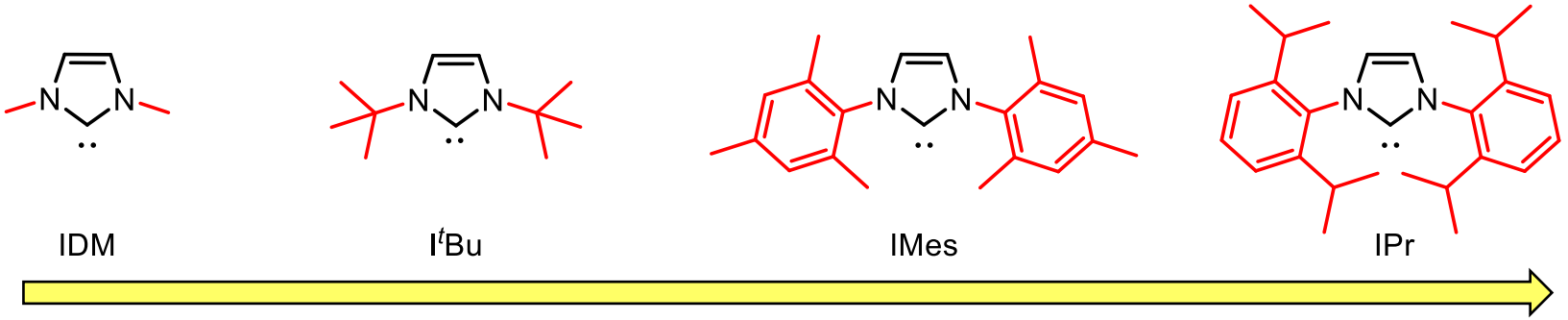
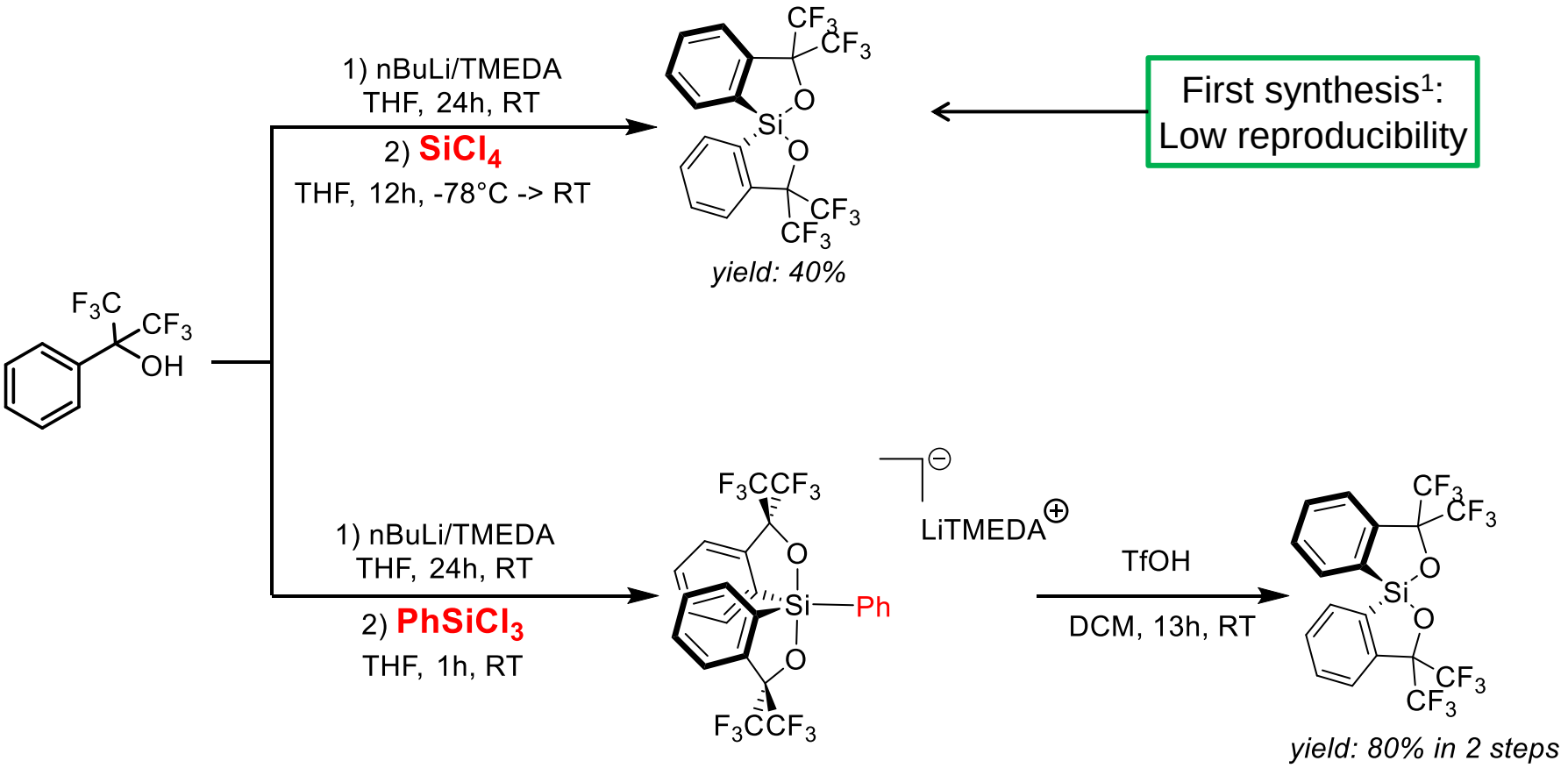


partially formed adduct
"Frustrated"

The NHC-Carbene taken into consideration are the following:



Martin's Spirosilane: Synthesis Update



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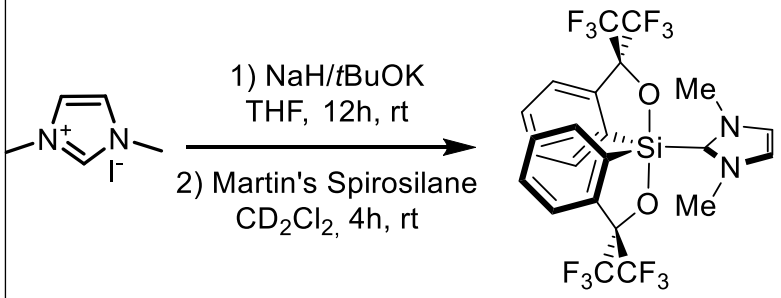
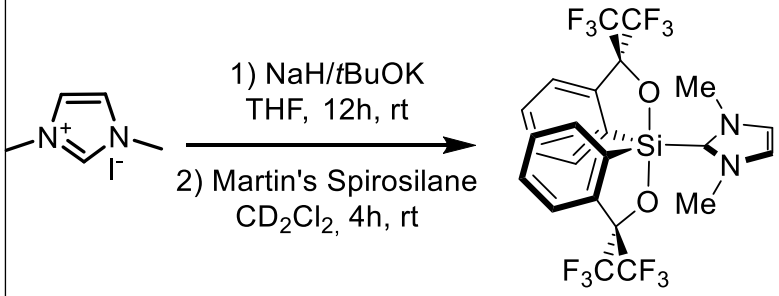
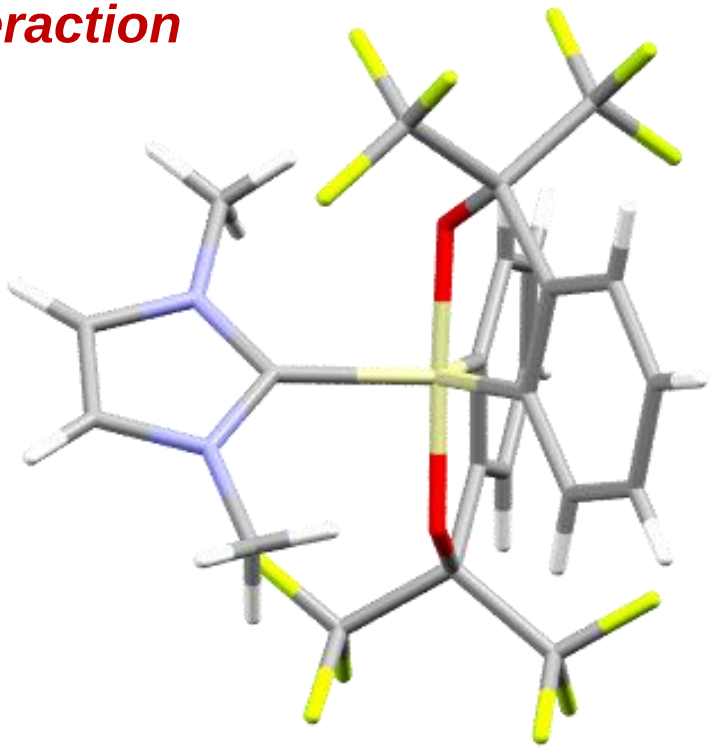
NHC-Spirosilane Interaction



NHC-Spirosilane Interaction





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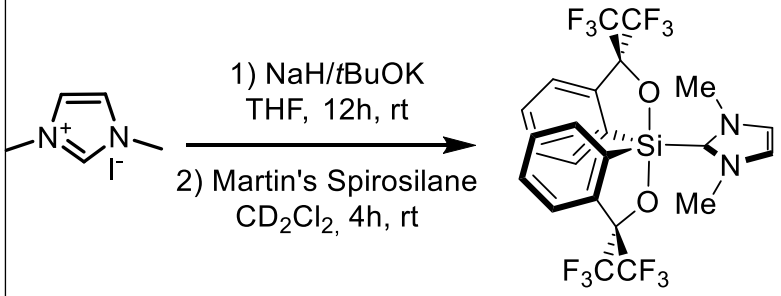

