



Prof. Holger Braunschweig

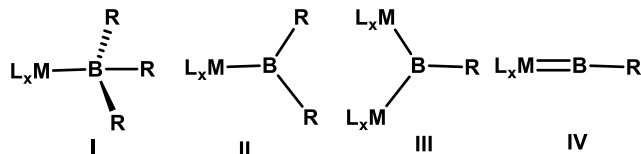
Holger Braunschweig is head and chair of Inorganic Chemistry at the University of Würzburg. He obtained his PhD and Habilitation with Prof. P. Paetzold (RWTH Aachen). He was post-doc with Prof. M. F. Lappert at Sussex and held a position as Reader at Imperial College, London.

He carried out seminal work on metal boron complexes, boron heterocycles, and boron-boron multiple bonds. His work was published in over 500 publications, the majority of which appeared in first ranking journals.

He was awarded the Gottfried Wilhelm Leibniz award (2009), the RSC Main Group Chemistry Award (2014), and received the Arduengo, Steinhofer, Bruker, and ScotCHEM named visiting lectureships. He is a member of the Bavarian Academy of Sciences, the German National Academy of Sciences (Leopoldina), the North Rhine-Westphalian Academy of Sciences, and the DFG advisory panel for molecular inorganic chemistry.

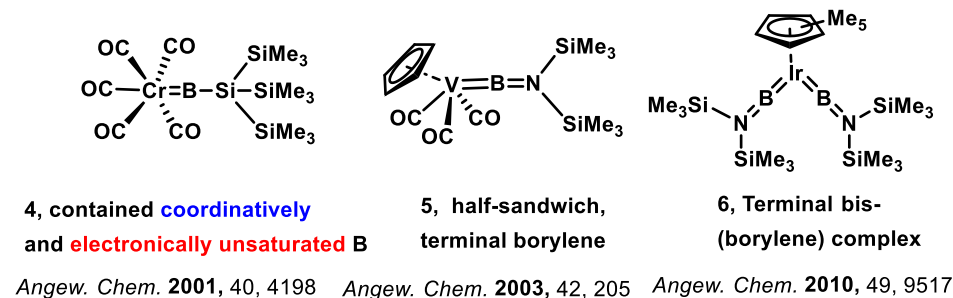
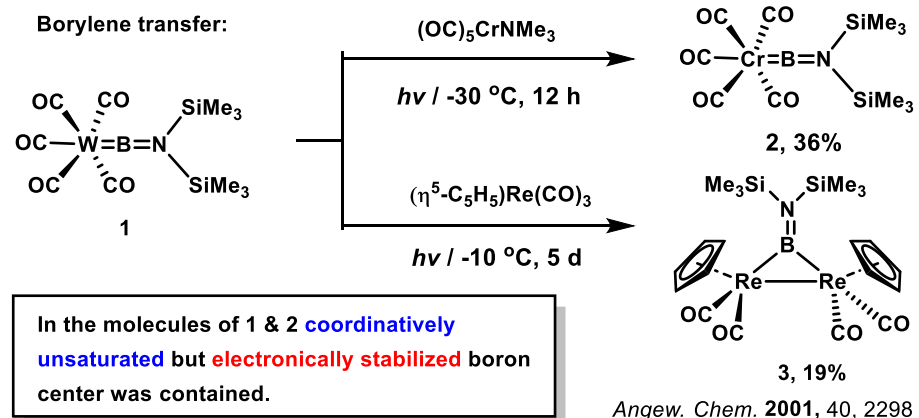
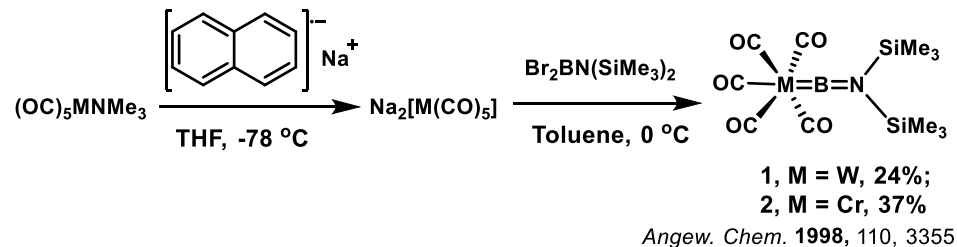


Research in the Braunschweig group covers a wide range of organometallic and main group element chemistry.

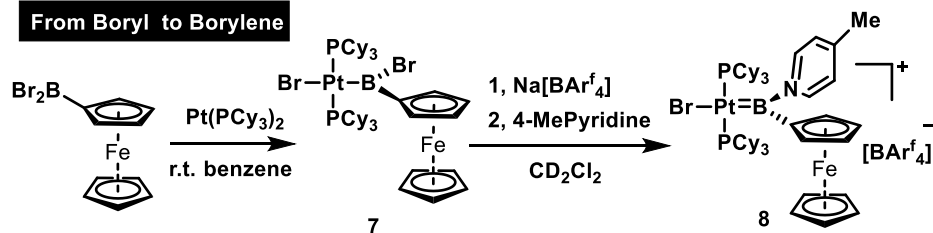


Transition metal complexes of boron; borane- (I), boryl- (II), bridged borylene (III), and terminal borylene complexes (IV)

