Literature Report

Stable Analog of Carbenes: Borylenes, Nitrenes and Phosphinidenes

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Supervisor: Prof. Zhang-Jie Shi

Fudan University
2022.06.03

Content

- Background
- Stable Analog of Carbenes
  - Borylenes
  - Nitrenes
  - Phosphinidenes
- Summary

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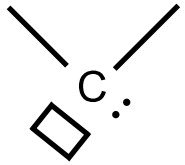
Background

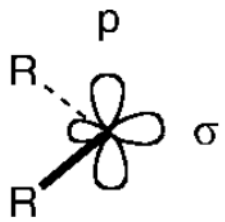
Carbene

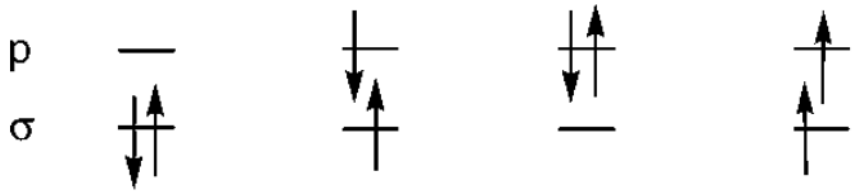


Six valence electrons

Reactive intermediates

Electronic configurations of carbenes





Lewis acid & Lewis base

$S_0(\sigma^2)$ $S_1(\sigma^1p^1)$ $S_2(p^2)$ $T_1(\sigma^1p^1)$

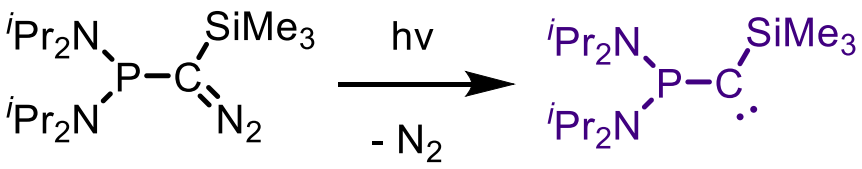
Diradicals

Singlet Singlet Singlet Triplet

Hirai, K. et al. *Chem. Rev.* **2009**, *109*, 3275-3332.

Background

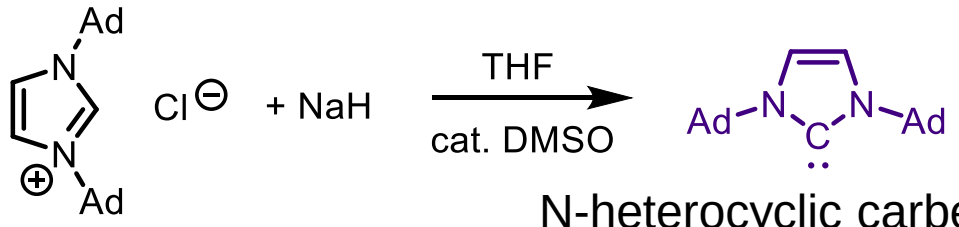
The First Stable Carbene



Push-pull mesomeric substitution pattern

(Phosphino)(silyl)carbene

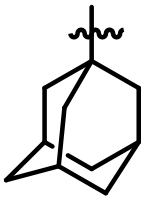
Bertrand, G. et al. *J. Am. Chem. Soc.* **1988**, *110*, 6463-6466.

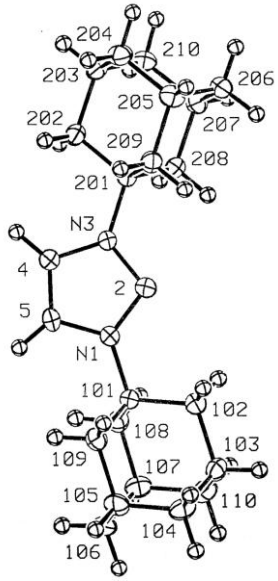


Push-push mesomeric substitution pattern

N-heterocyclic carbene (NHC)

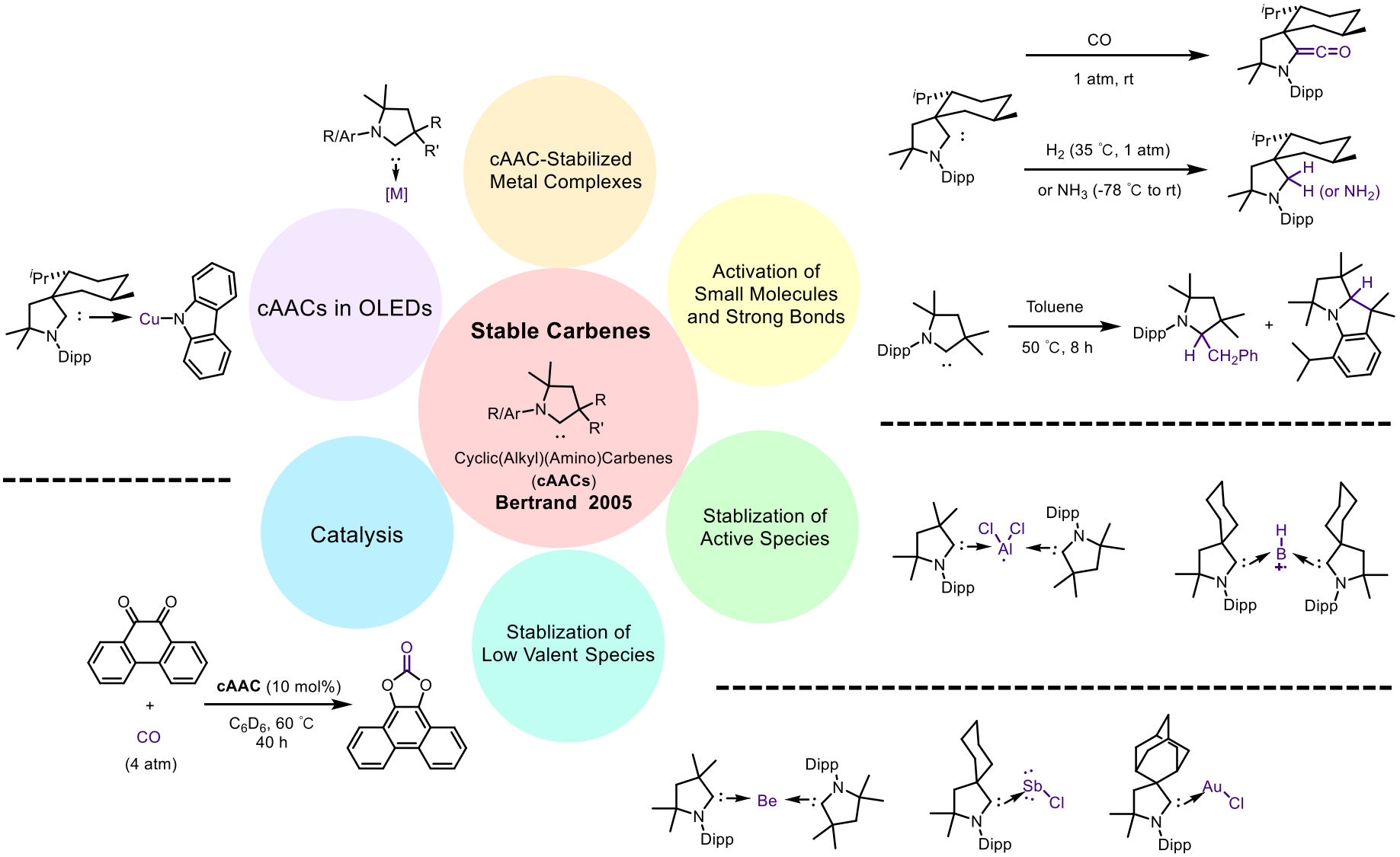
Ad =





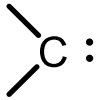
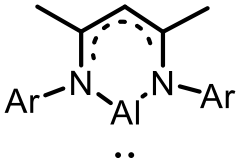
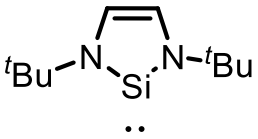
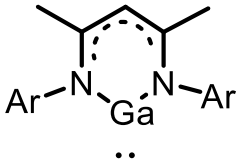
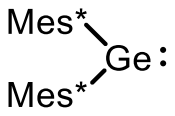
Arduengo, A. J. et al. *J. Am. Chem. Soc.* **1991**, *113*, 361-363.

Areas of Stable Carbenes Chemistry



Roesky, H, W. et al. *Chem Asian J.* **2022**,*17*, e2021013.

Main Group Element Analogues of Carbenes

Group 13 (III A)	Group 14 (IV A)	Group 15 (V A)
B —B : borylene	**C**  carbene	**N**  nitrene
Al  **Roesky 2000**	**Si**  **Weidenbruch 1994**	**P**  phosphinidene
Ga  **Power 2000**	**Ge**  **Lange 1987**	**As**

Roesky, H. W. et al. *Angew. Chem. Int. Ed.* **2000**, *39*, 4274-4276.

Power P. P. et al. *Chem. Commun.* **2000**, 1991-1992.

Weidenbruch, M. et al. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1846-1848.

Lange, L. et al. *J. Organomet. Chem*. **1987**, *329*, C17-C20.