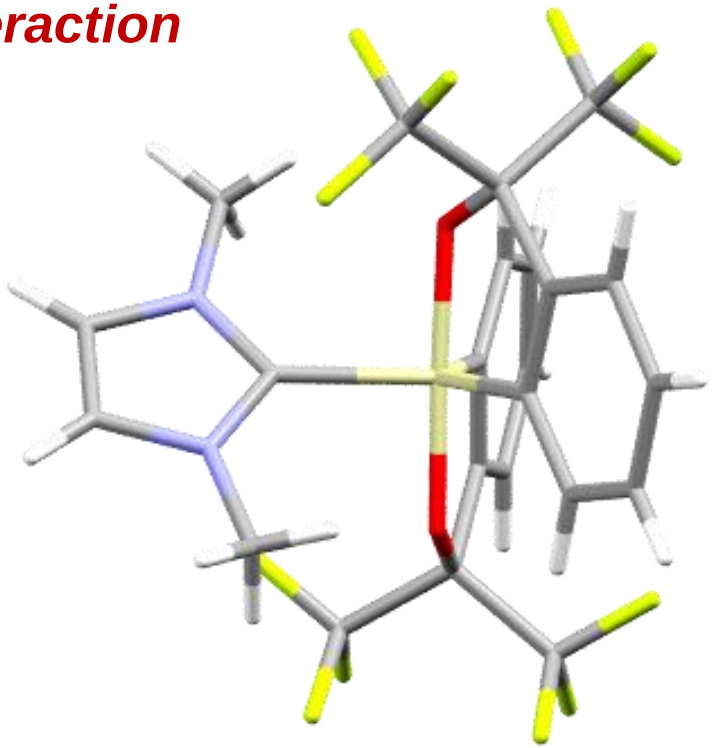

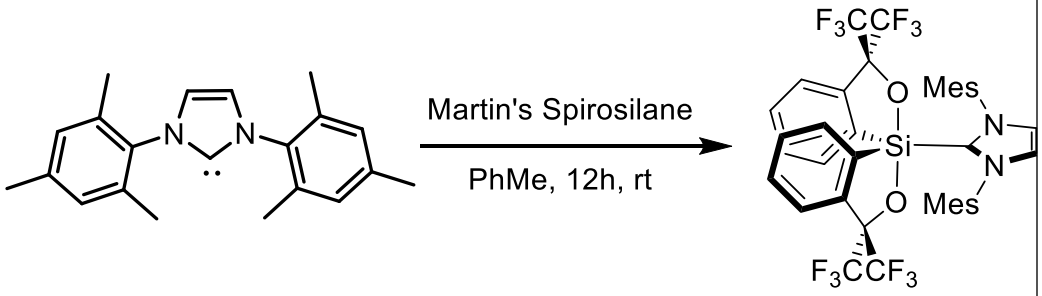

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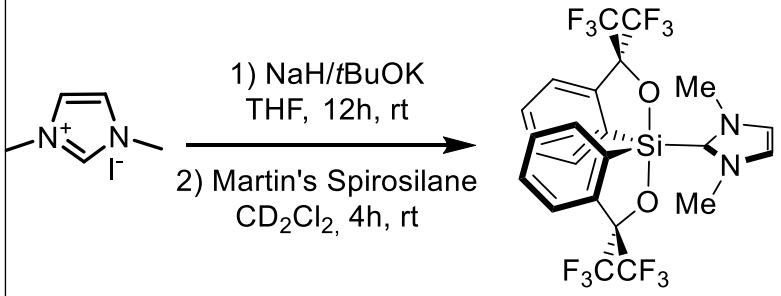

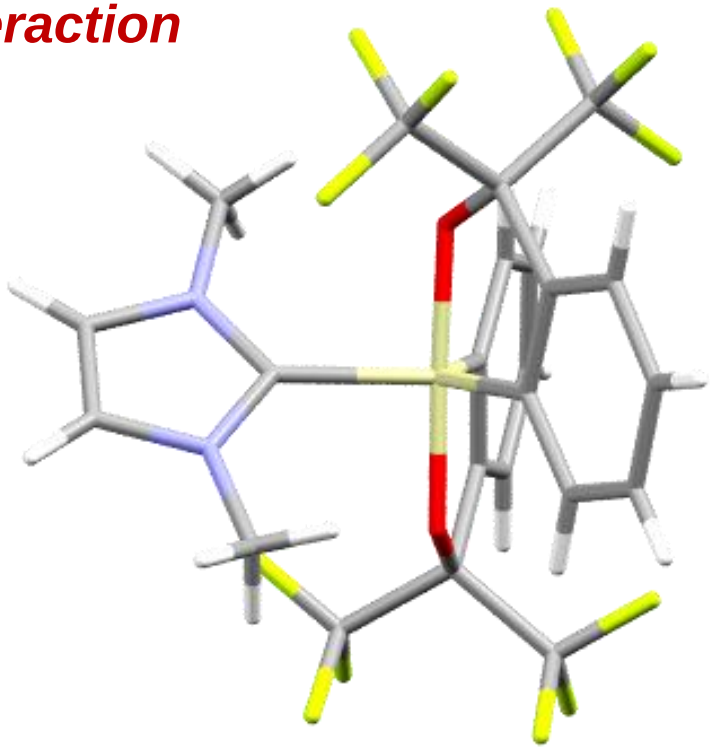

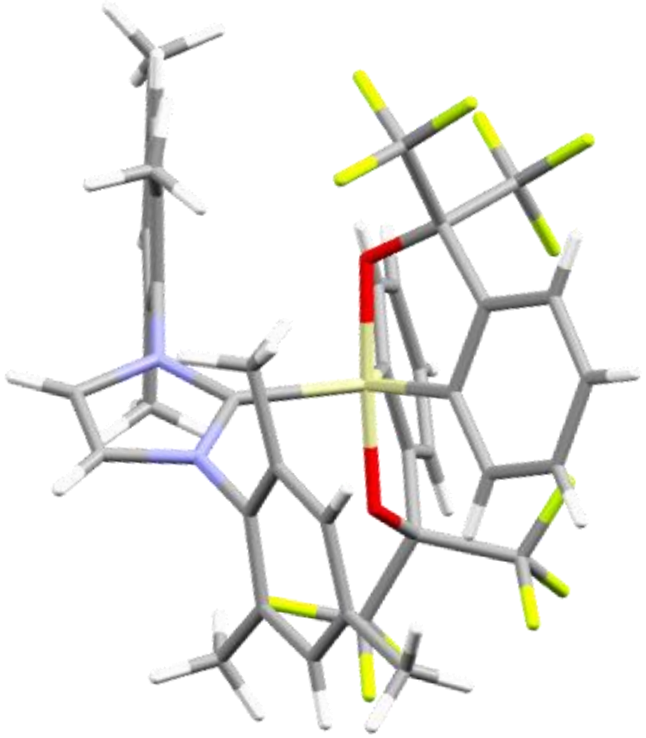

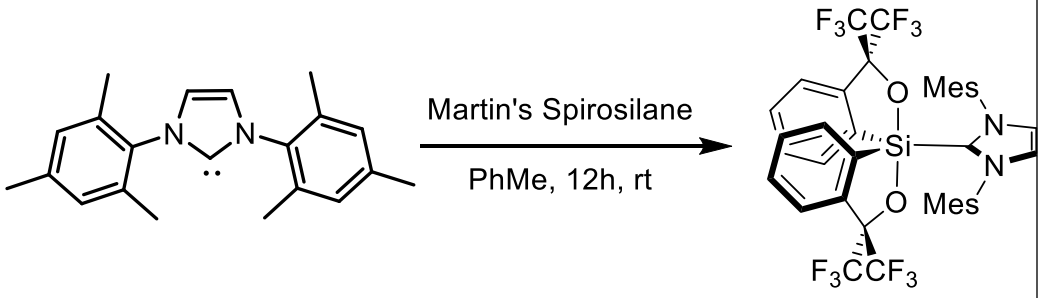

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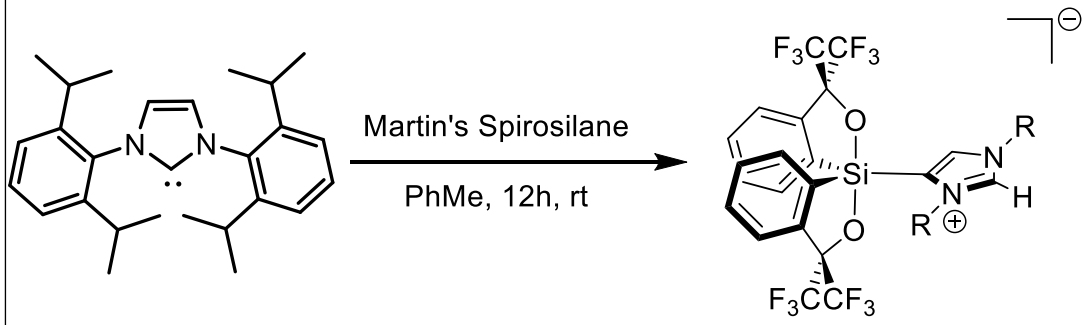
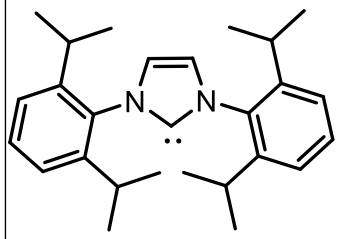


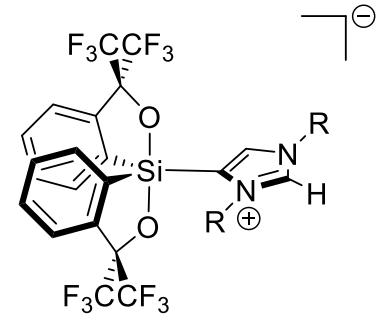
R = 2,6-diisopropylphenyl

NHC-Spirosilane Interaction



Martin's Spirosilane

PhMe, 12h, rt



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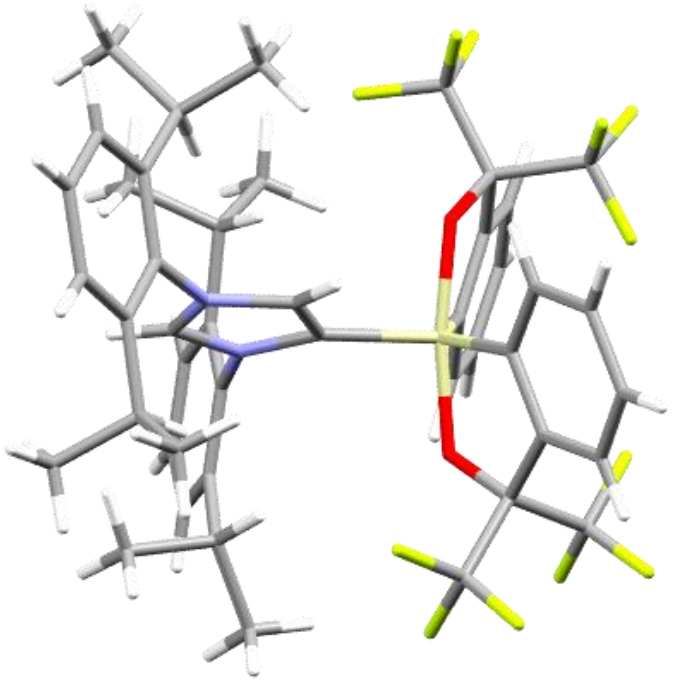
Abnormal Adduct!



