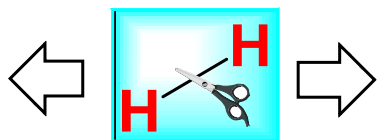
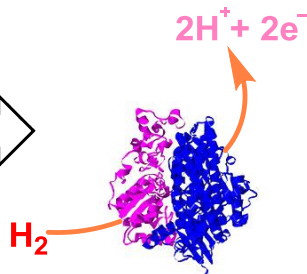




In industry



cleavage of dihydrogen

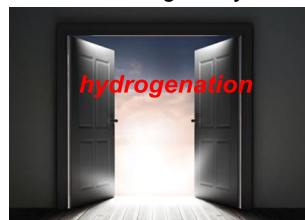


In biological system

- ◆ In 1926, Sabatier (1912 Nobel Prize winner in chemistry) discovered amorphous metals can catalyze hydrogenations.

Ind. Eng. Chem. **1926**, *18*, 1005

- ◆ From that time on, tremendous development of homogeneous hydrogenation.



hydrogenation

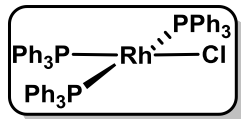
Representative paper:

J. Am. Chem. Soc. **1939**, *61*, 2330. *Nature*, **1965**, *208*, 1203. *J. Am. Chem. Soc.* **1976**, *98*, 2143.

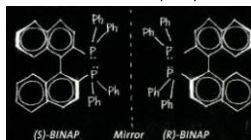
J. Am. Chem. Soc. **1976**, *98*, 4450. *J. Am. Chem. Soc.* **1976**, *98*, 2134.

Angew. Chem., Int. Ed. **2002**, *41*, 1998

Angew. Chem., Int. Ed. **2002**, *41*, 2008



Wilkinson catalyst



asymmetric hydrogenation

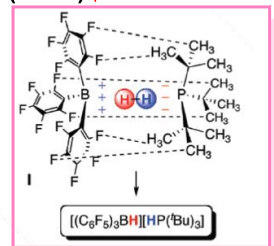
- ◆ Recently, earth abundant metals can perform hydrogenation.

(Fe, Co) *Science*, **2013**, *342*, 1054.

- ◆ From 2005, main group elements. **First paper:** *JACS*, **2005**, *127*, 12232.

Frustrated Lewis Pairs (FLPs) (Not covered in this review)

(FLPs) (Not covered in this review)



main-group element compounds

(in low oxidation states)

(Focus on this review)

• like an "encounter complex" stabilized by noncovalent interactions and dispersion forces that creates an electric field in the pocket;

• This electric field polarizes H₂, leading to cleavage of the H-H bond.

group 13, 14, 15
elements: C(II), Si(II), Ge(I),
Sn(I), P(II), B(O), B(II), Al(I),
Ga(I).

See reviews:

ACIE, **2015**, *54*, 6400.

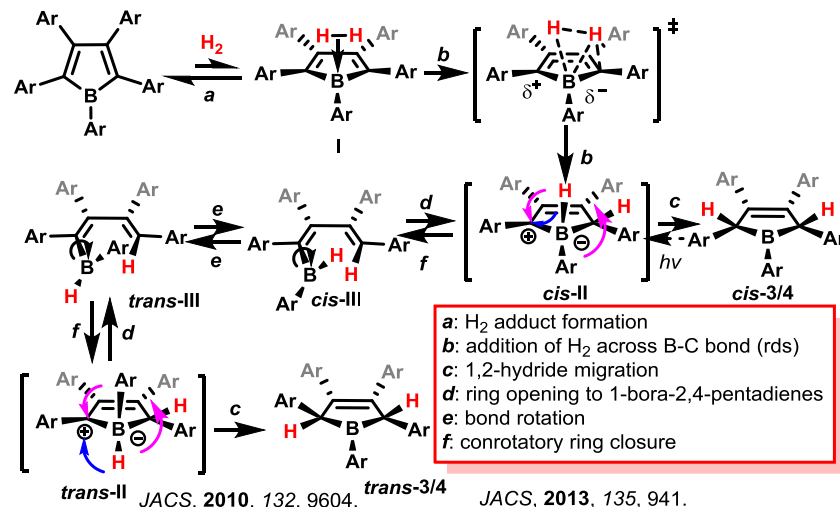
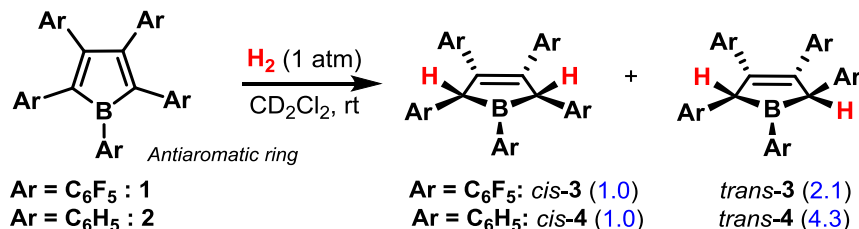
Acc. Chem. Res. **2015**, *48*, 306.