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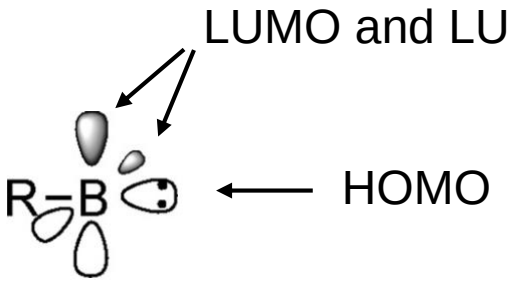
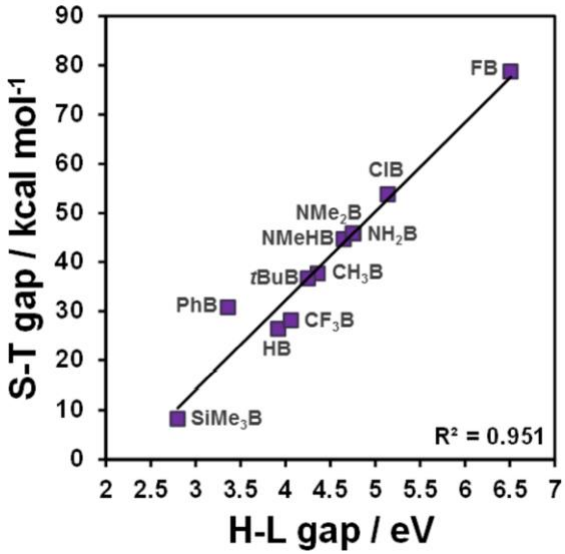
Borylenes



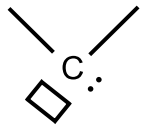
Electronic structure of singlet borylenes



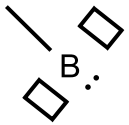
Bettinger H. F. et al. *J. Phys. Chem. A* **2016**, *120*, 6332-6341.

Computed at the B3LYP/def2-TZVP level of theory

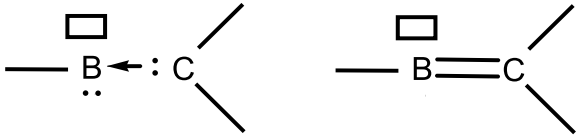
Group 13 element analogues of carbenes



Carbene



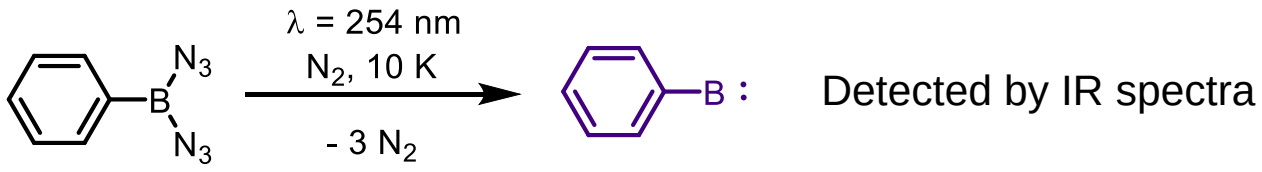
Borylene



Mono(Lewis base)-stabilized borylenes

Borylenes

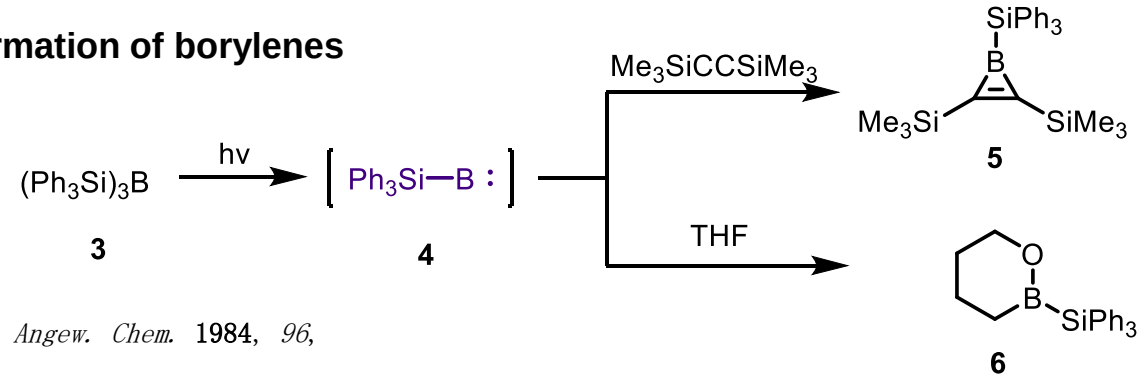
Spectroscopically characterized borylene



1 **2**

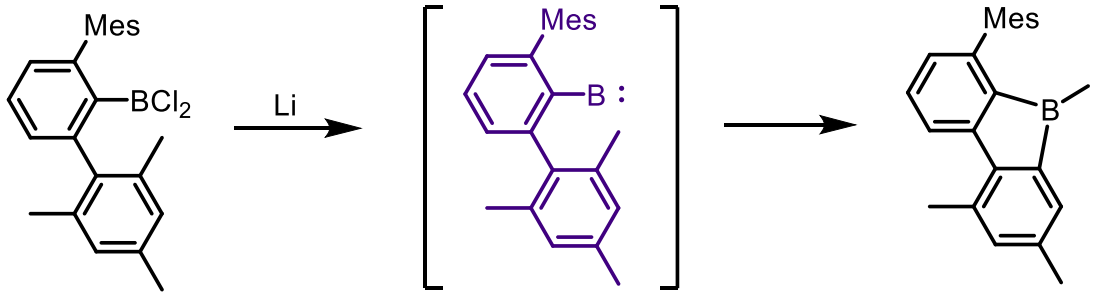
Bettinger, H. F. et al. *J. Am. Chem. Soc.* **2006**, *128*, 2534-2535.

Transient formation of borylenes



3 **4** **5** **6**

West R. et al. *Angew. Chem.* **1984**, *96*, 444.

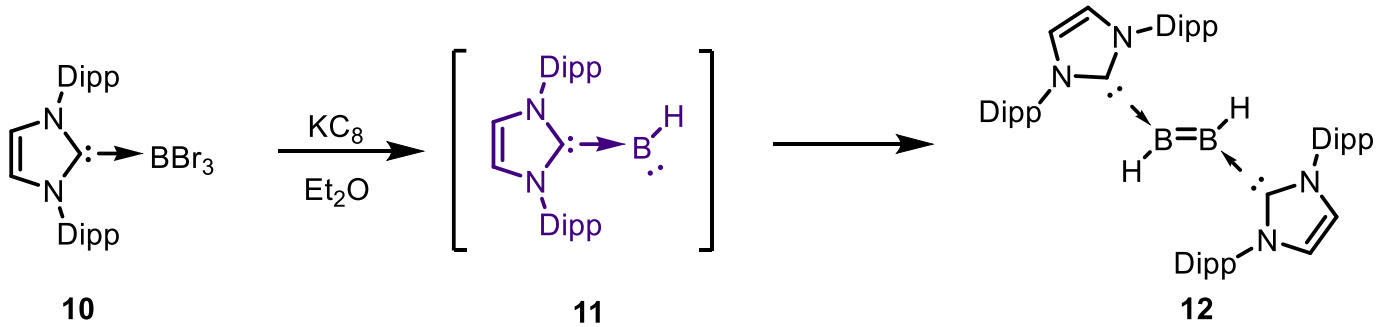


7 **8** **9**

Power, P. P. et al. *J. Am. Chem. Soc.* **1996**, *118*, 7981-7988.

Mono(Lewis base)-Stabilized Borylenes

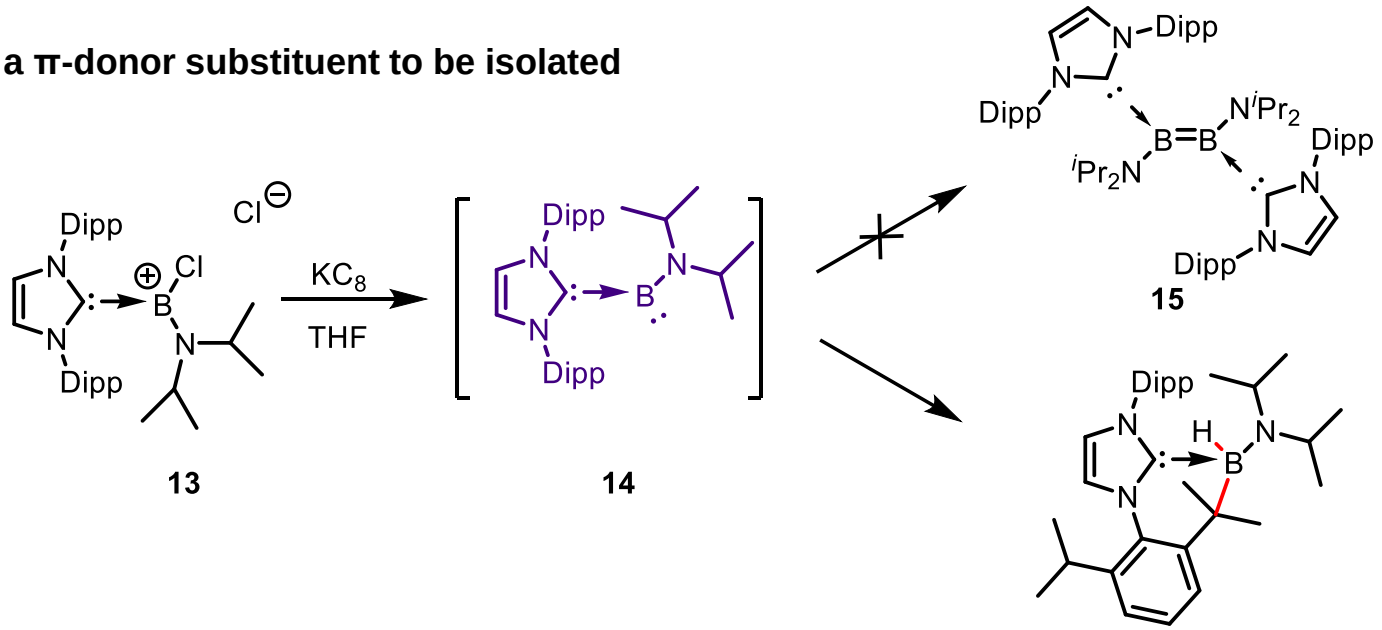
The first attempt to isolate mono(Lewis base)-stabilized borylene



Robinson, G. H. et al. *J. Am. Chem. Soc.* **2007**, *129*, 12412-12413.