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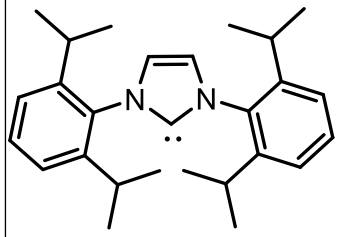

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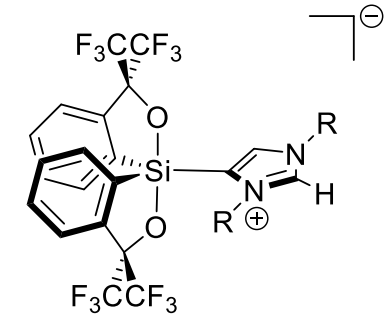

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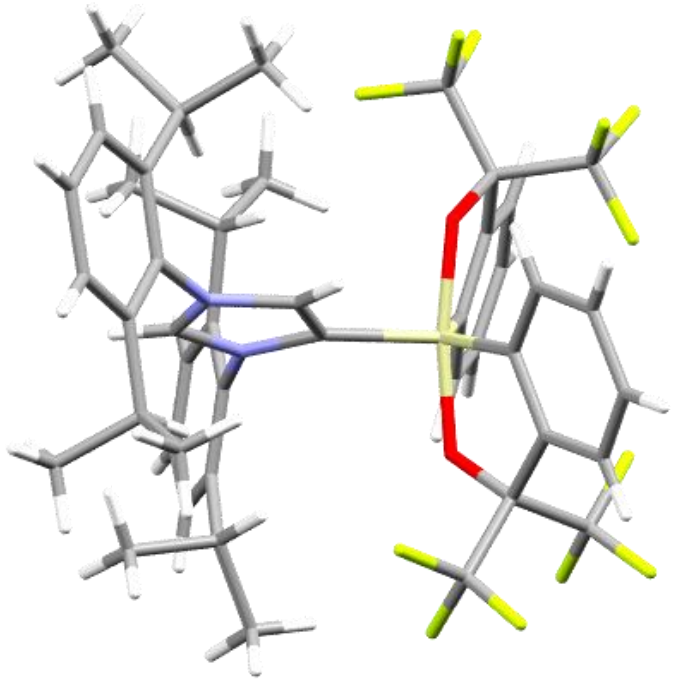

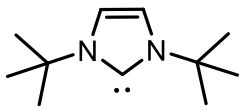

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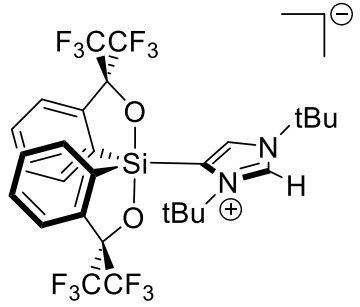
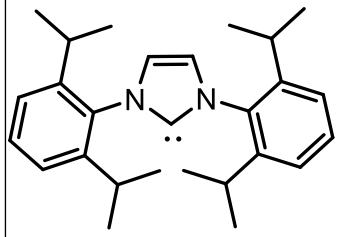


NHC-Spirosilane Interaction



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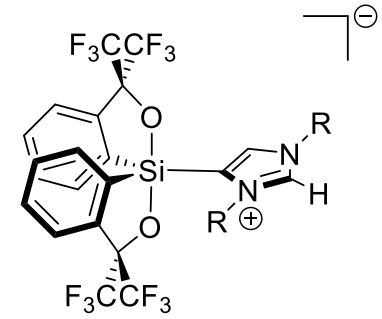

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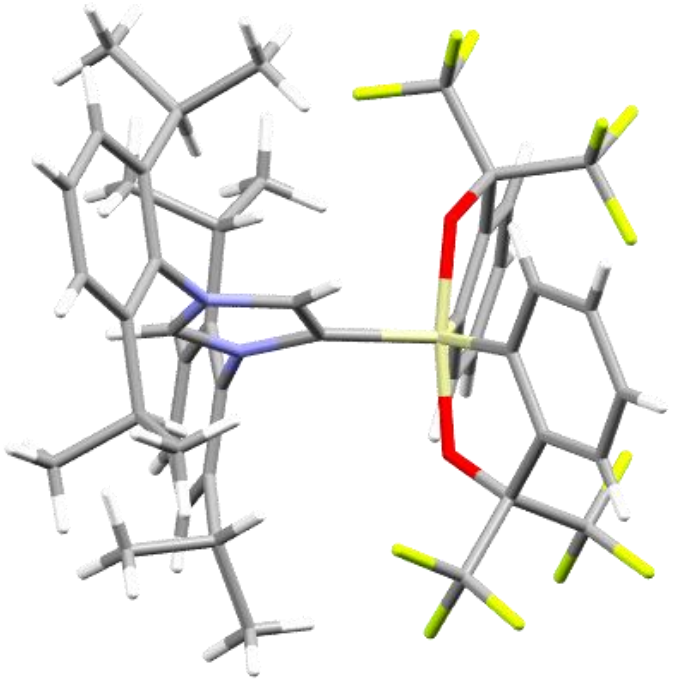

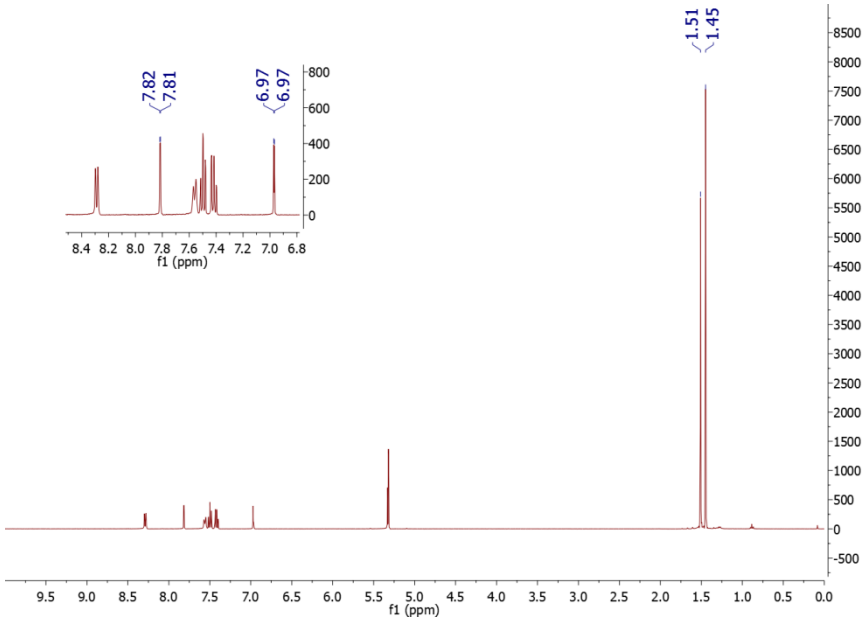

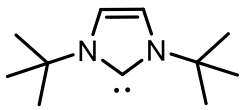

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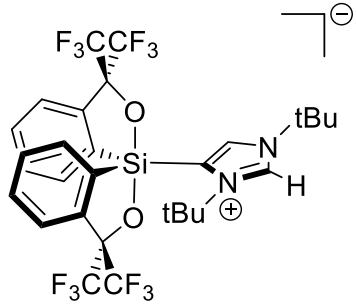
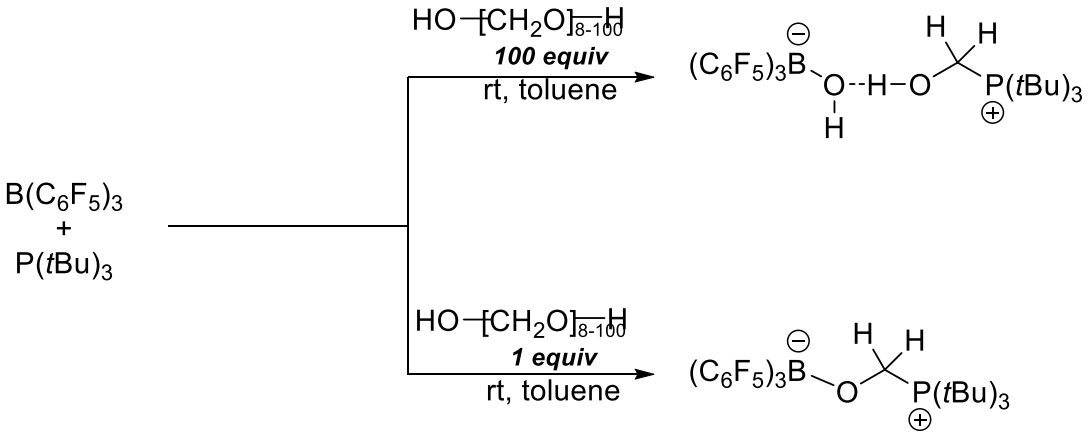


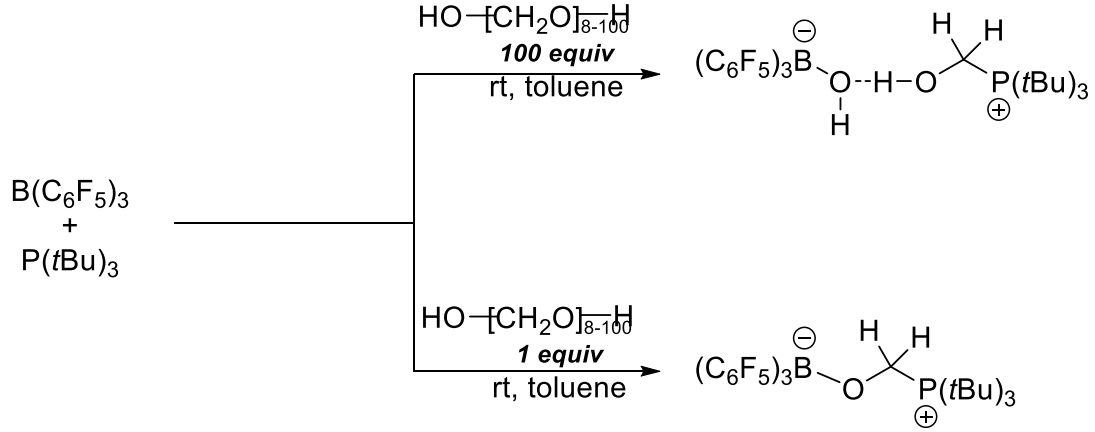
Abnormal Adduct!

NHC-Spirosilane and Paraformaldehyde



G. Ghattas, C. Bizzarri, M. Hoelscher, J. Langanke, C. Gürtler, W. Leitner, M. A. Subhani, *Chem. Commun.* **2017**, *53*, 3205-3208.