Synthesis of Terminal Borylene

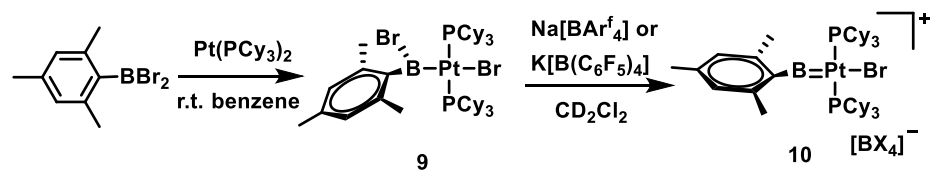


From Boryl to Borylene



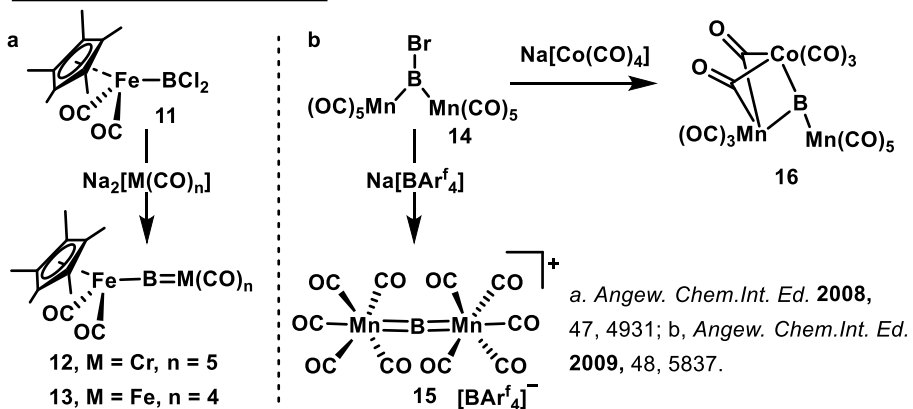
Organometallics. 2004, 24, 5545
Angew. Chem.Int. Ed. 2005, 44, 5651

Important Principle: Intramolecular, particularly α -hydrogen, migrations within organometallic compounds are thought to be **kinetically favorable**, if through the shift a coordinatively unsaturated species can be converted into coordinatively more strongly saturated compound.

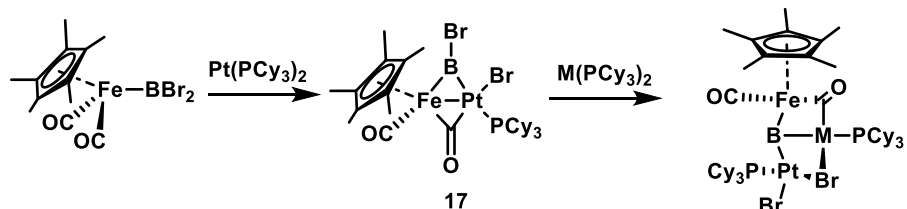


Angew. Chem.Int. Ed. 2006, 46, 3979

Boron as a Bridging Ligand



a. *Angew. Chem.Int. Ed.* 2008, 47, 4931; b. *Angew. Chem.Int. Ed.* 2009, 48, 5837.

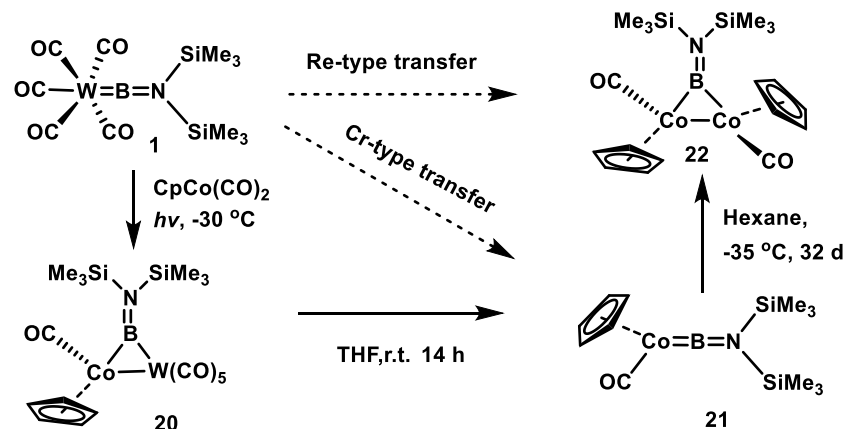


According to the DFT calculations result, the molecular orbitals that are involved in bonding with the boron center are composed of rather **complicated mixtures of boron s and p orbitals**.

Angew. Chem.Int. Ed. 2006, 45, 1066

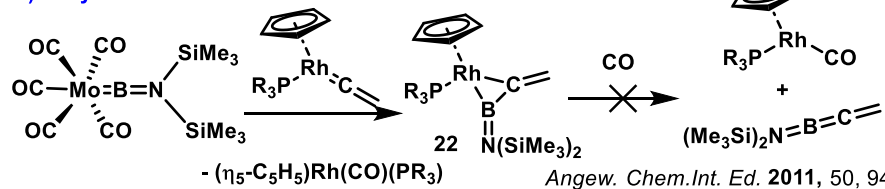
Reactions of Terminal Borylene with Metal Complex

a) Stepwise research of intermetal borylene transfer.



Angew. Chem.Int. Ed. 2007, 46, 5212

b) Borylene transfer to metal-carbon double bond.