The first stable neutral diborene

Need a π-donor substituent to be isolated

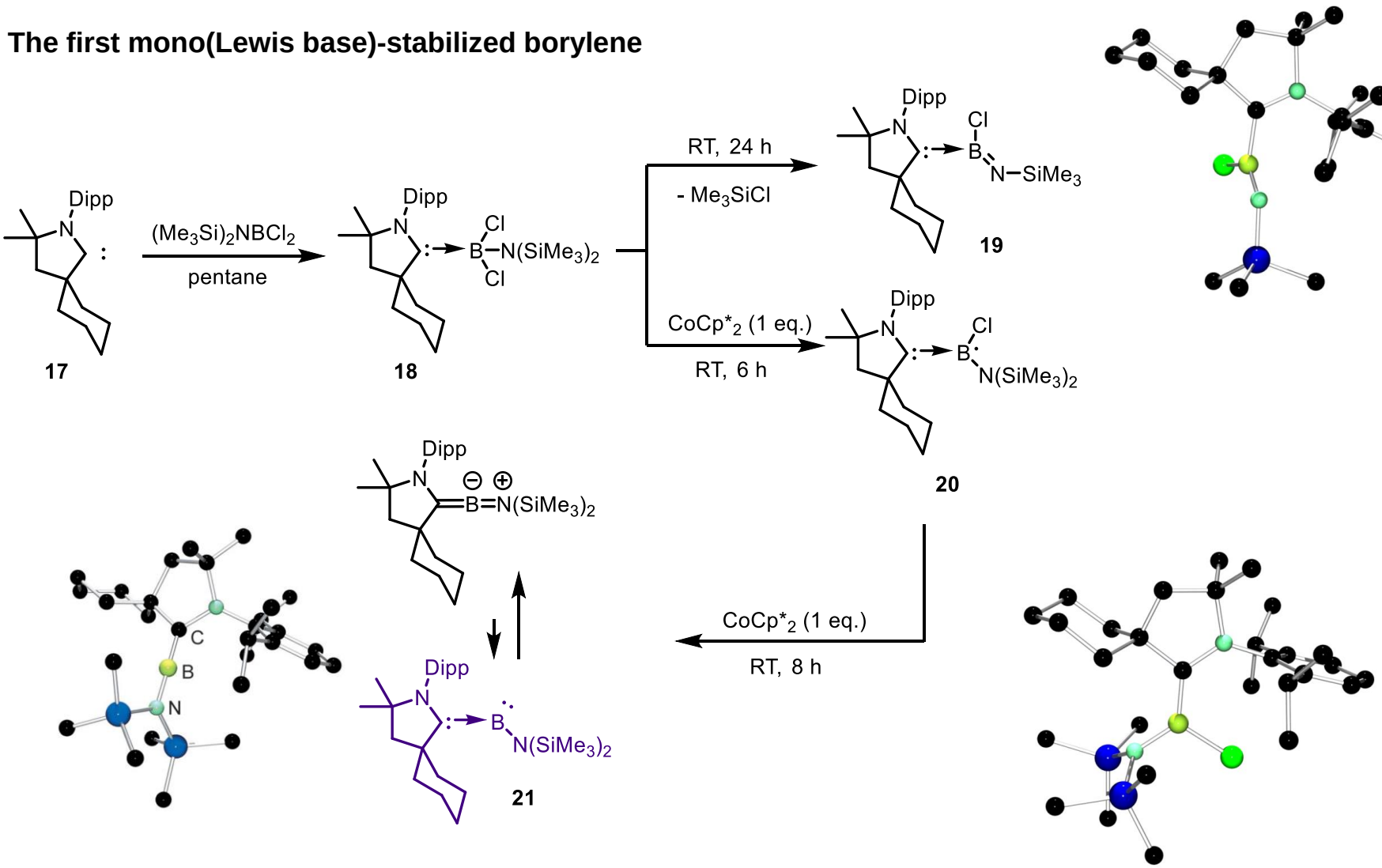


Robinson, G. H. et al. *Inorg. Chem.* **2011**, *50*, 12326-12337.

intramolecular CH insertion

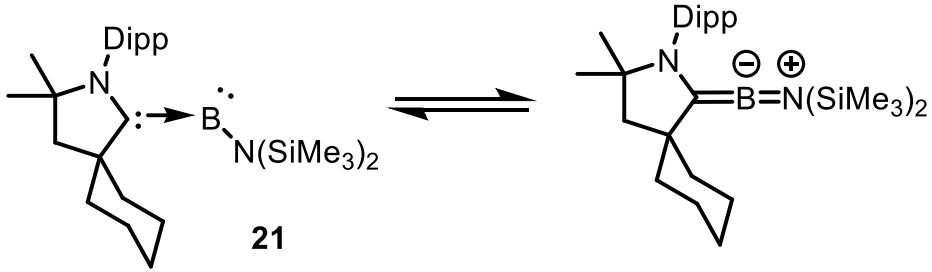
Mono(Lewis base)-Stabilized Borylenes

The first mono(Lewis base)-stabilized borylene



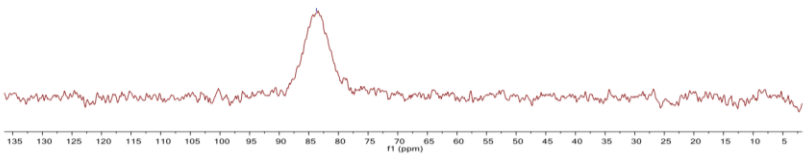
Bertrand, G. et al. *Angew. Chem. Int. Ed.* **2014**, *53*, 13159-13163.

Mono(Lewis base)-Stabilized Borylenes

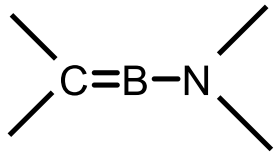


21

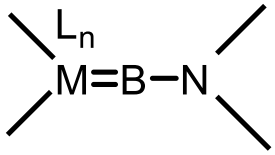
83.72



The ^{11}B NMR spectrum of **21**

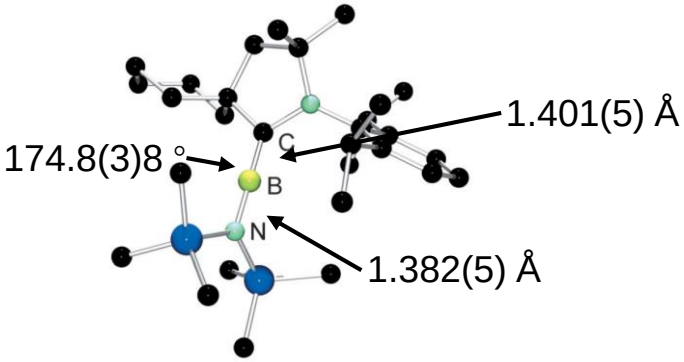


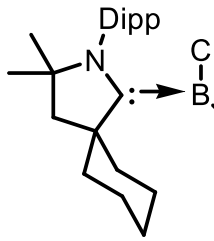
Aminoboraalkenes
^{11}B NMR +59 ~ +71 ppm



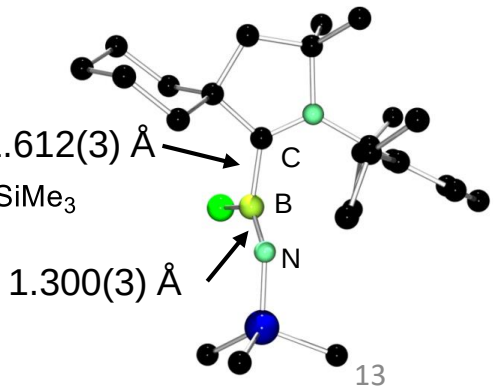
Transition-metal-stabilized terminal aminoborylenes
^{11}B NMR +67 ~ +92 ppm