NHC-Spirosilane and Paraformaldehyde



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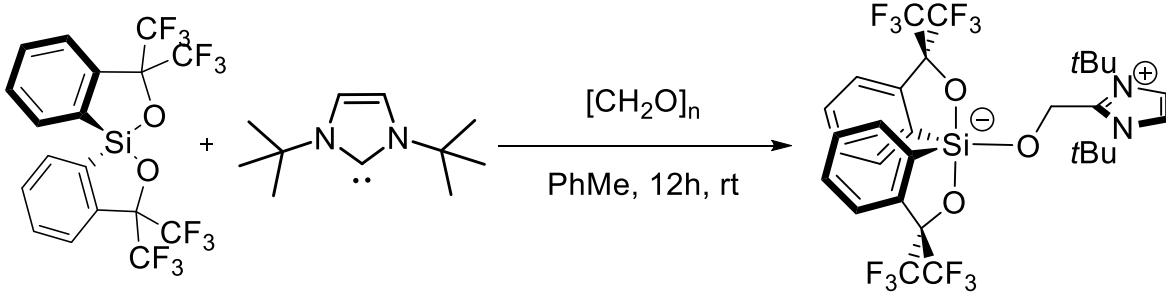
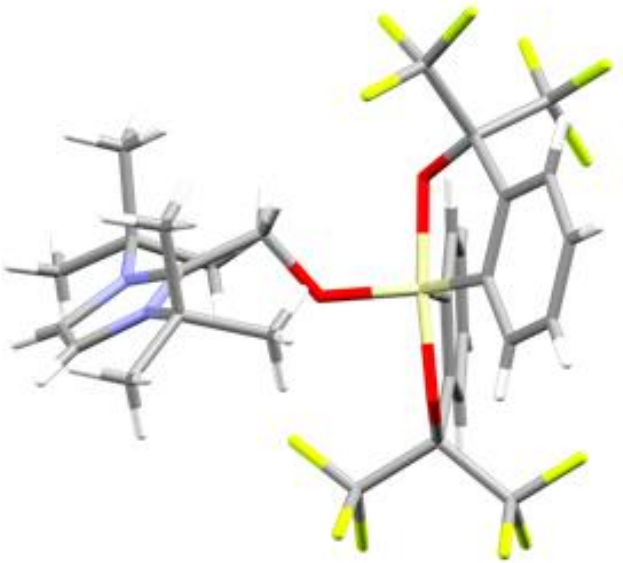
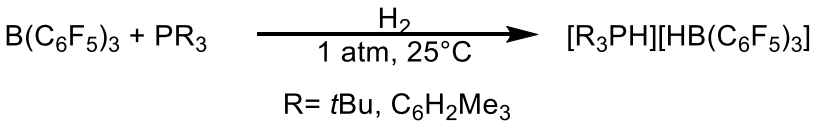


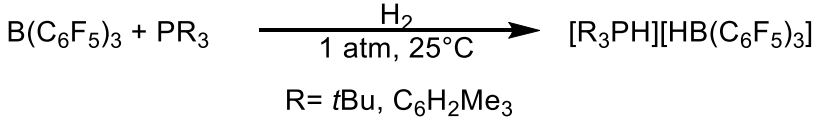


Hydrogenation

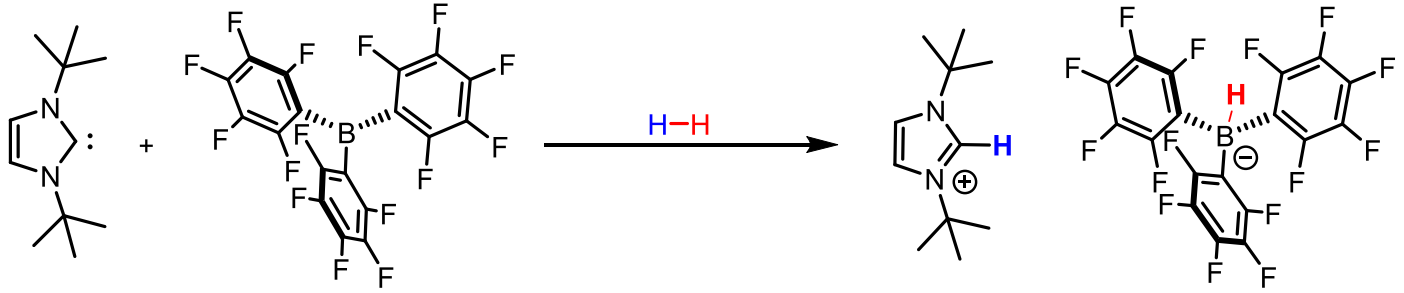


G. C. Welch, D. W. Stephan, *J. Am. Chem. Soc.*, **2007**, *129*, 1880-1881

Hydrogenation



G. C. Welch, D. W. Stephan, *J. Am. Chem. Soc.*, **2007**, *129*, 1880-1881



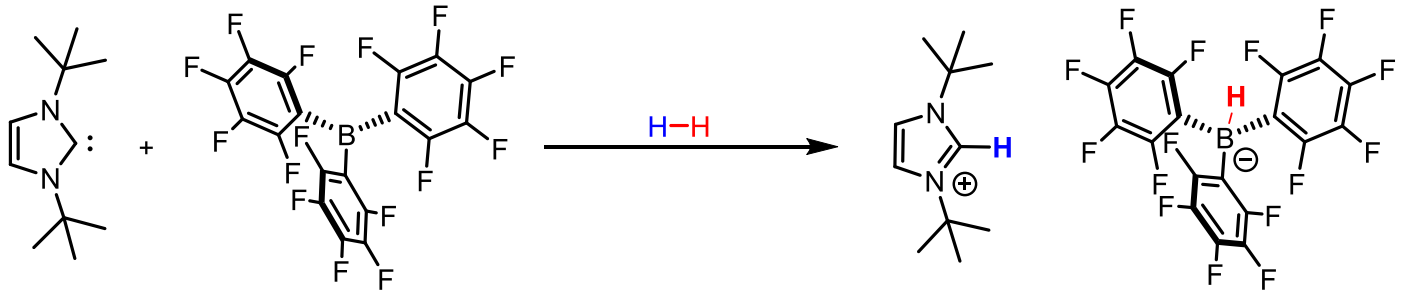
D. Holschumacher, T. Bannenberg, C. G. Hrib, P. G. Jones, M. Tamm, *Angew. Chem. Int. Ed.*, **2008**, *47*, 7428 –7432

Hydrogenation

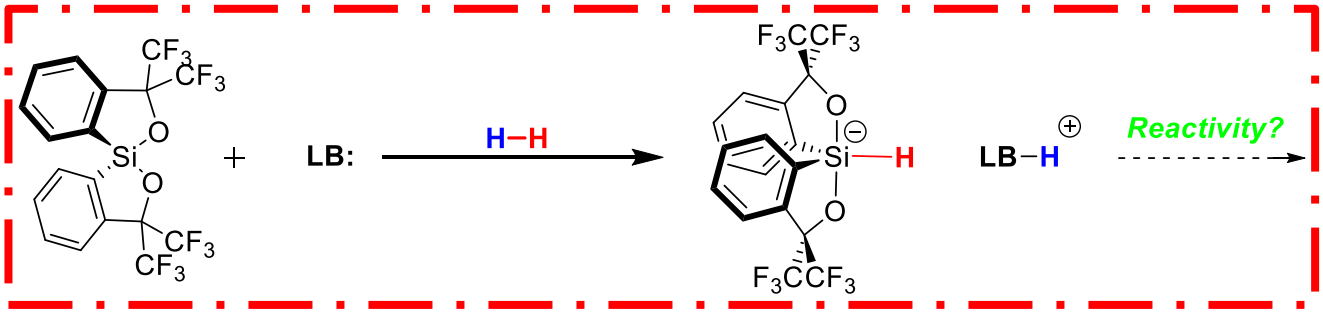
$B(C_6F_5)_3 + PR_3 \xrightarrow[1\ atm,\ 25°C]{H_2} [R_3PH][HB(C_6F_5)_3]$

R= *t*Bu, $C_6H_2Me_3$

G. C. Welch, D. W. Stephan, *J. Am. Chem. Soc.*, **2007**, *129*, 1880-1881

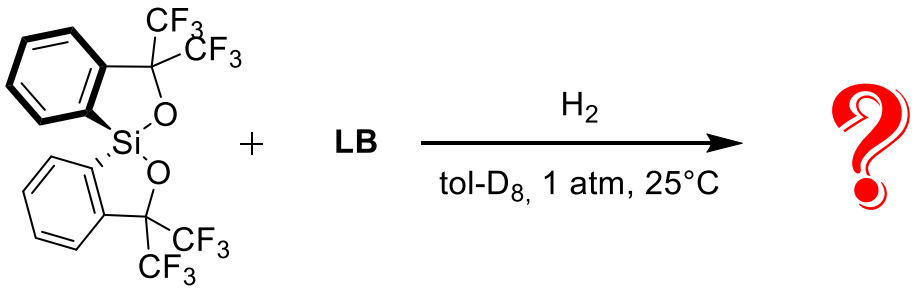


D. Holschumacher, T. Bannenberg, C. G. Hrib, P. G. Jones, M. Tamm, *Angew. Chem. Int. Ed.*, **2008**, *47*, 7428 –7432

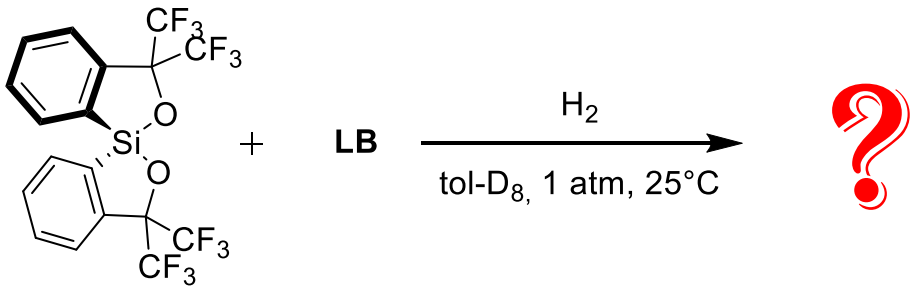


For other examples: D. Chen, Y. Wang, J. Klankermayer, *Angew. Chem. Int. Ed.* **2010**, *49*, 9475–9478; T. Mahdi, Z. M. Heiden, S. Grimme, D. W. Stephan, *J. Am. Chem. Soc.* **2012**, *134*, 4088–4091; V. Morozova, P. Mayer, G. Berionni, *Angew. Chem. Int. Ed.* **2015**, *54*, 14508–14512; M. Bakos, Á. Gyömöre, A. Domján, T. Soós, *Angew. Chem. Int. Ed.* **2017.**

Hydrogenation

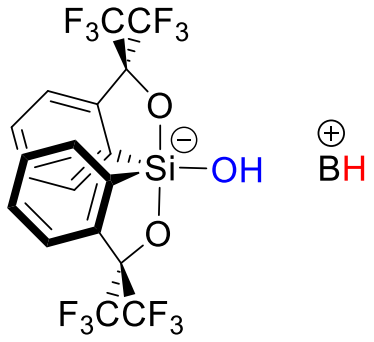


Hydrogenation

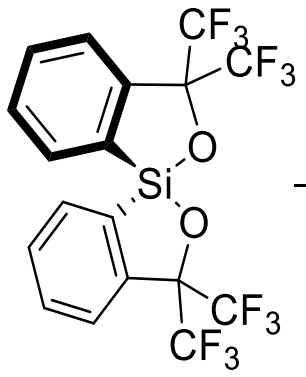


Lewis Base	*Time*	*Results*
IPr	10’ bubbling then 24h	Hydroxy*
IPr	10’ bubbling then NMR	Hydroxy*
P(*i*Pr)$_3$	10’ bubbling then 24h	Hydroxy*
P(*i*Pr)$_3$	10’ bubbling then NMR	Hydroxy*

*«Hydroxy»:



Hydrogenation

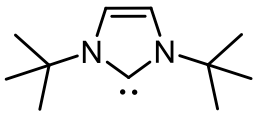


+ **LB**

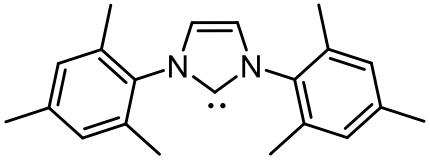
"Dry" H_2, additive

solvent, P, T, τ

Lewis Base

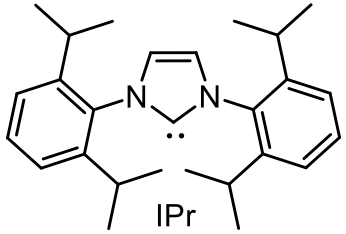


I*t*Bu

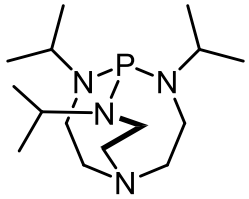


IMes

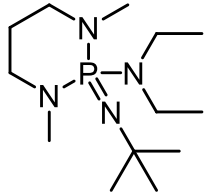
Pka(CH_3CN): 20 - 24



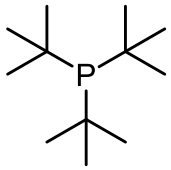
IPr

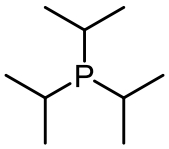


iPr-Verkade's superbase
Pka(CH_3CN): 33.6

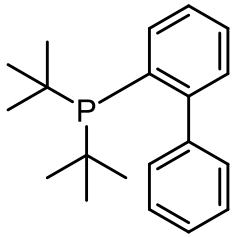


BEMP
Pka(CH_3CN): 27.6



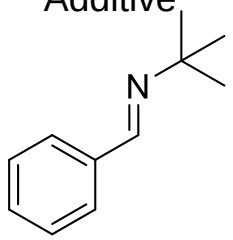


Pka(H_2O): 8 - 12

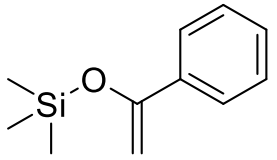


P: 1, 5, 15, 25, 50 bar
Solvents: PhMe, C_6H_5Br, CH_2Cl_2
T: rt, 80°C, 110°C
t: 10', 1h, 4h, 24h

Additive

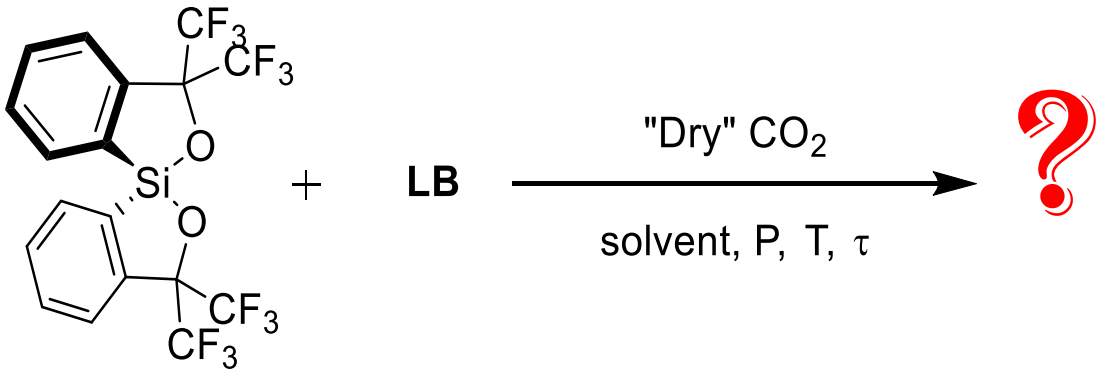


(E)-N-Benzylidene-tert-butylamine

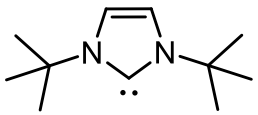


1-Phenyl-1-trimethylsiloxyethylene

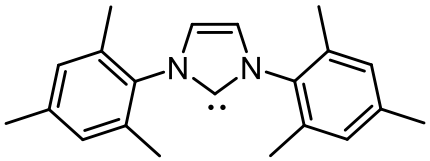
Carbon dioxide activation



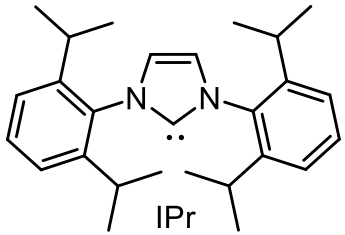
Lewis Base



I*t*Bu

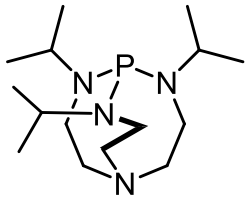


IMes



IPr

Pka(CH_3CN): 20 - 24



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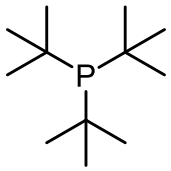
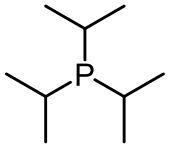
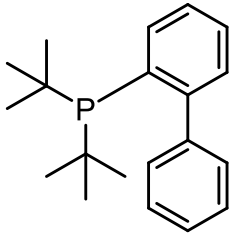
Pka(CH_3CN): 33.6



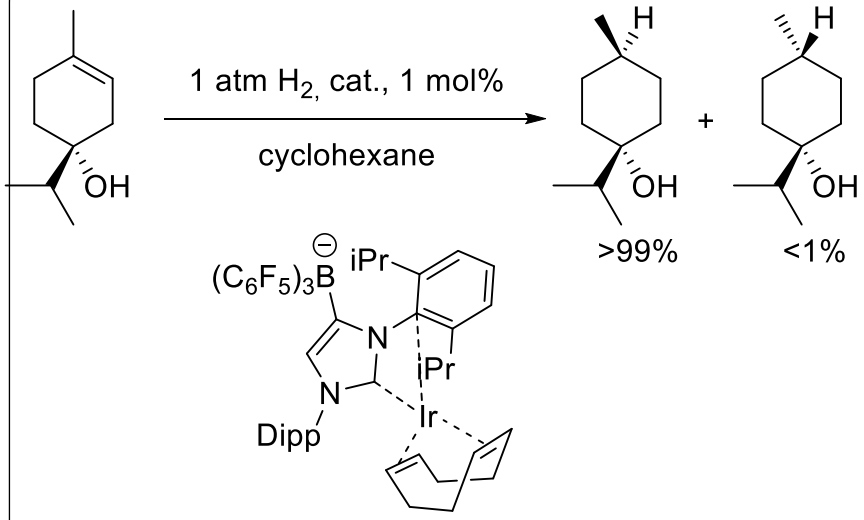


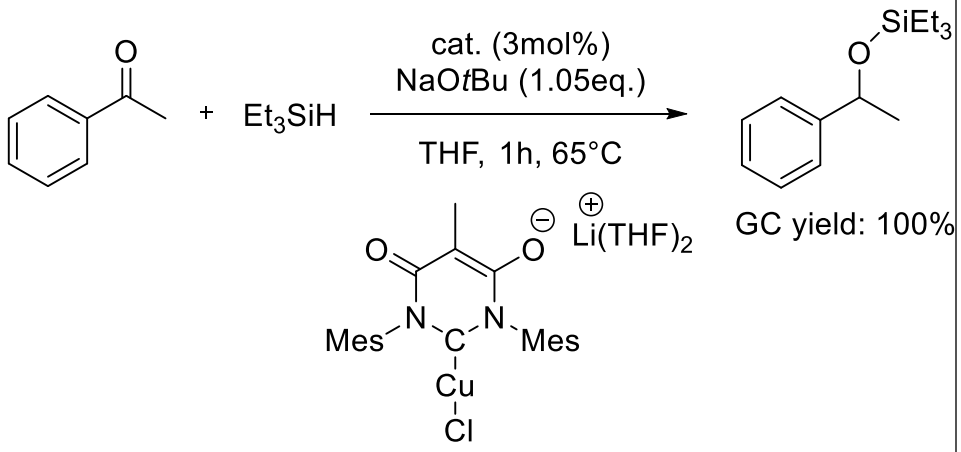


Pka(H_2O): 8 - 12

Abnormal adducts and metal

Abnormal adducts and metal



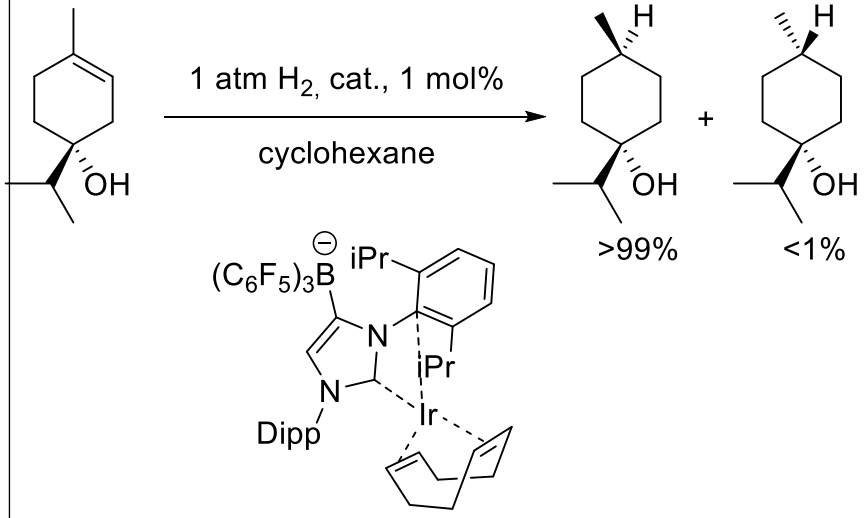


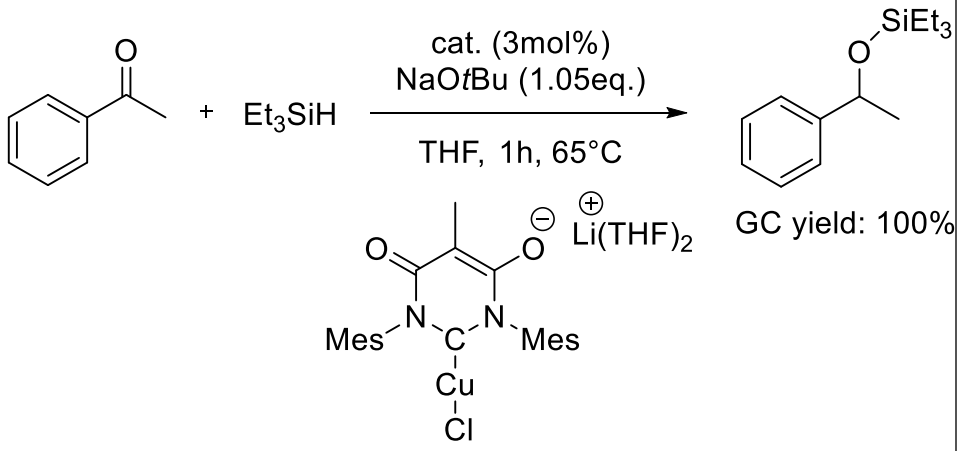
E. L. Kolychev, S. Kronig, K. Brandhorst, M. Freytag, P. G. Jones, M. Tamm, *J. Am. Chem. Soc.*, **2013**, *135*, 12448−12459

V. César, C. Barthes, Y. C. Farré, S. V. Cuisiat, B. Y. Vacher, R. Brousses, N. Lugan, G. Lavigne, *Dalton Trans.* **2013**, *42*, 7373–7385.

For a review on anionic carbene: A. Nasr, A. Winkler, M. Tamm, *Coordination Chemistry Reviews*, **2016**, *316*, 68–124

Abnormal adducts and metal





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V. César, C. Barthes, Y. C. Farré, S. V. Cuisiat, B. Y. Vacher, R. Brousses, N. Lugan, G. Lavigne, *Dalton Trans.* **2013**, *42*, 7373–7385.