- (η⁵-C₅H₅)Rh(CO)(PR₃)
Angew. Chem.Int. Ed. 2011, 50, 9462

c) Reactions of M=B=M type borylene

Background

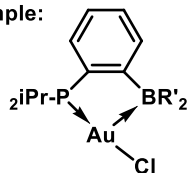
Two typical boron-gold coordination modes

Borane Gold complexes

Discovered by Bourissou Group

Borane ligand as pure σ -acceptor

Example:

*J. Am. Chem. Soc.* **2006**, 128, 12056

Tethered phosphine groups bind

orthogonally to the B-Au axis

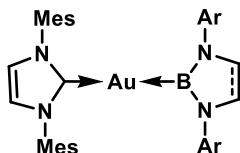
(B-Au-L : 79 - 84 °)

Boryl Gold complexes

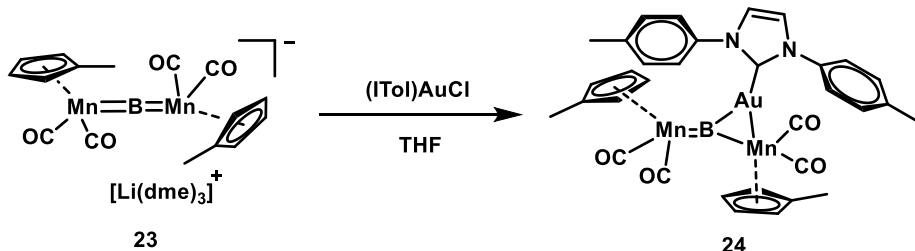
Discovered by Yamashita & Nozaki

Boryl ligand as pure σ -donor

Example:

*Angew. Chem.* **2007**, 119, 6830

The B-Au-L axis is effectively linear

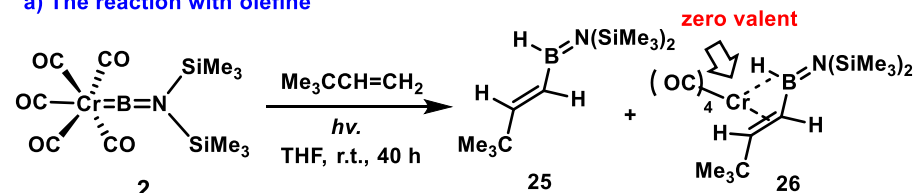


The parameters of 24 which are related to the gold-boron moiety bisect those of known boryl gold and borane gold systems.

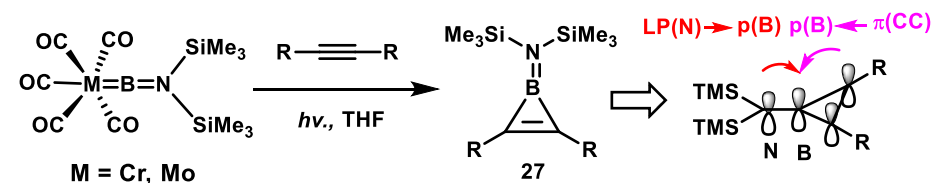
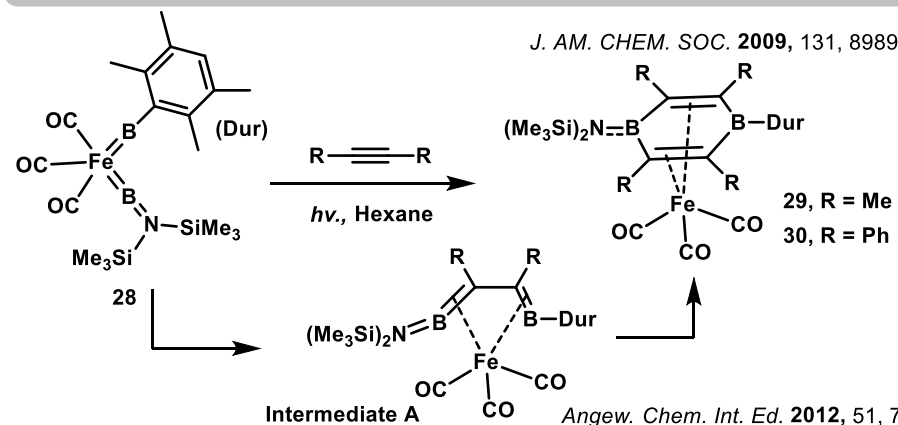
Angew. Chem. Int. Ed. **2009**, 48, 9735

Reactions of Terminal Borylene with Unsaturated Compound

a) The reaction with olefine

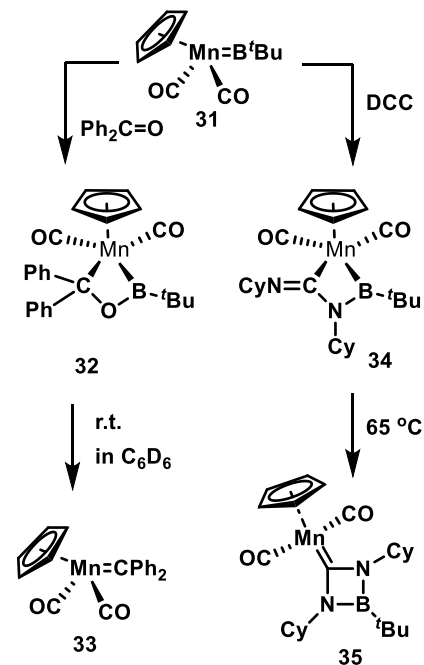
*Angew. Chem. Int. Ed.* **2008**, 47, 5978

b) The reactions with alkyne

Two-electron stabilizing donation from the $\pi(\text{CC})$ molecular orbital to the pz-atomic orbital at boron in borirene is substantially higher than the corresponding electronic donation from the nitrogen atom lone pair LP(N).*J. AM. CHEM. SOC.* **2009**, 131, 8989Intermediate A *Angew. Chem. Int. Ed.* **2012**, 51, 7839