Allenic Structure





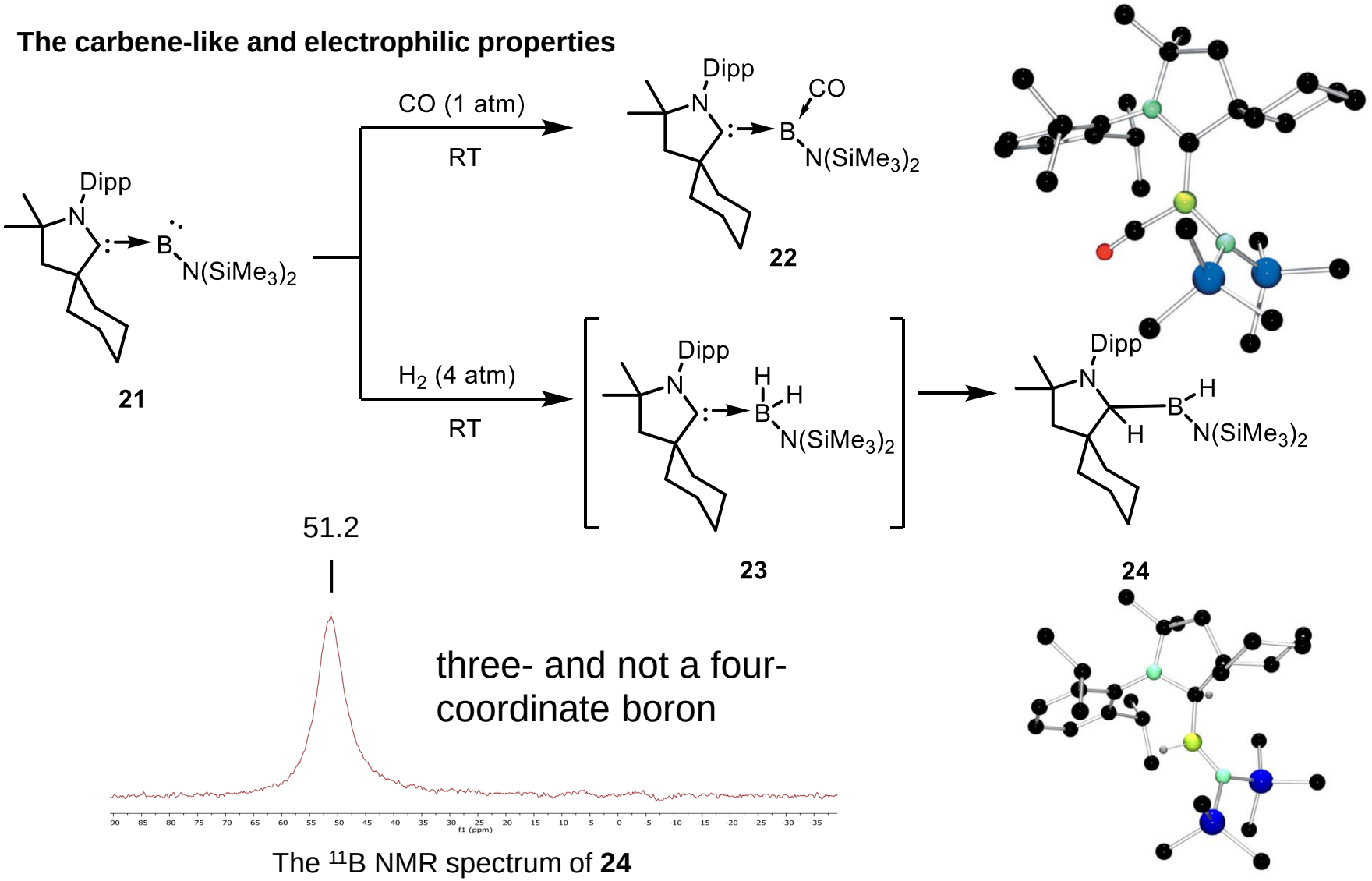
19



Bertrand, G. et al. *Angew. Chem. Int. Ed.* **2014**, *53*, 13159-13163.

Mono(Lewis base)-Stabilized Borylenes

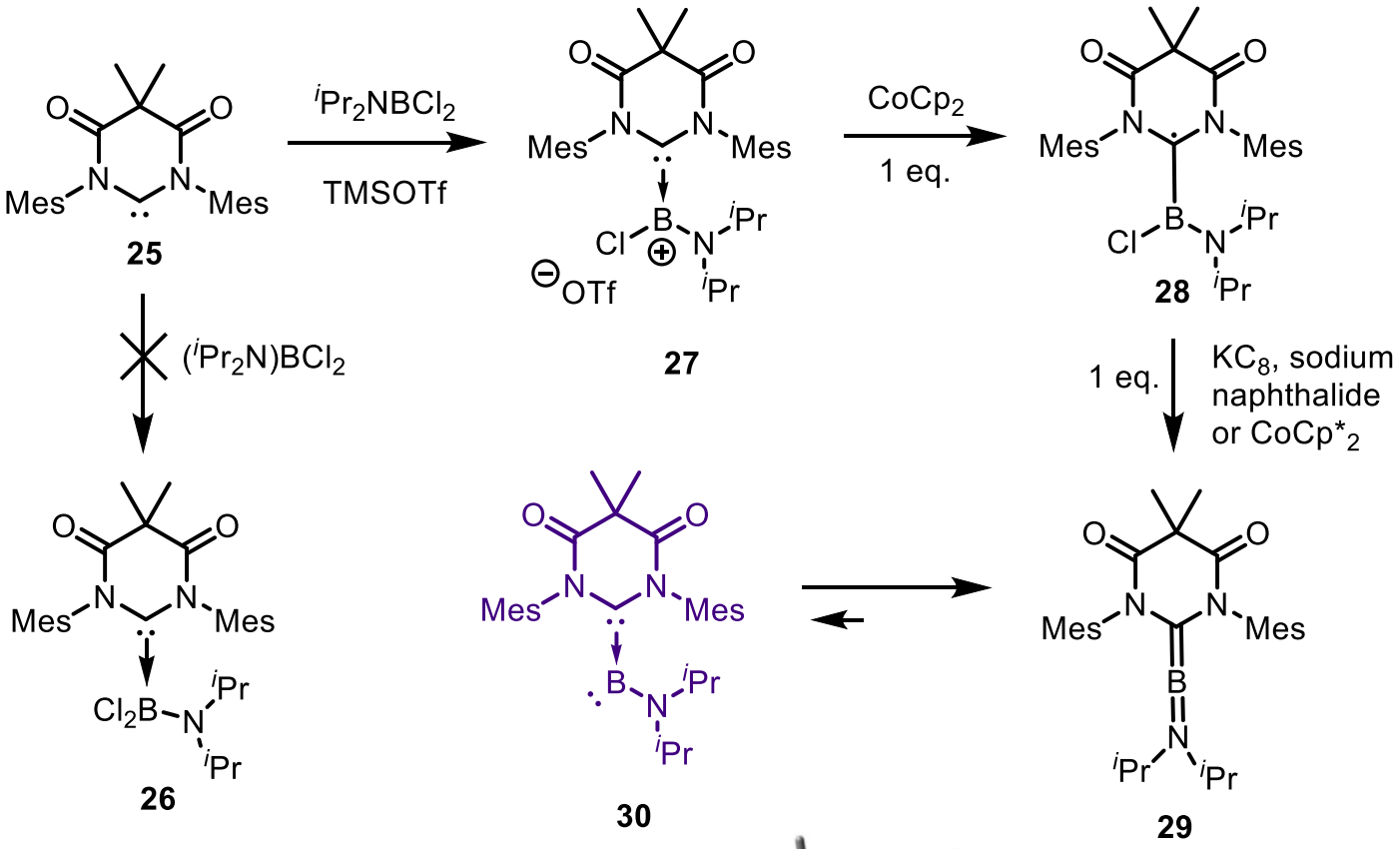
The carbene-like and electrophilic properties