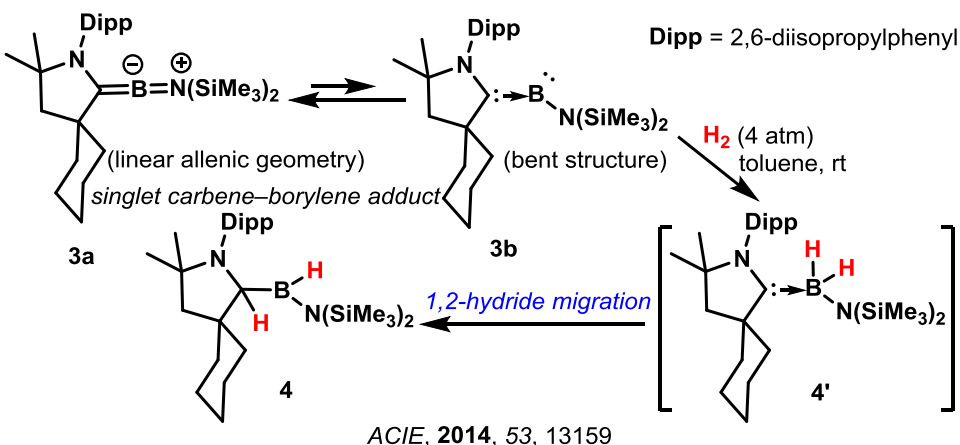
Transition-metal compounds	VS	Main-group compounds
Usually have partially occupied valence <i>d</i> orbitals that are often relatively close in energy.		The valence <i>s</i> or <i>p</i> orbitals are either fully occupied or empty and are far apart energetically.
Often coloured as a consequence of small orbital energy separations.		Usually colourless.
Often interact with small molecules such as CO, C ₂ H ₄ or H ₂ .		Generally do not interact strongly with CO, C ₂ H ₄ or H ₂ .
Often paramagnetic.		Usually diamagnetic.
Stereochemical electron pair character less pronounced.		Have stereochemically active electron pairs which form the basis of VSEPR theory.
Antiferromagnetic coupling is common.		Antiferromagnetic coupling in stable compounds not common.

Stoichiometric Reaction

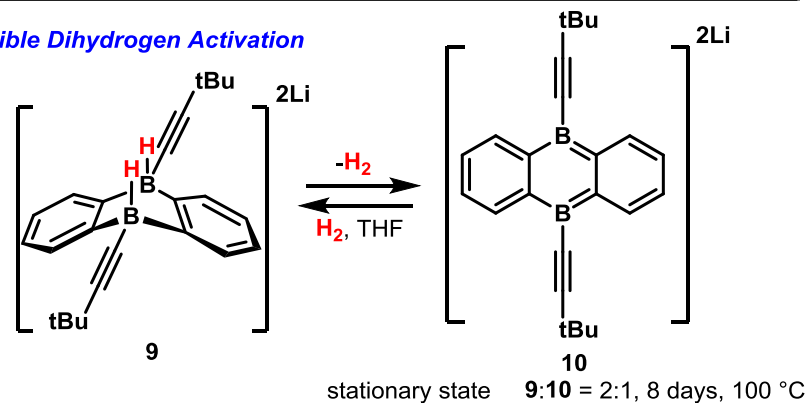
Nature, **2010**, *463*, 171.