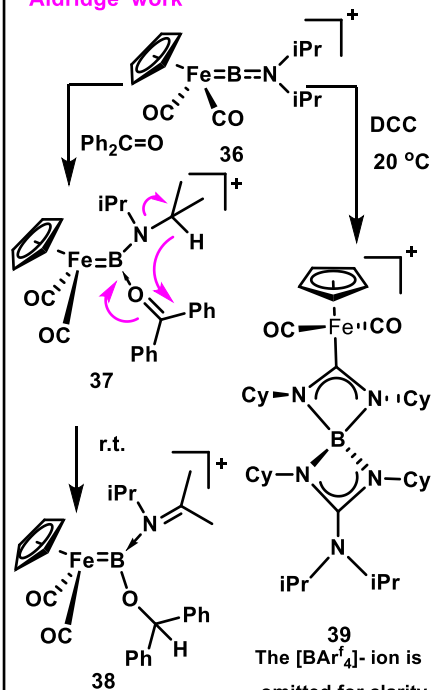
c) Borylene metathesis

Braunschweig' work

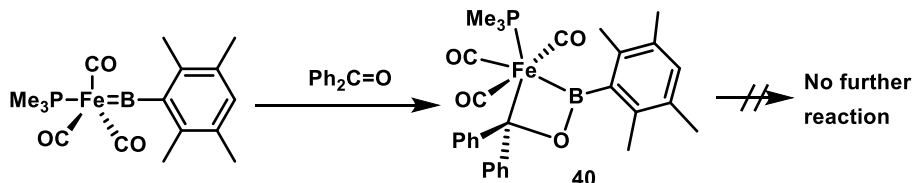


Angew. Chem. Int. Ed. **2007**, 46, 8071
J. Am. Chem. Soc. **2013**, 135, 8726

Aldridge' work

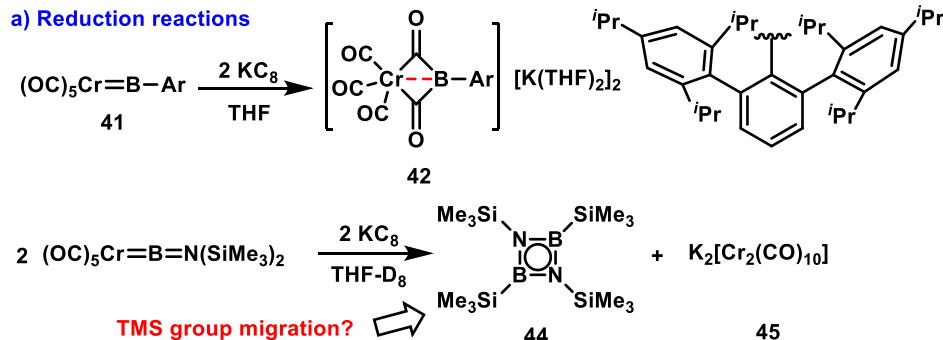


Angew. Chem. Int. Ed. **2006**, 45, 3513
Angew. Chem. Int. Ed. **2007**, 46, 2043