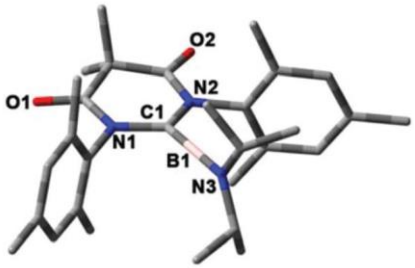


The ^{11}B NMR spectrum of **24**

Mono(Lewis base)-Stabilized Borylenes

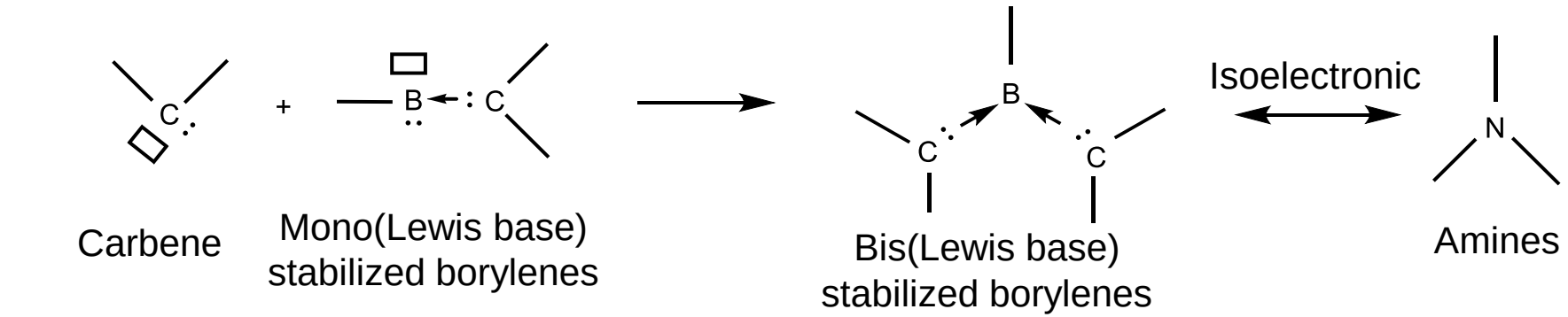
DAC-Stabilized Borylene

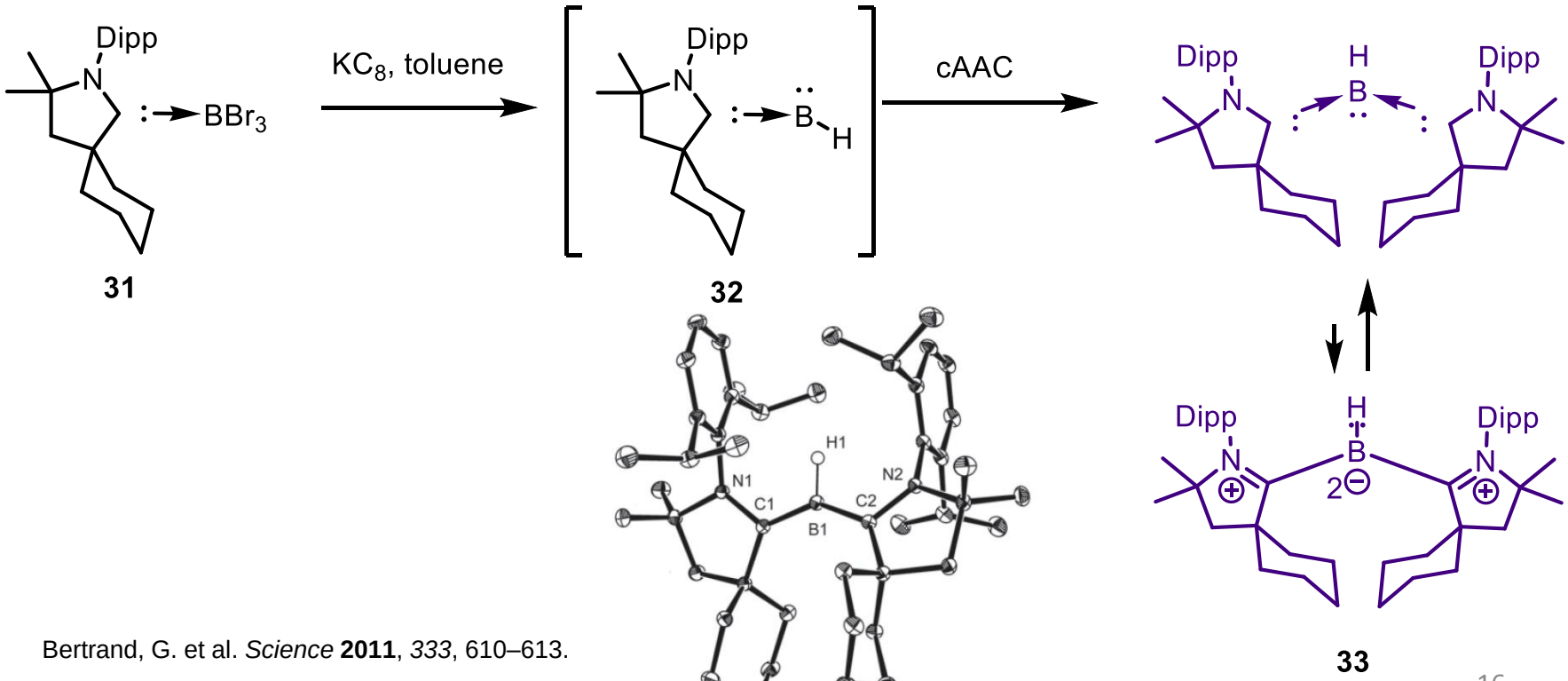




Hudnall T. W. et al. *Dalton Trans.* **2016**, *45*, 9820-9826.

Bis(Lewis base)-Stabilized Borylenes

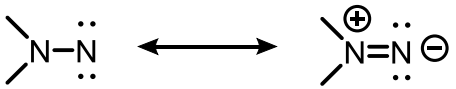


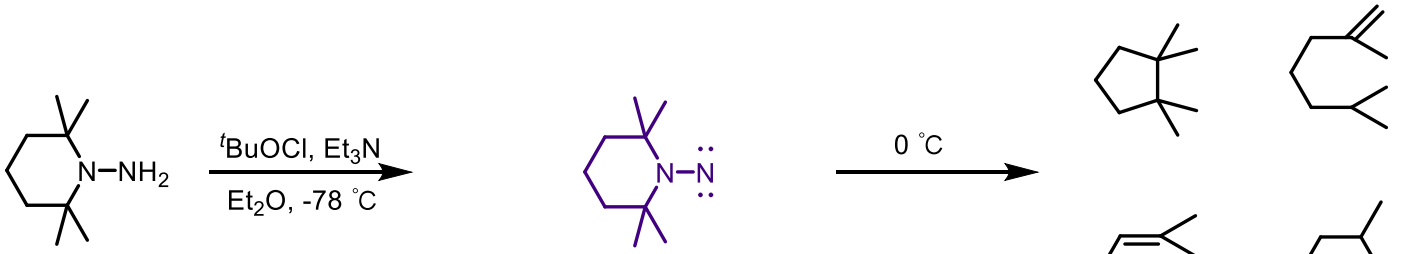


Bertrand, G. et al. *Science* **2011**, *333*, 610–613.

Stable Nitrenes

metallonitrenes $L_nM{-}\ddot{N}: \longleftrightarrow L_nM{\equiv}N:$ metal-nitrido complexes

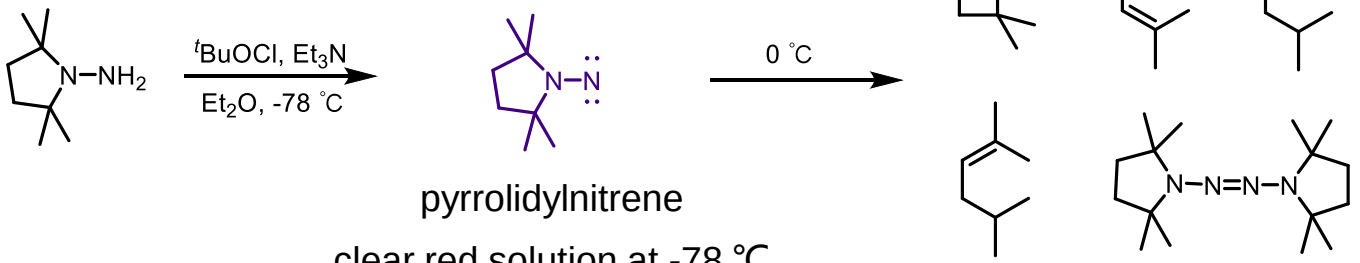
the most stable nonmetallic nitrenes  aminonitrene



piperidylnitrene

clear purple solution at -78 ℃

spectroscopic characterization and purification by low-temperature chromatography



pyrrolidylnitrene

clear red solution at -78 ℃

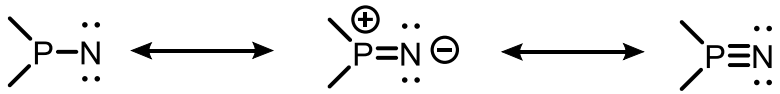
Dervan, P. et al. *J. Am. Chem. Soc.* **1978**, *100*, 1608-1610.

Schultz, P. et al. *J. Am. Chem. Soc.* **1980**, *102*, 878-880.

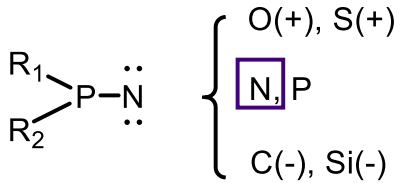
Hinsberg, W. D. et al. *J. Am. Chem. Soc.* **1982**, *104*, 766-773.

Dervan, P. et al. *J. Am. Chem. Soc.* **1981**, *103*, 1120-1122.

Stable Nitrenes

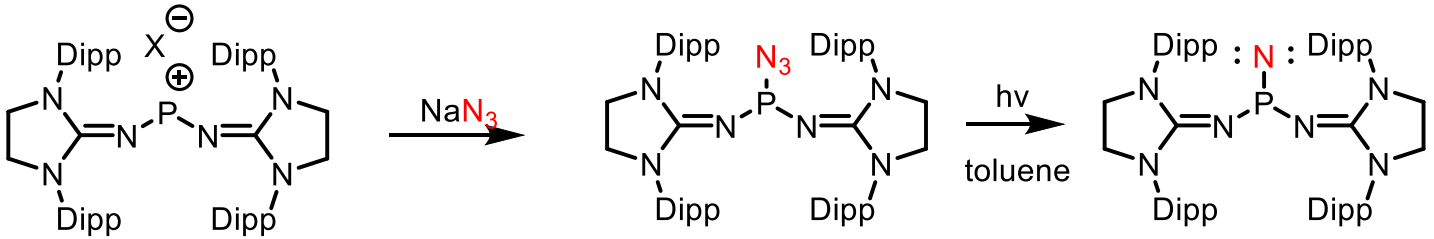


Phosphinonitrene



Substituents, which bear an imino function in the α-position to the phosphorus atom, e.g.,the phosphaniminato group" would be the best choice