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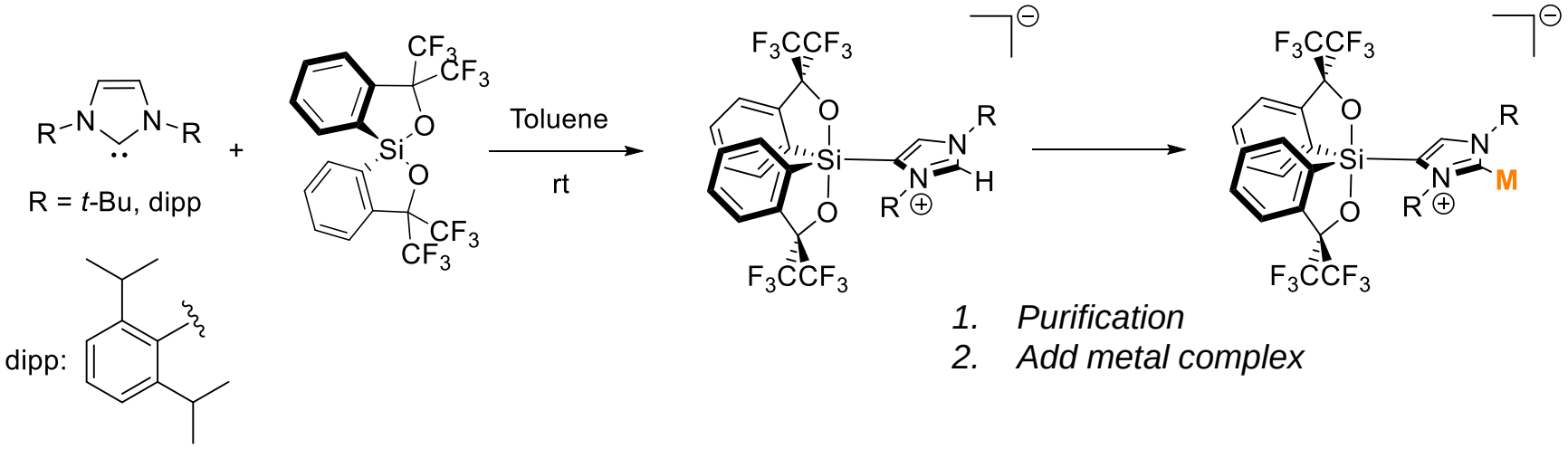
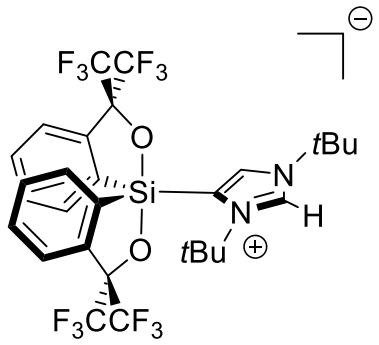


1. *Purification*
2. *Add metal complex*

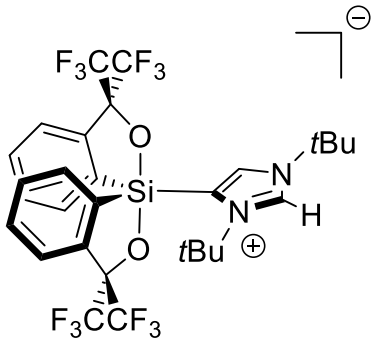
Abnormal adducts and metal: purification