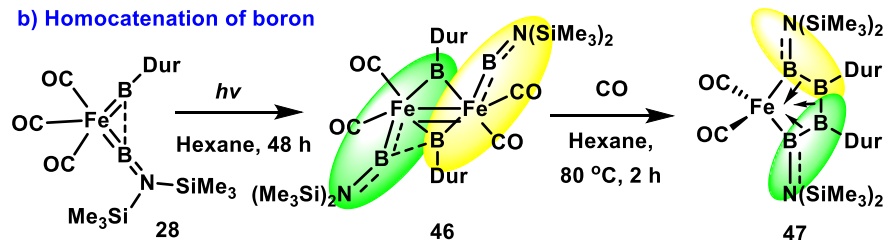
Other Types of Reactions

a) Reduction reactions



Angew. Chem. Int. Ed. **2013**, 52, 10120

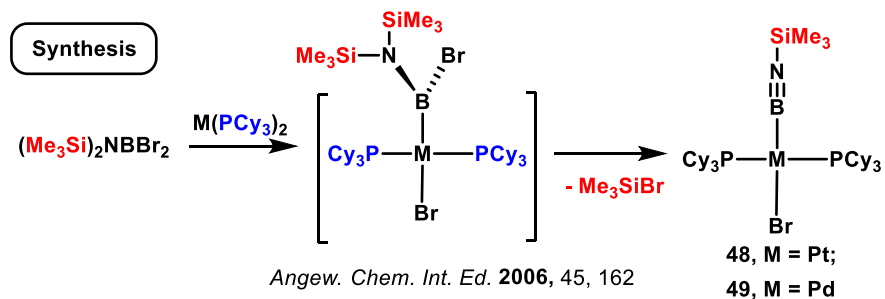
b) Homocatenation of boron



Nat. Chem. **2012**, 4, 563

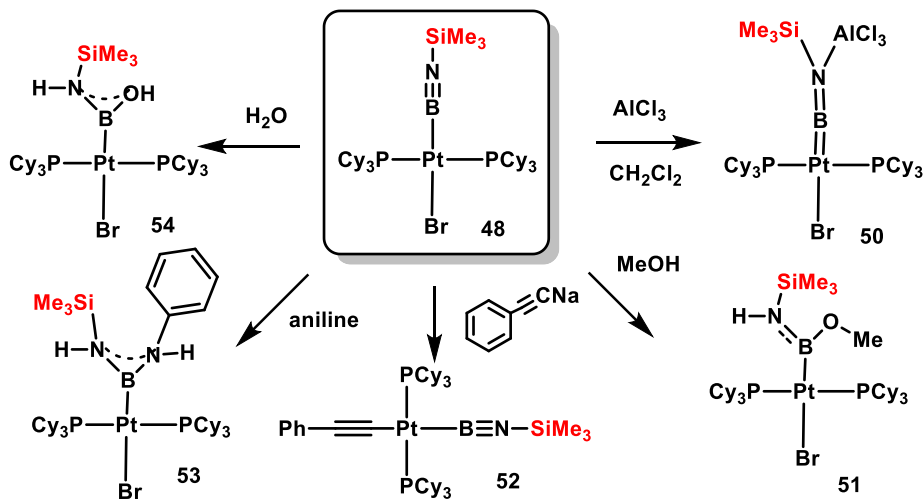
Iminoboryl Complexes

Synthesis



Angew. Chem. Int. Ed. **2006**, 45, 162

Examples of reactions

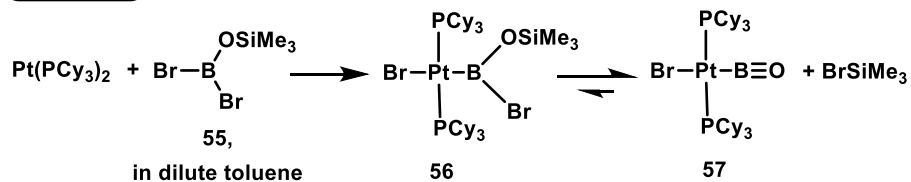


JACS. 2007, 129, 10350

JACS. 2008, 130, 7974

Boron-Oxygen Triple Bonds

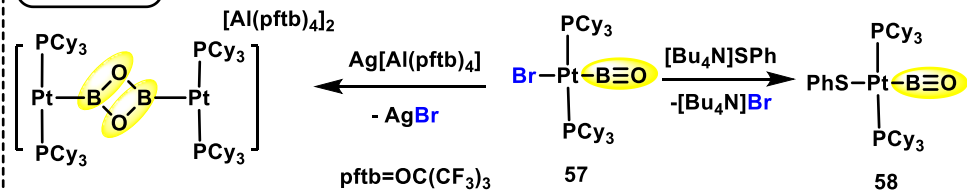
Synthesis



At room temperature, the reaction reaches a stationary point, with the two reaction products 56 and 57 in a ratio of approximately 1:4. Removal of all volatile components in high vacuum at ambient temperature and redissolution of the residue affords complete conversion of 56 to 57.

Science, 2010, 328, 345

Reactivity

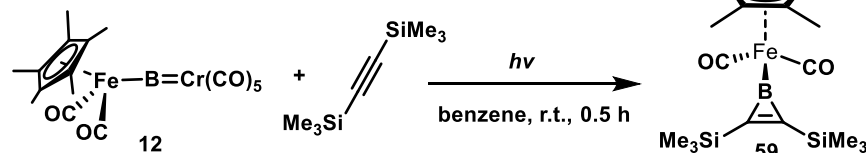


The dramatic consequences of abstracting the bromide ligand trans to BO triple bond should be considered as the subtle influence the platinum fragment exerts on the oxoboryl moiety rather than an innocuous spectator ligand.

Angew. Chem. Int. Ed. 2010, 49, 5993

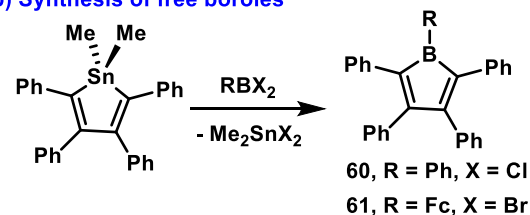
Boron Heterocycles

a) Synthesis of a ferroborene



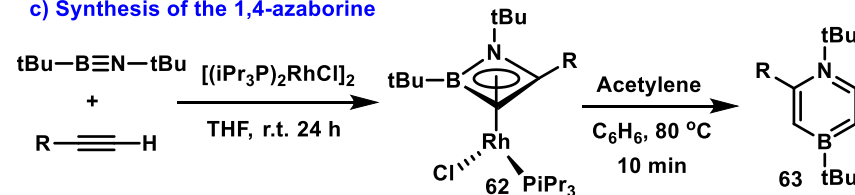
Angew. Chem. Int. Ed. 2007, 46, 5215

b) Synthesis of free boroles



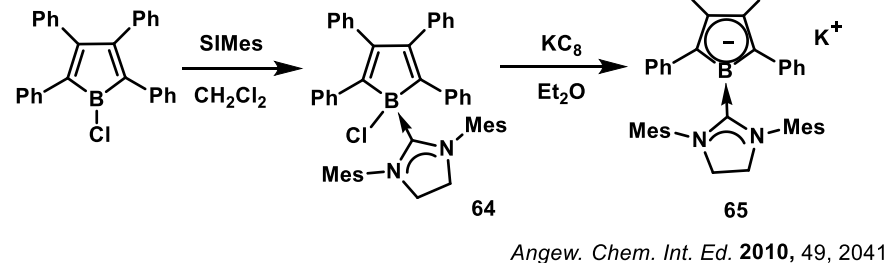
The boroles are antiaromatic. Moreover, the antiaromatic character of 60 is more pronounced than the one of 61