Group 13 Compounds (B, Al, Ga,)

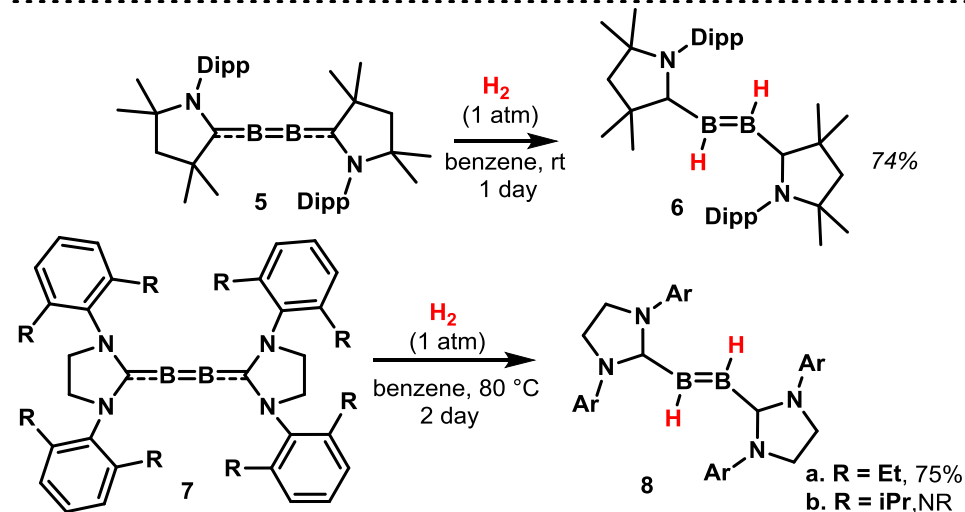
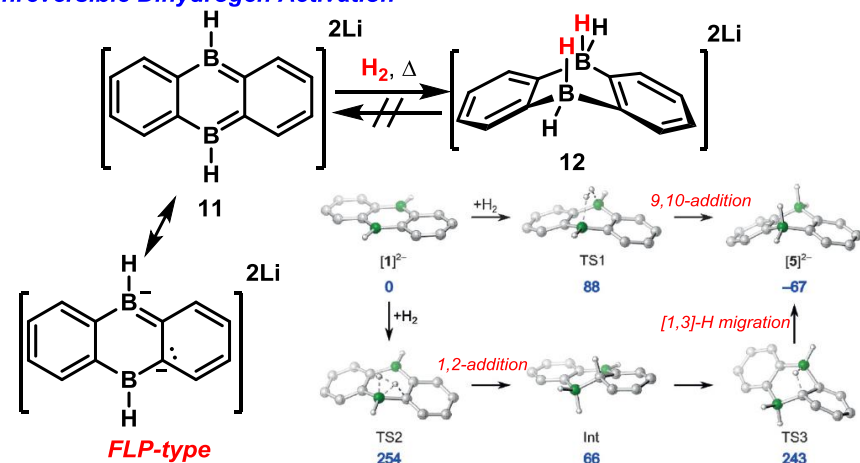