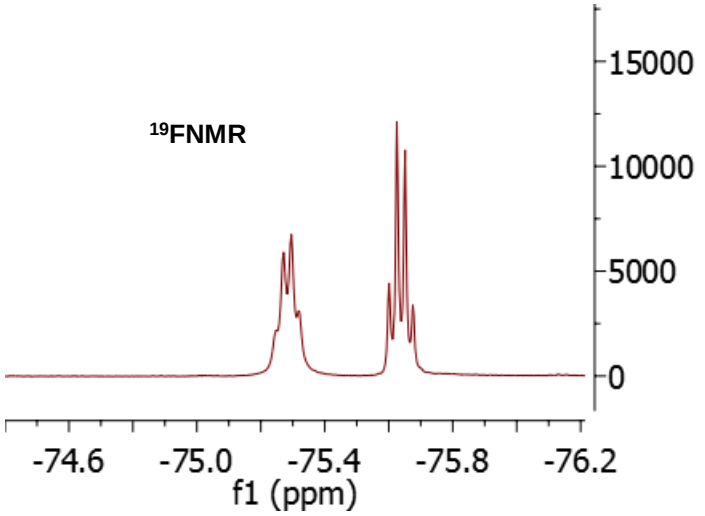
Eluent: DCM
Rf: 0,71

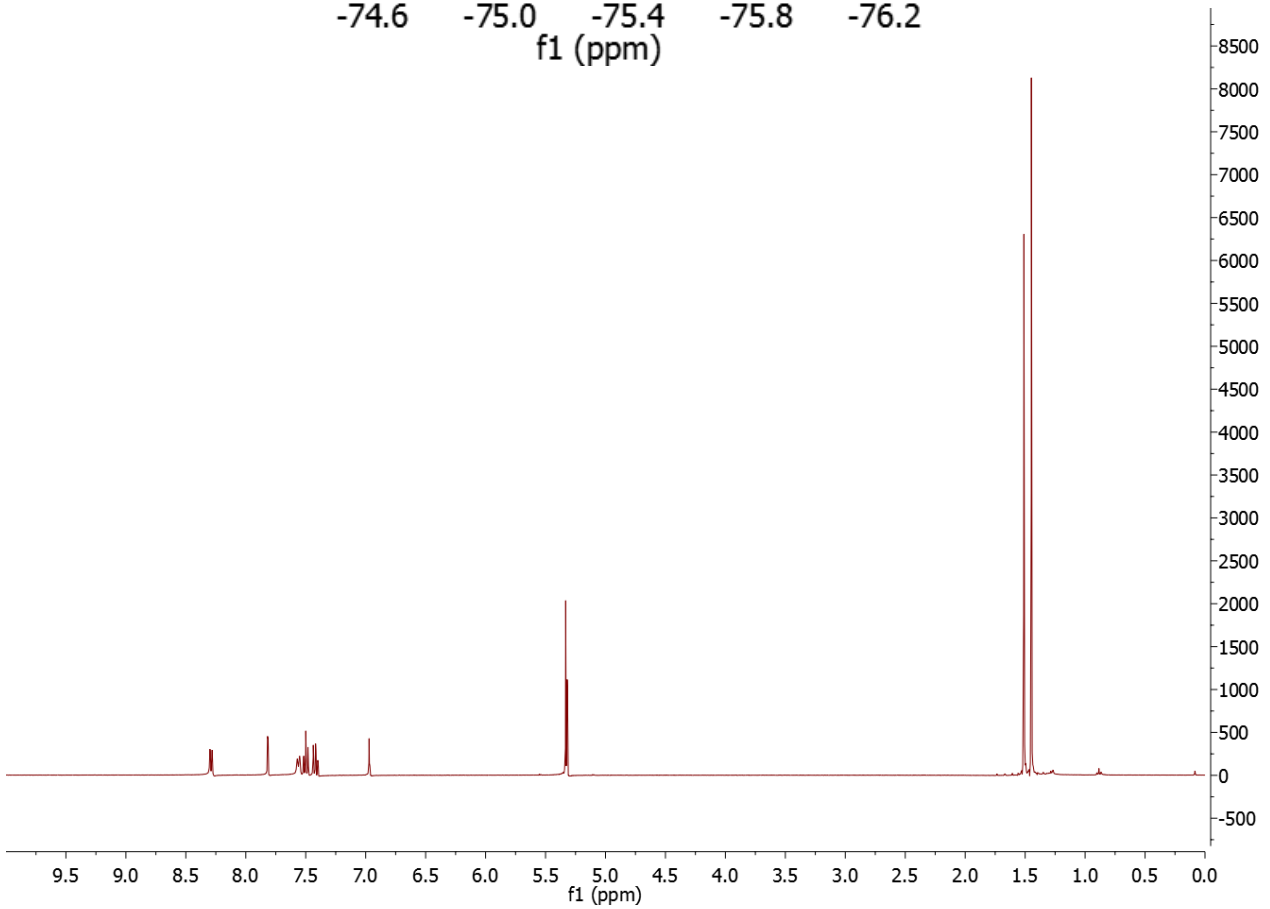


Abnormal adducts and metal: purification

Eluent: DCM
Rf: 0,71

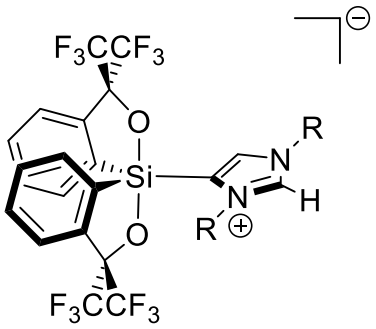




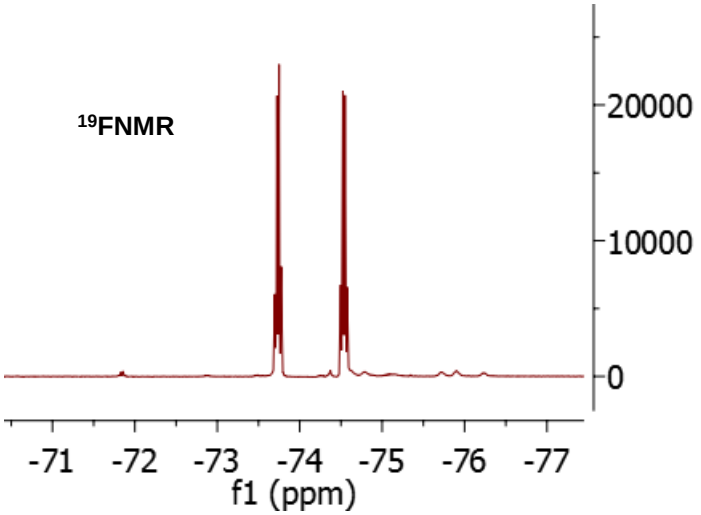


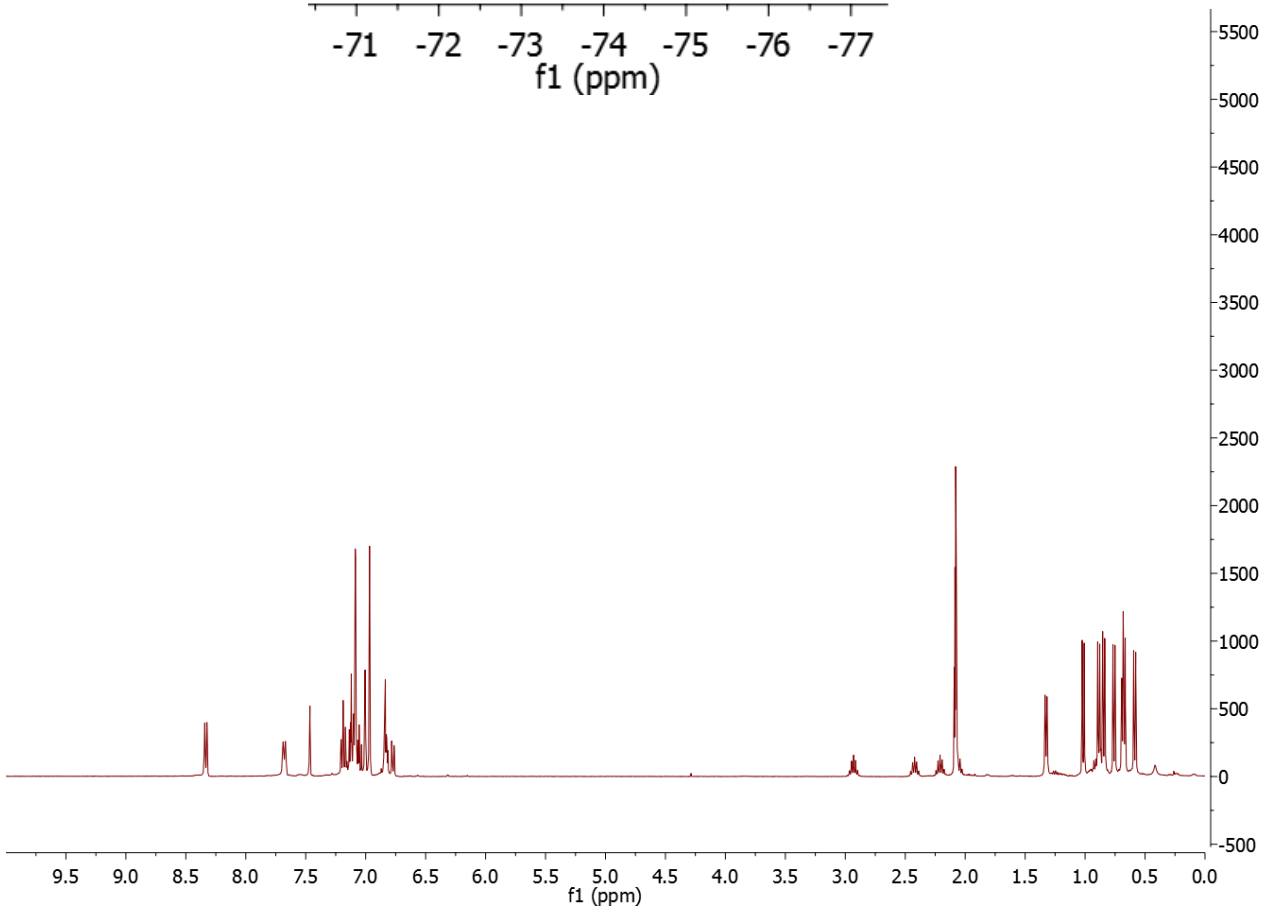
Abnormal adducts and metal: purification

Eluent: DCM
Rf: 0,75



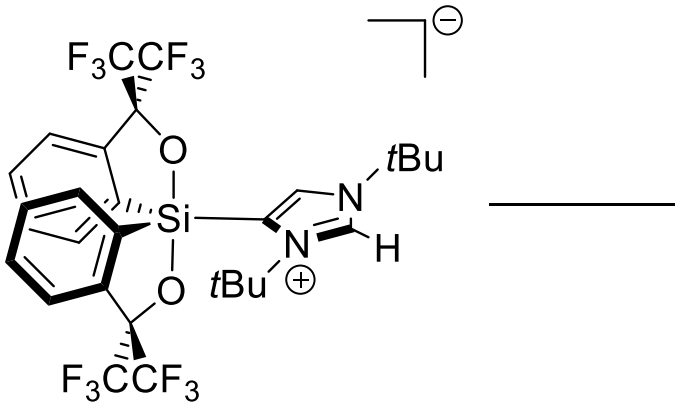
R = dipp





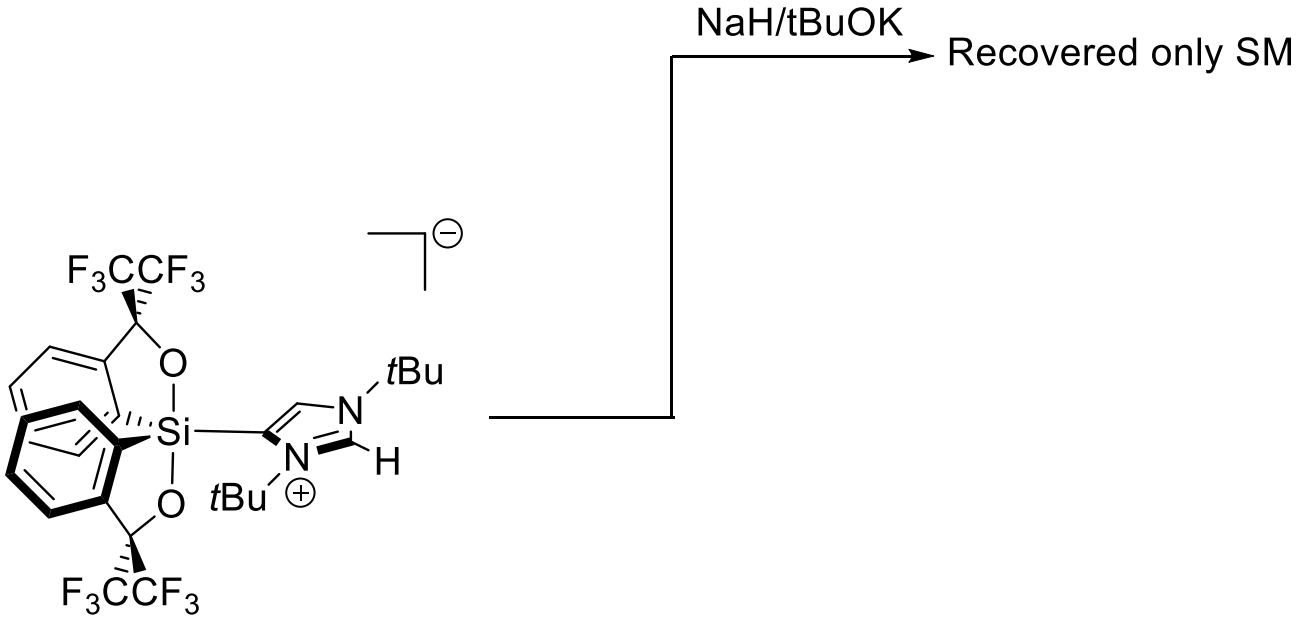
Abnormal adducts and metal: metal addition

- Deprotonation



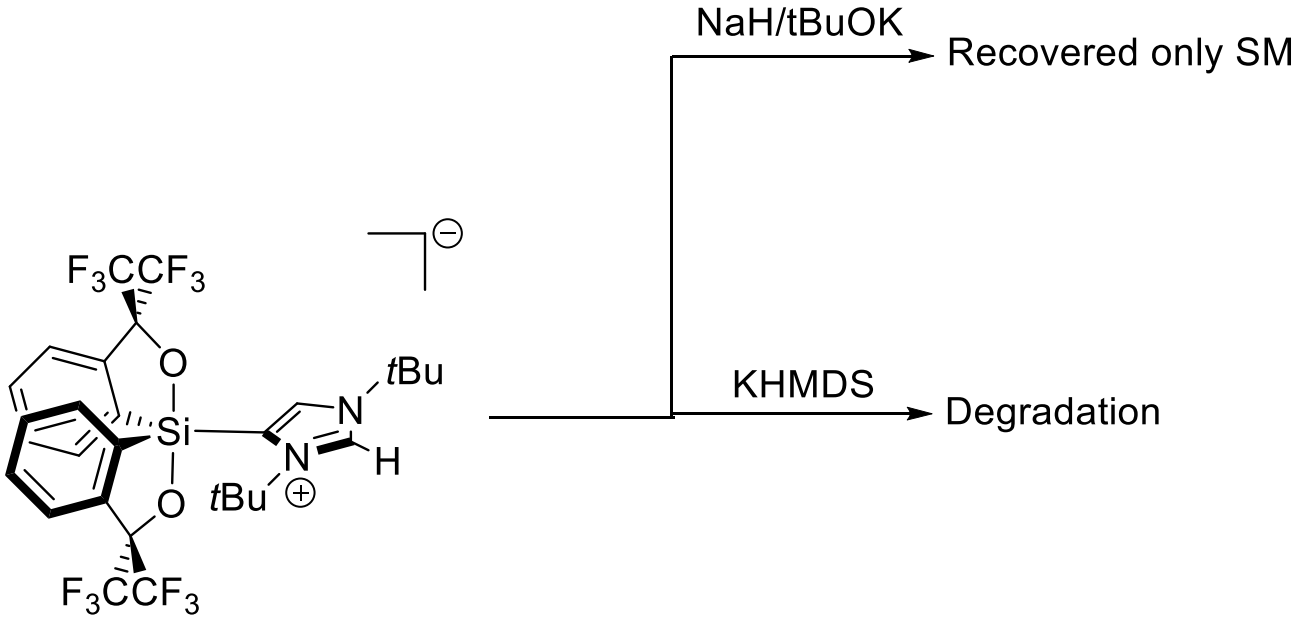
Abnormal adducts and metal: metal addition

- ***Deprotonation***



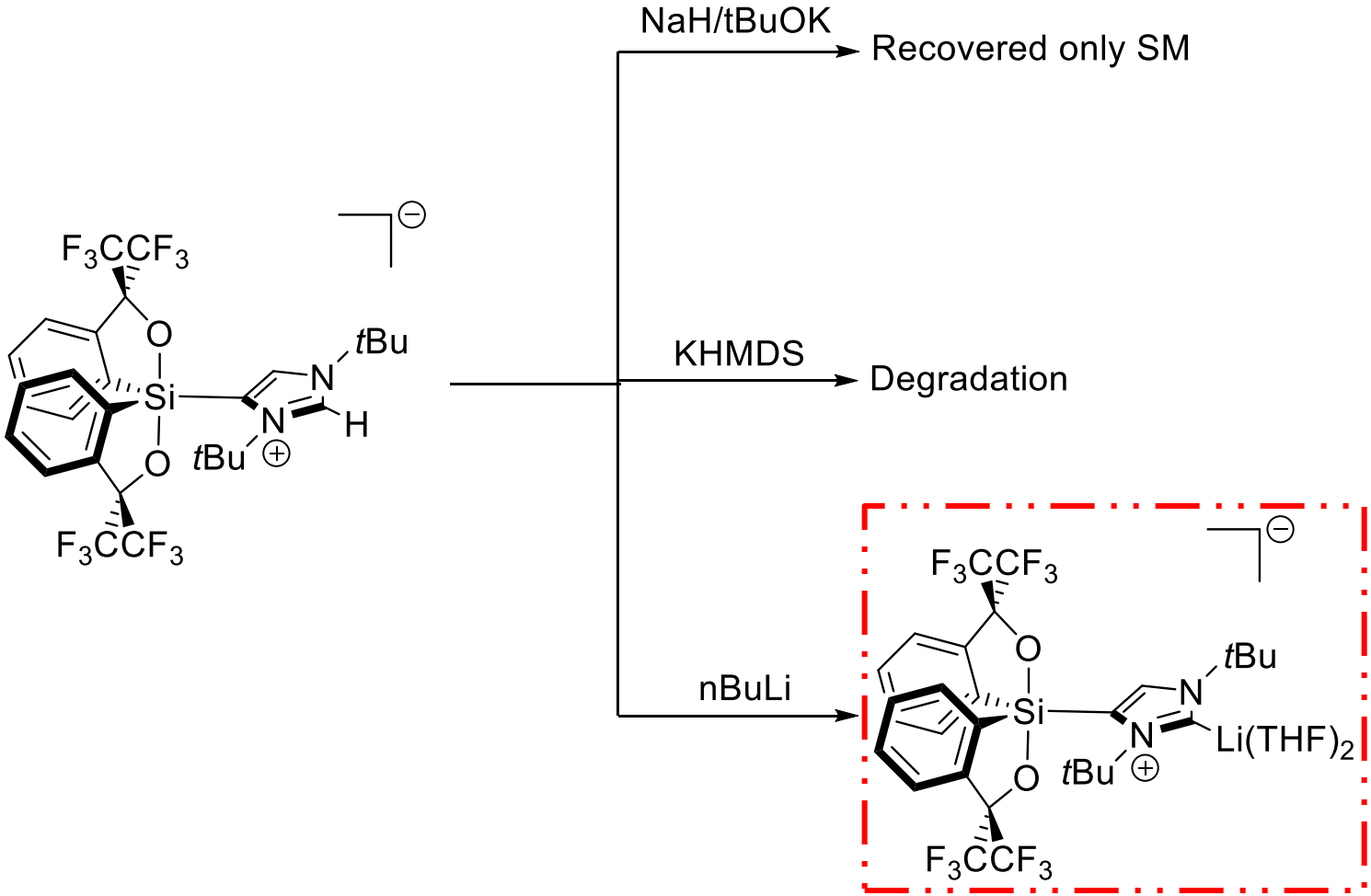
Abnormal adducts and metal: metal addition