c) Synthesis of the 1,4-azaborine

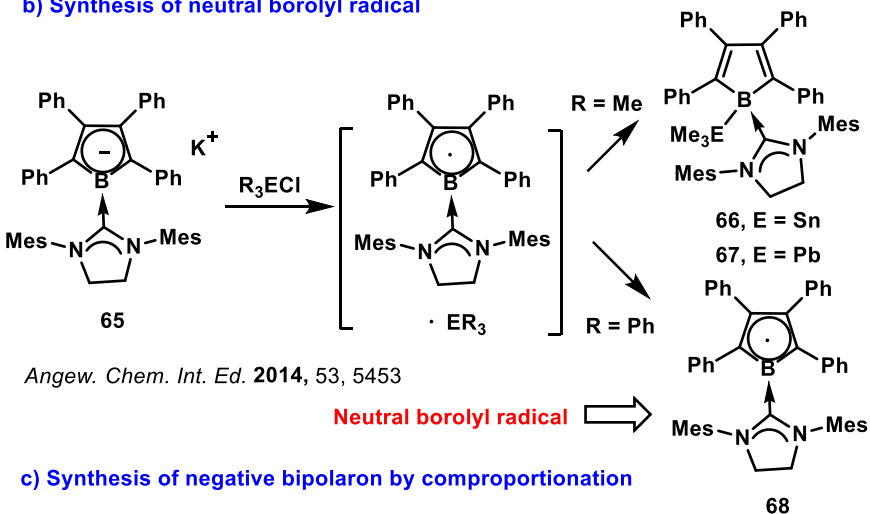


J. Am. Chem. Soc. 2016, 138, 8212

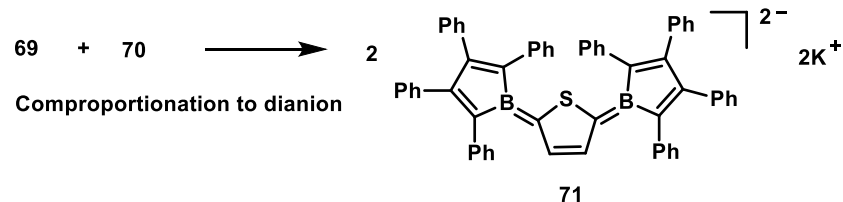
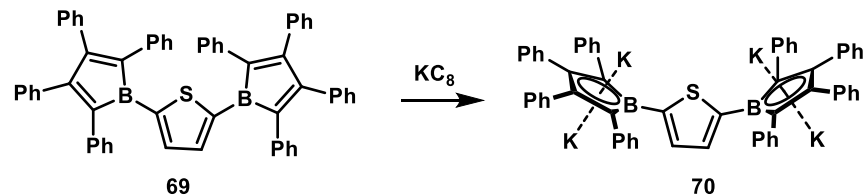
Reduction reactions of boron heterocycles

a) Synthesis of carbene-stabilized π -boryl anion

b) Synthesis of neutral borolyl radical



c) Synthesis of negative bipolaron by comproportionation

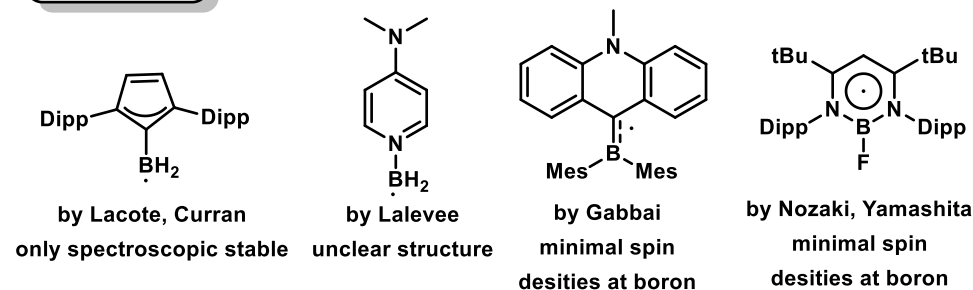


Angew. Chem. Int. Ed. 2013, 52, 12852

CAAC-Stabilized Neutral Boryl Radical

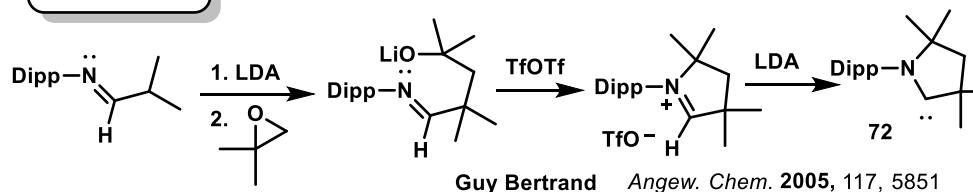
Background 1

Previous report about the neutral boryl radicals

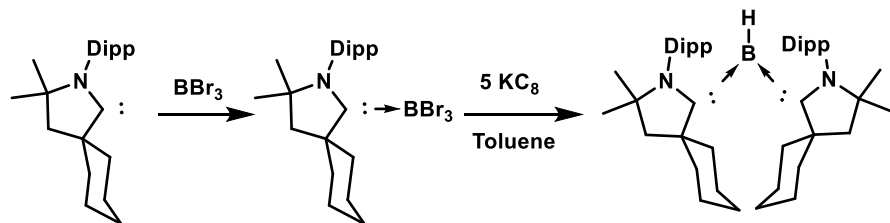


Background 2

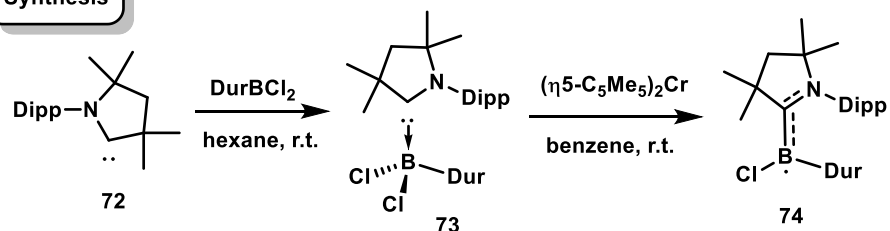
Cyclic (alkyl)(amino)carbenes (CAACs)



CAACs have been widely utilized as ligands for **stabilizing unusual reactive molecules**, such as **phosphorus radicals**, a parent borylene, and a boryl anion. It is characteristic for CAACs to exert **stronger σ -donating and π -accepting properties** than NHCs, and moreover, the steric demand of CAACs is different from that of NHCs owing to the presence of a **quaternary carbon atom next to the carbene center**.