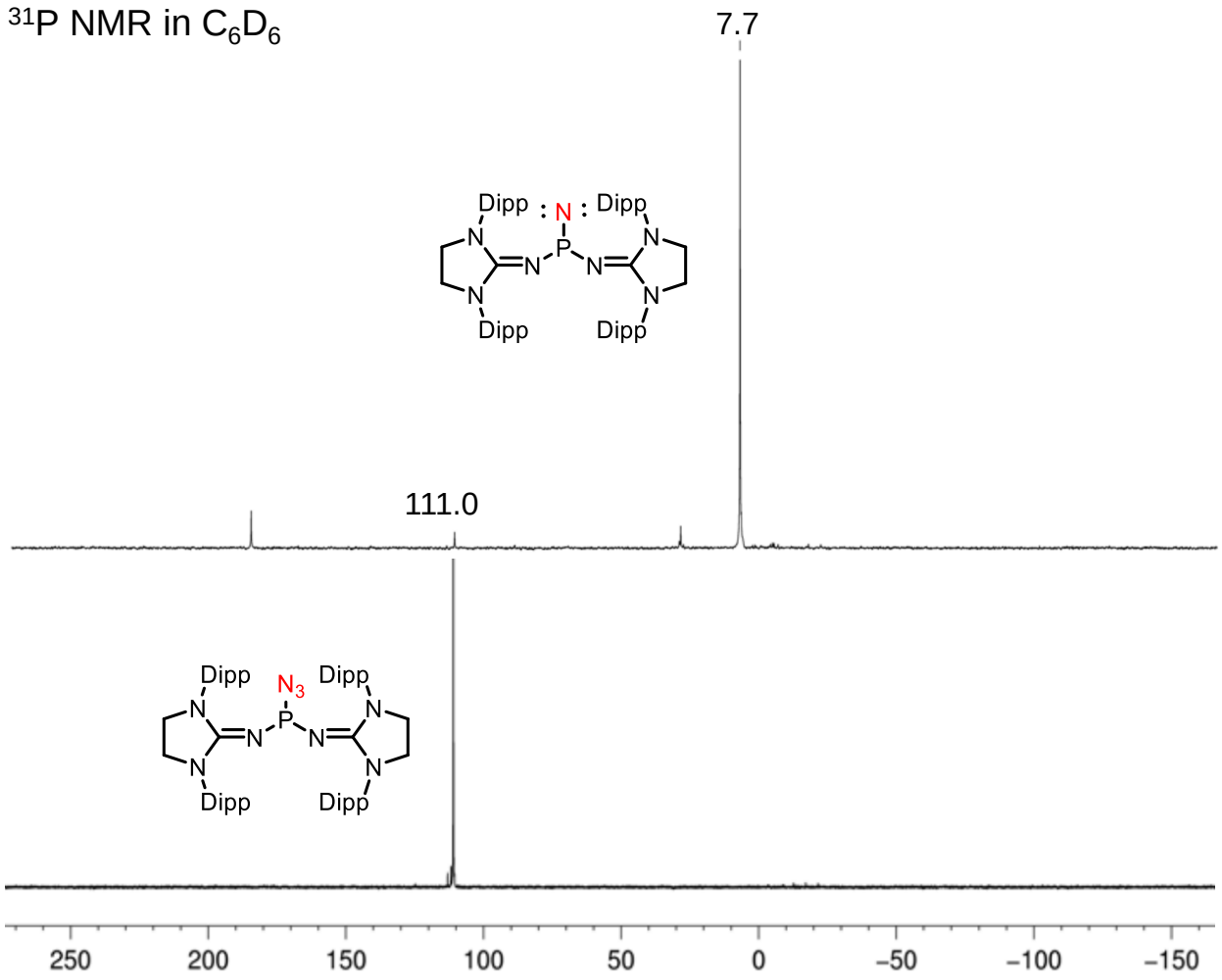
Schoeller, W. et al. *Eur. J. Inorg. Chem.* **2001**, *2001*, 845-850.



34 **35** **36**

Bertrand, G. et al. *Science* **2012**, *337*, 1526-1528.

Stable Nitrenes



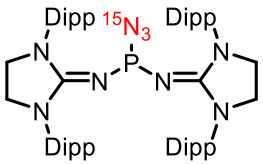
Hypervalent phosphorus center

Bertrand, G. et al. *Science* **2012**, *337*, 1526-1528.