- Deprotonation

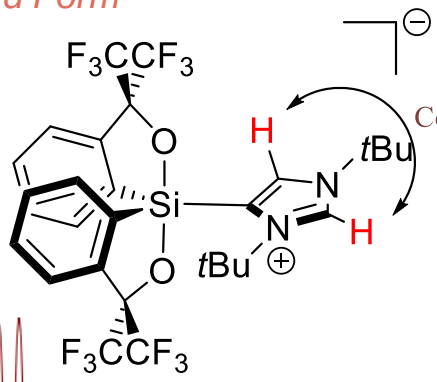


Abnormal adducts and metal: metal addition

- Deprotonation

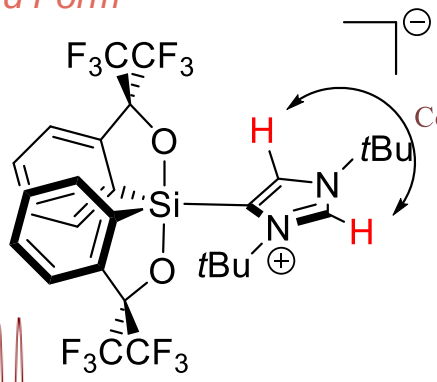


Protonated Form



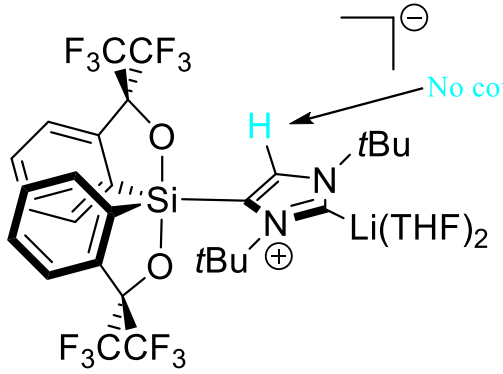
Copling: two doublets

Protonated Form



Copling: two doublets

Deprotonated Form



No coupling: one singlet

Conclusion

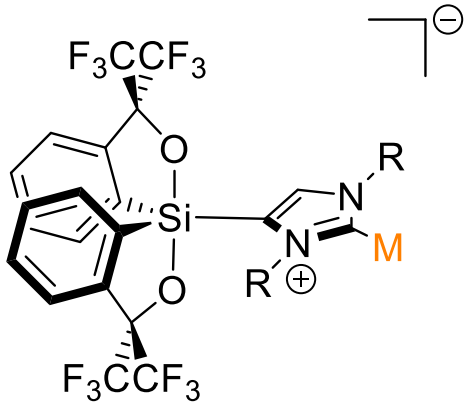
- *Optimisation of the Martin's spirosilane synthesis*
- *Isolation and characterisation of pentacoordinate complexes with different NHC-Carbene*
- *Synthesis of one of the first «abnormal» adduct with a tetravalent spirosilane not halogenated*
- *Investigation of the FLP properties with H_2 and CO_2*
- *Succesfull deprotonation of the "abnormal" adduct.*

Perspectives

- *Completion of studies regarding activation of H_2 and CO_2*

Perspectives

- *Completion of studies regarding activation of H_2 and CO_2*
- *Deprotonation of the "Abnormal" IPr adduct*
- *Starting of the studies of metals coordination at "abnormal" adducts…*

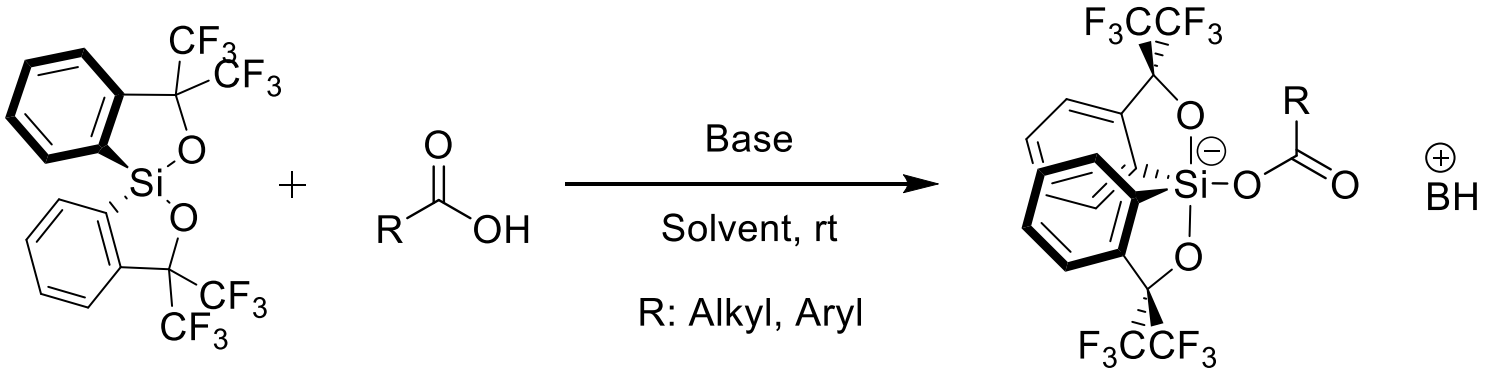


M: [Au], [Ag], [Rh], [Cu]...

- *…and their reactivity*

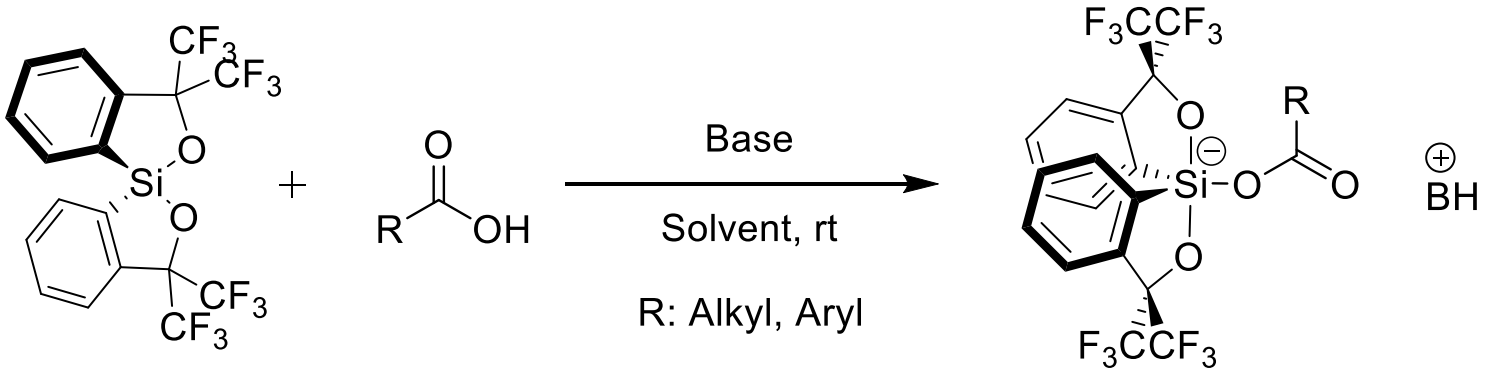
Perspectives

- *Investigations of new pentacoordinate complex with carboxylate…*

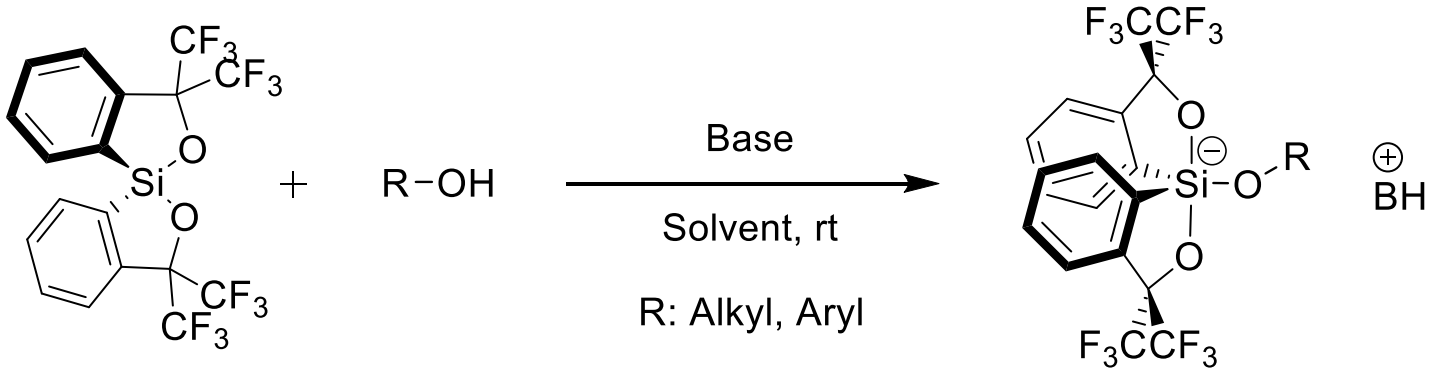


Perspectives

- *Investigations of new pentacoordinate complex with carboxylate…*



- *…and alcohol*



Acknowledgments

- *Pr. Louis Fenstrbank*
- *Dr. Gilles Lemiére*
- *Geoffrey Gontard for X-ray structure*

- MACO team

sec 54

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RESEARCH UNIVERSITY PARIS

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Thank You for Your Attention