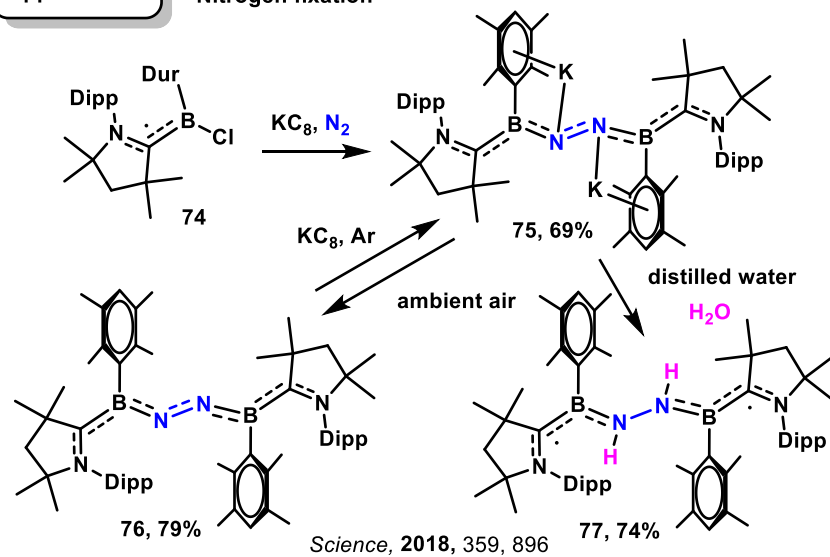
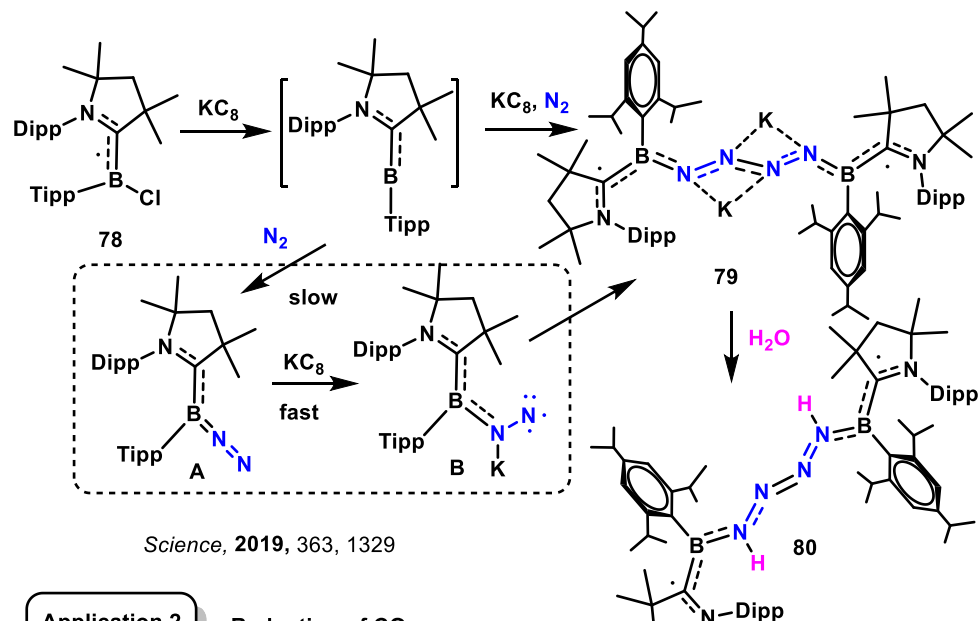
Guy Bertrand *Science*, 2011, 333, 610