Stable Nitrenes

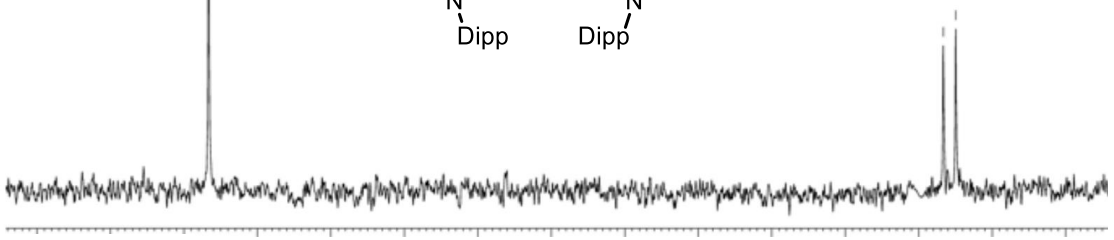
^{15}N NMR in C_6D_6

196.6



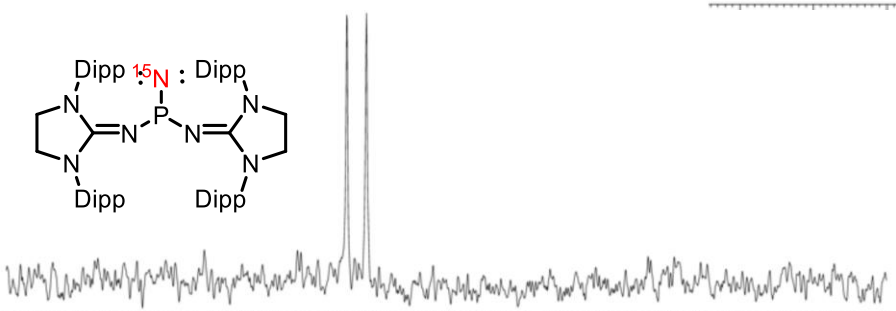
J_{PN} =103 Hz

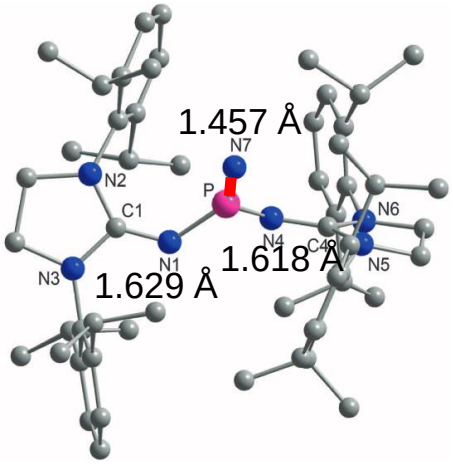
96.6 95.0



J_{PN} =144 Hz

267.2 264.8



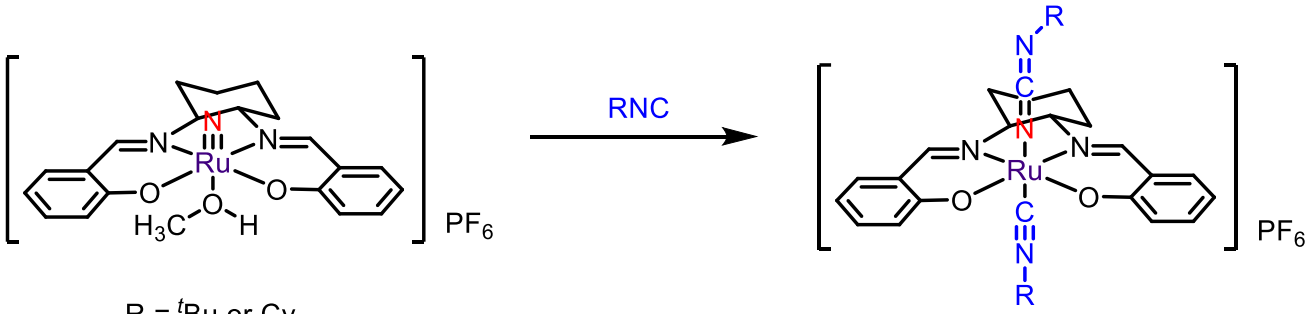


PN multiple bond

Reported PN double bonds are in the range of 1.50 to 1.60 Å

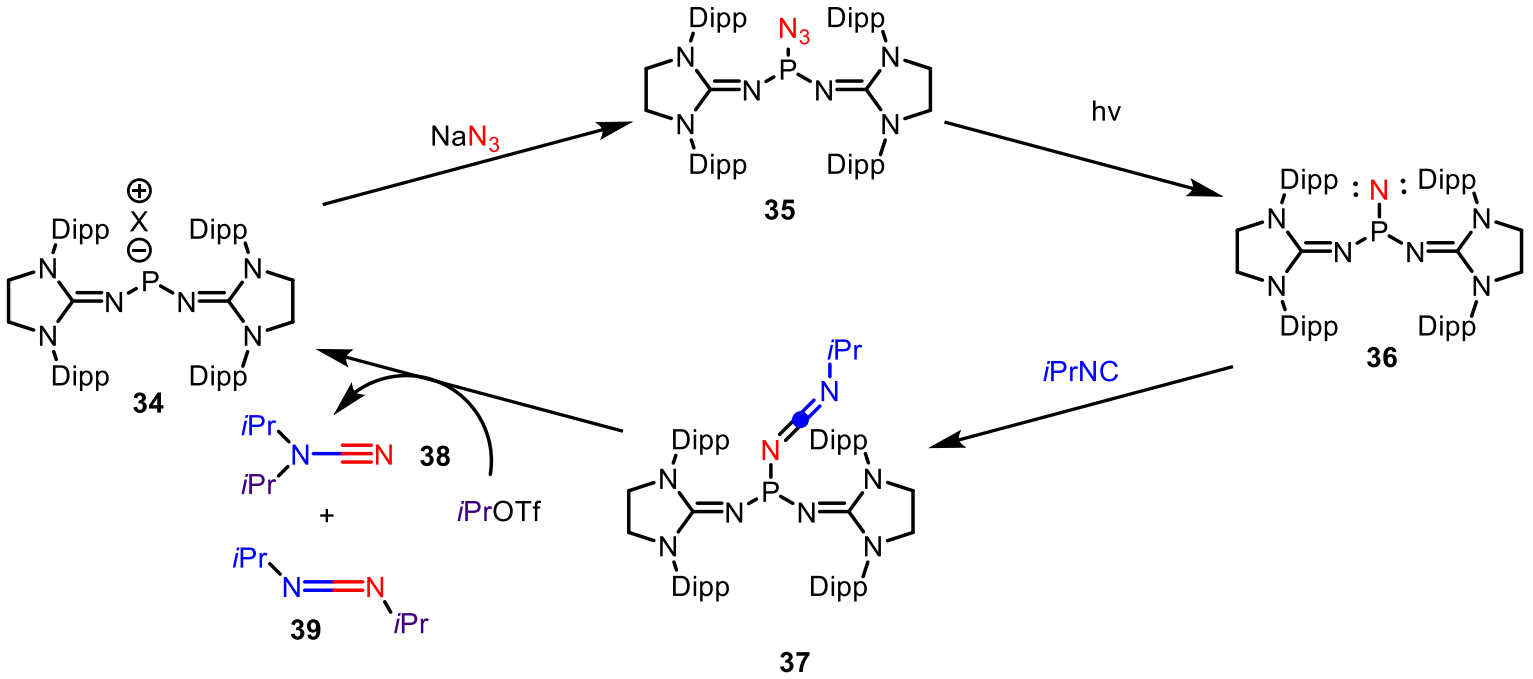
Bertrand, G. et al. *Science* **2012**, *337*, 1526-1528.

Stable Nitrenes



R = ^{t}Bu or Cy

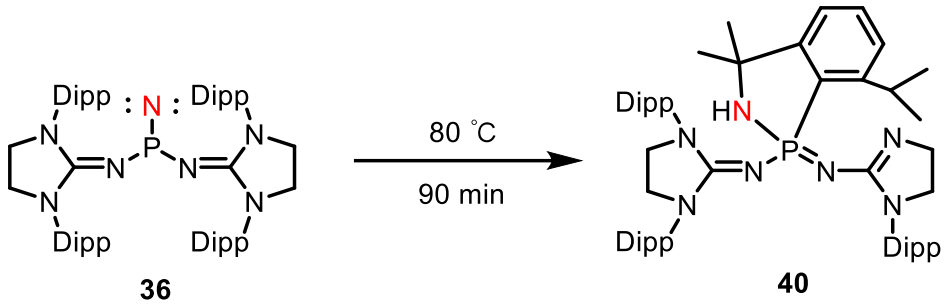
Lau, T. C. et al. *Inorg. Chem.* **2009**, *48*, 3080-3086.



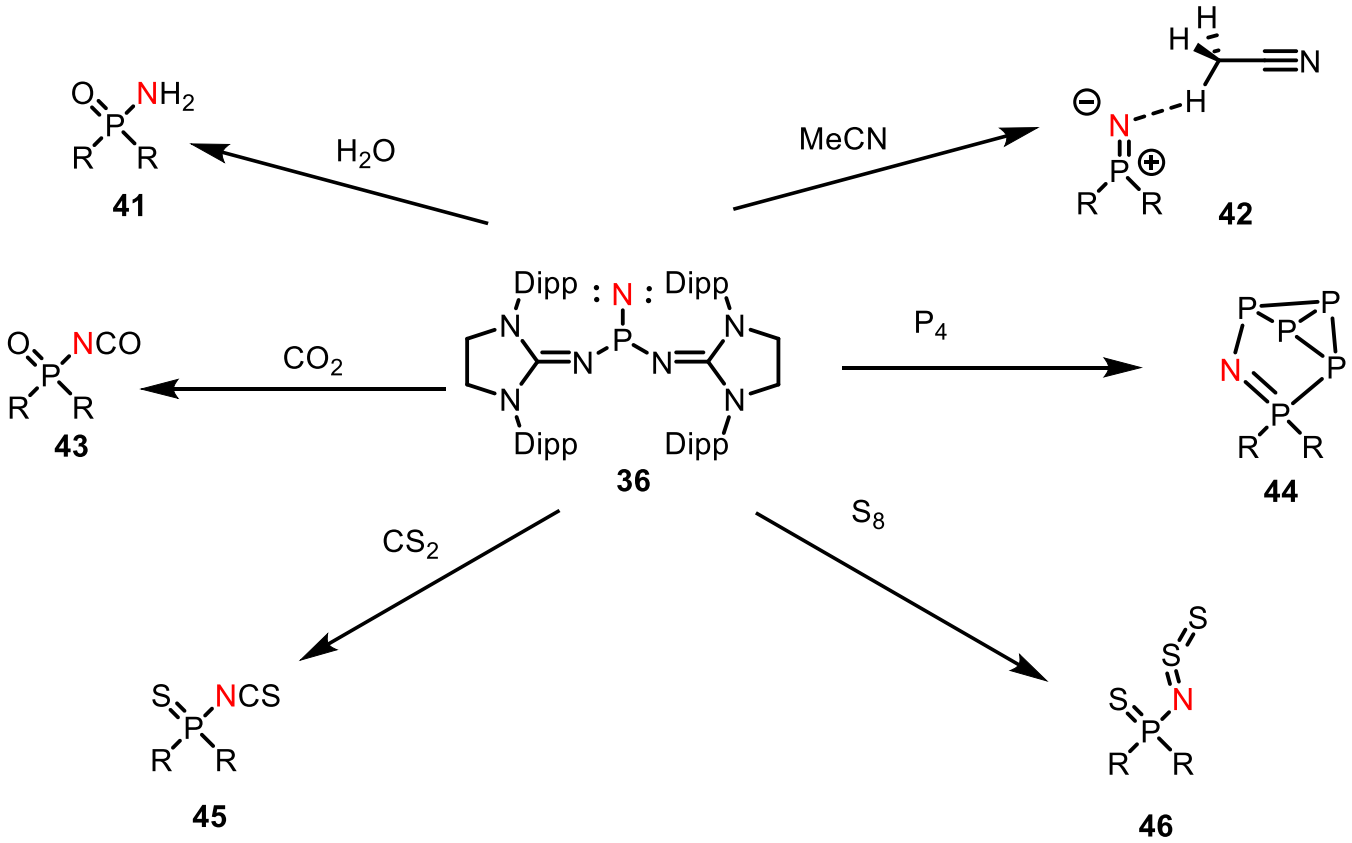
Mimic the chemical behavior of transition metals

Bertrand, G. et al. *Science* **2012**, *337*, 1526-1528.

Stable Nitrenes



36 40

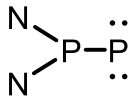


41 42 43 36 44 45 46

Bertrand, G. et al. *Chem. Eur. J.* **2015**, *21*, 191-198.

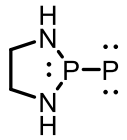
Stable Phosphinidene

Phosphinidenes

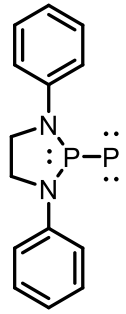


Amino groups in the β position of phosphino-phosphinidenes would be the best choice

Nguyen, M. T. et al. *J. Org. Chem.* **1996**, *61*, 7077-7084.



47



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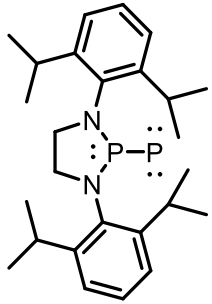
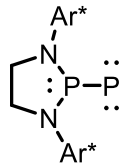


49



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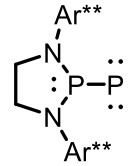


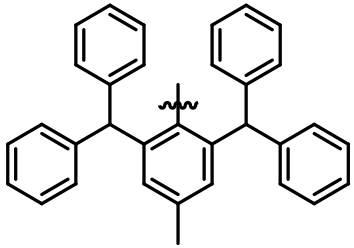
51

Singlet-triplet gap (kcal/mol)

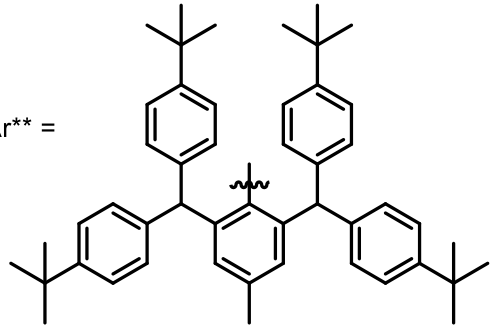
47	48	49	50	51
17.4	8.2	17.2	23.5	

calculations at the M06-2X/Def2-SVP level

Ar* =



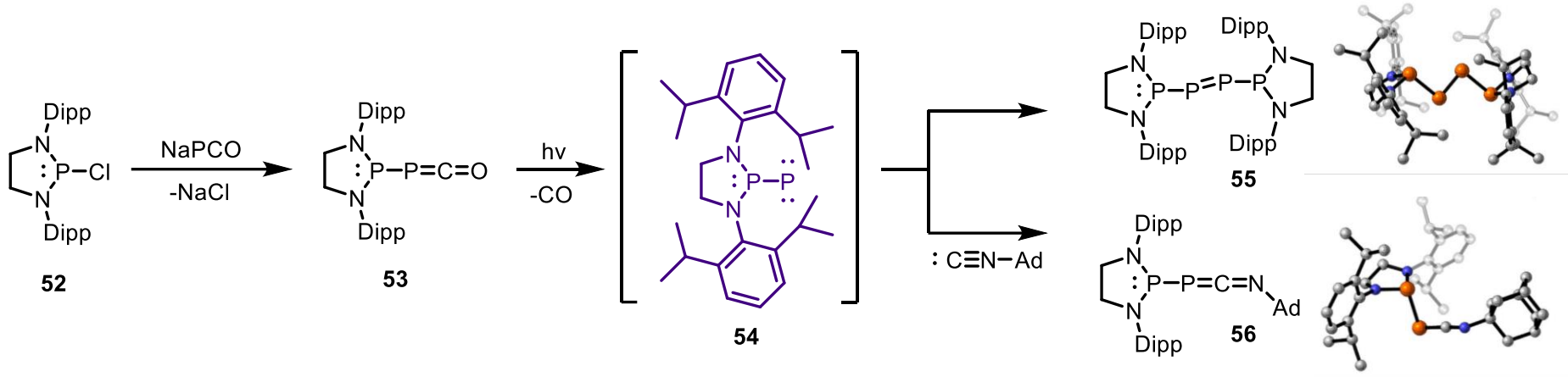
Ar** =

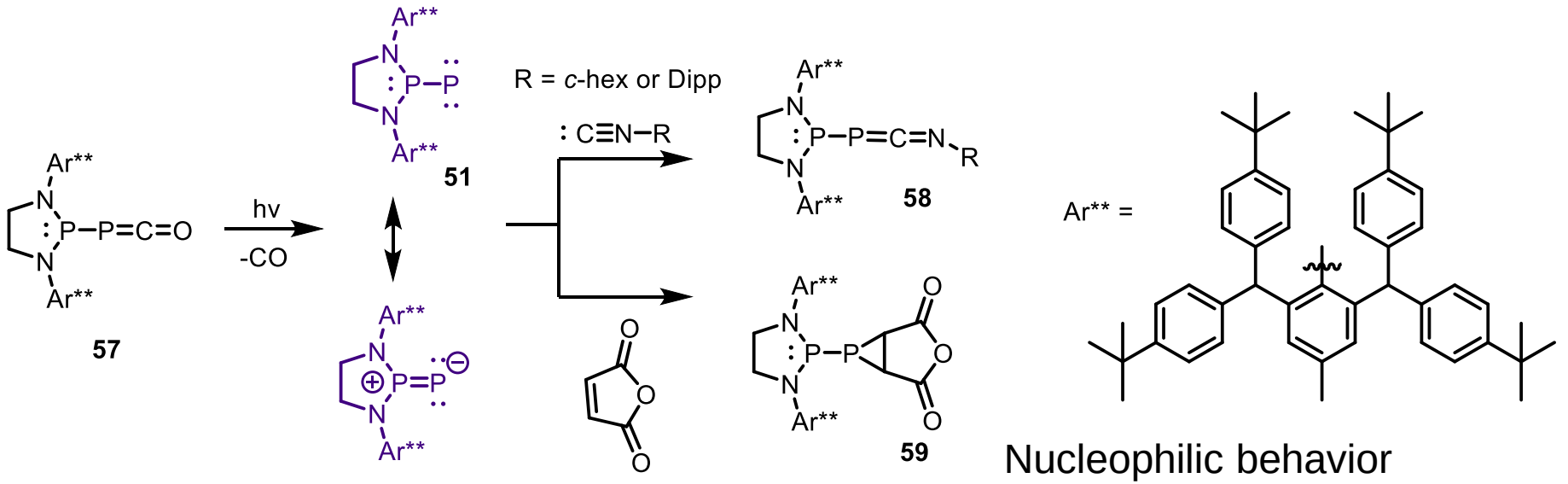


Bertrand, G. et al. *Chem* **2016**, *1*, 147-153.

Stable Phosphinidene

Dipp groups are not bulky enough to kinetically protect phosphinidene





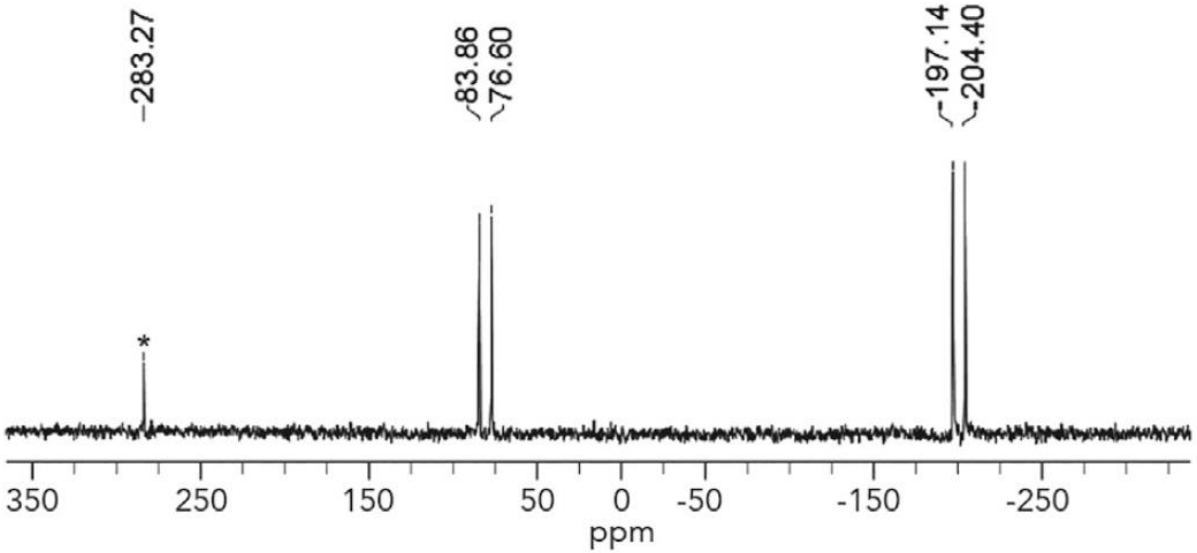
Nucleophilic behavior

Bertrand, G. et al. *Chem* **2016**, *1*, 147-153.

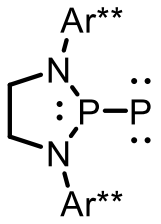
Stable Phosphinidene

^{31}P NMR in C_6D_6

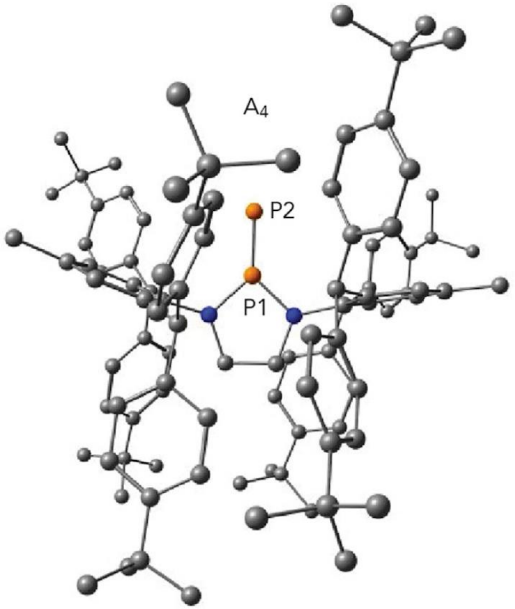
J_{PP} =883.7 Hz



(asterisk denotes unidentified impurity)



51



PP multiple bond

A negatively charged terminal phosphorus center

Planar Environment

Bertrand, G. et al. *Chem* **2016**, *1*, 147-153.

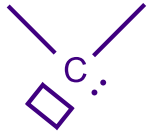
Content

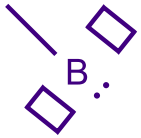
- Background
- Stable Analog of Carbenes
  - Borylenes
  - Nitrenes
  - Phosphinidenes
- Summary

Summary

Emerging Class of Compounds

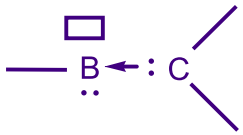
Stable Analog of Carbenes

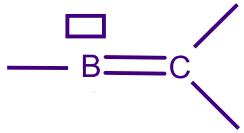


Borylenes 

Eluding by synthetic skills

Mono(Lewis base)-stabilized borylenes





Linear allenic structure

Nitrenes 

PX multiple bond

Planar Environment

Phosphinidenes 

Thanks!