Synthesis

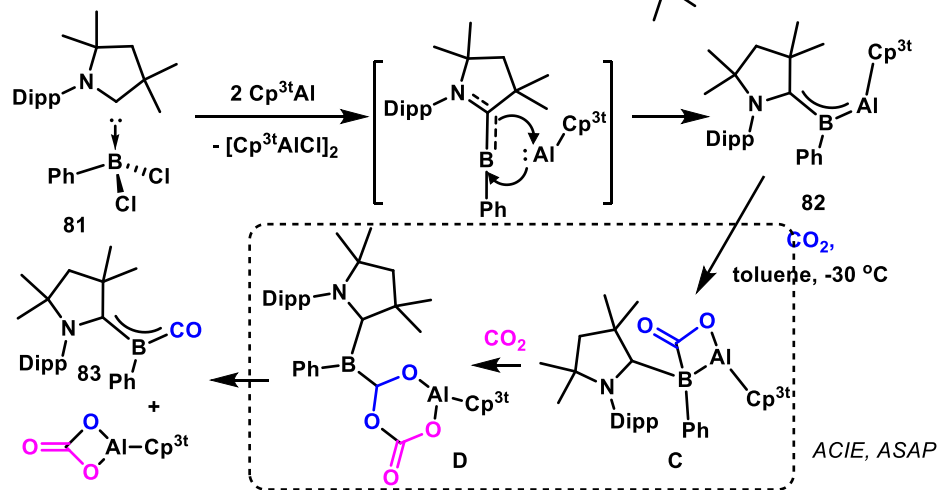
*Angew. Chem. Int. Ed.* 2014, 53, 7360

Application 1

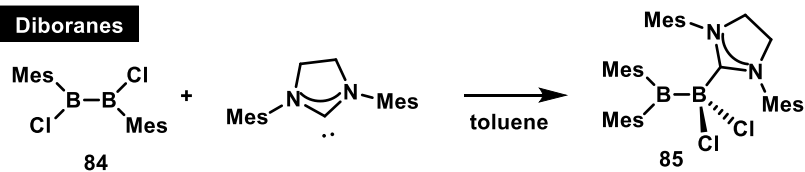
Nitrogen fixation

*Science*, 2018, 359, 896*Science*, 2019, 363, 1329

Application 2

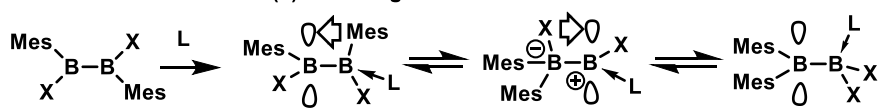
Reduction of CO_2 *ACIE, ASAP*

Diboranes

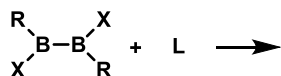


J. Am. Chem. Soc. **2011**, 133, 19044

Base-induced Diborane(4) Rearrangement

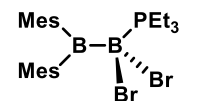
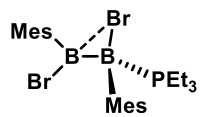


L = Lewis base

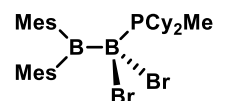
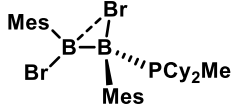


Different halides?
Different substituent group?
Different Lewis base?

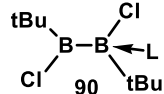
R = Mes, X = Br, L = PEt₃



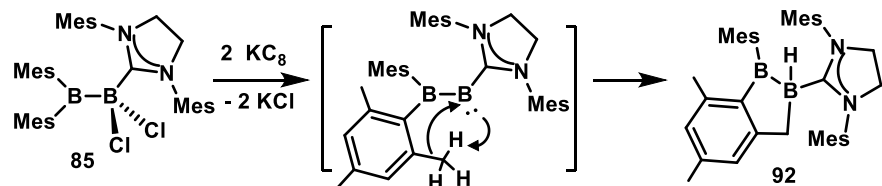
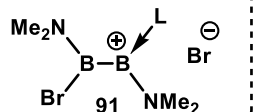
R = Mes, X = Br, L = PCy₂Me



R = tBu, X = Cl, L = NHC/P

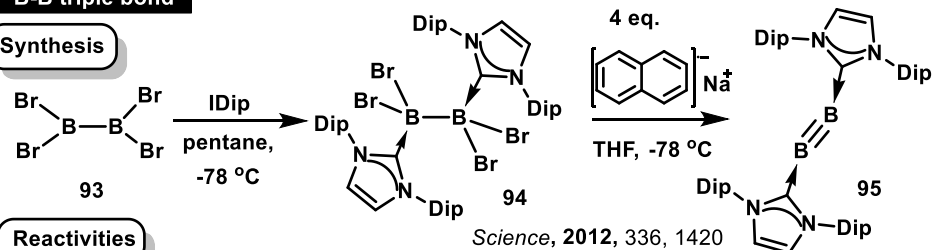


R = NMe₂, X = Br, L = SiMes

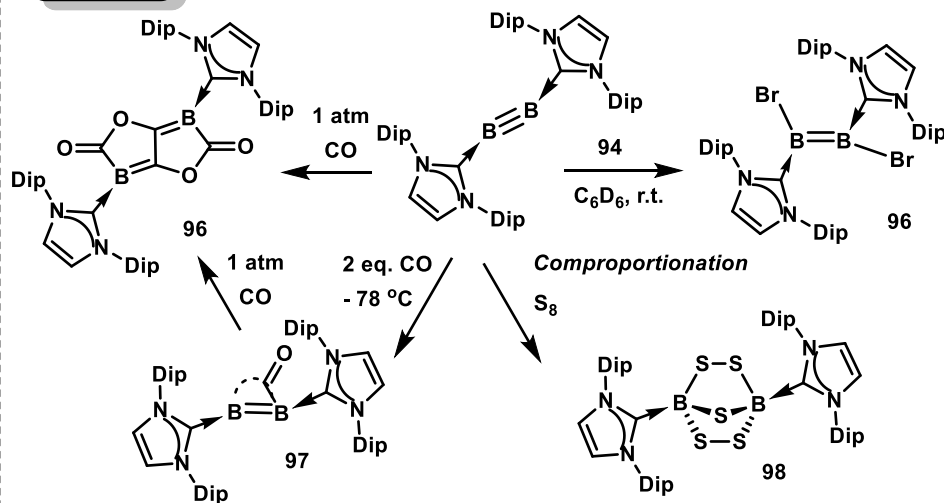


B-B triple bond

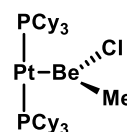
Synthesis



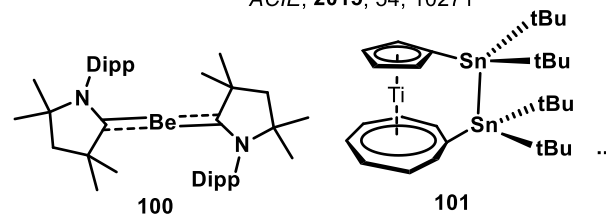
Reactivities



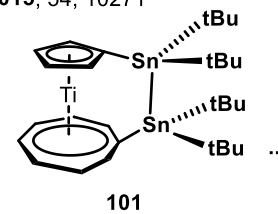
Besides B ...



ACIE, **2009**, 48, 4239



Nat. Chem., **2016**, 8, 890



Am. Chem. Soc. **2011**, 133, 5780