Reversible Dihydrogen Activation

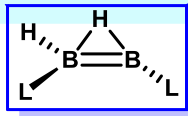


Irreversible Dihydrogen Activation

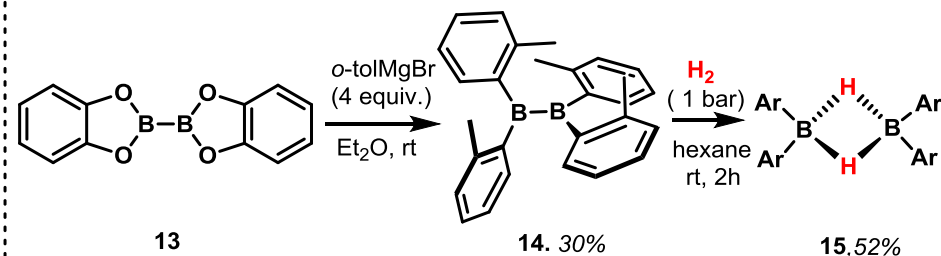


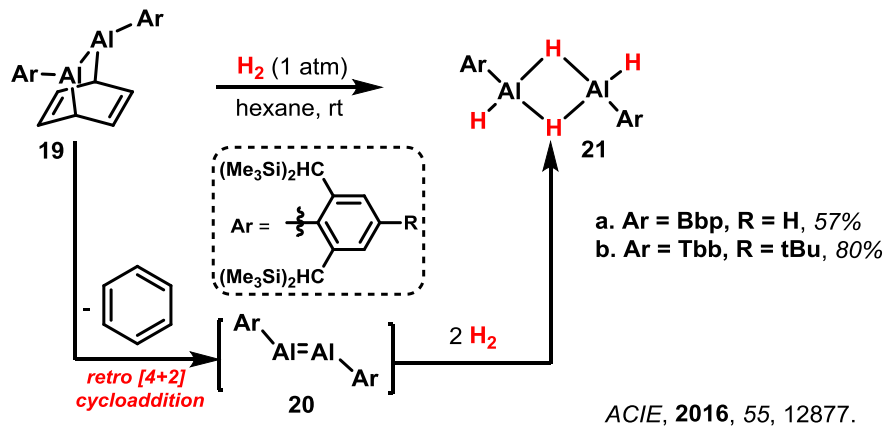
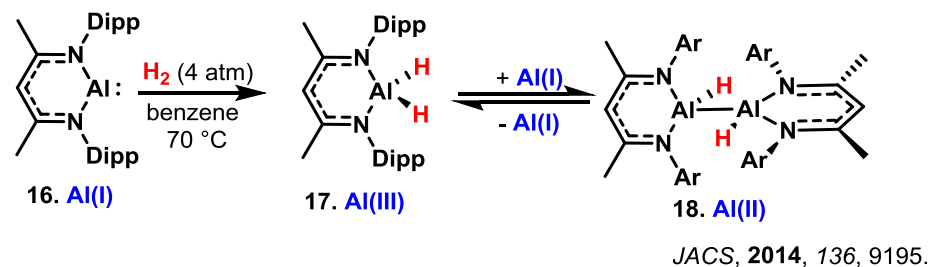
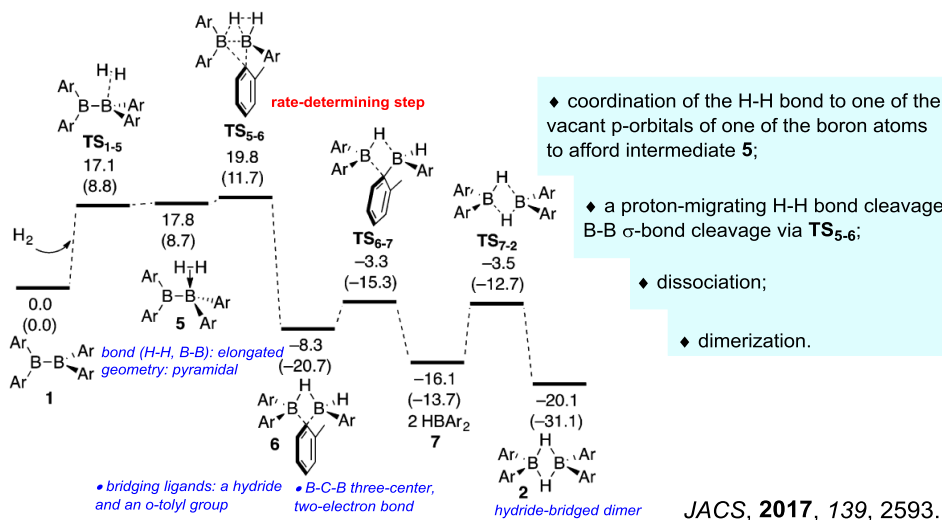
DFT calculations showed an overall exothermic ($\Delta G = 19.4 \text{ kcal mol}^{-1}$) two-step asynchronous H₂ addition mechanism proceeding via a bridging hydride intermediate.

increasing π -acidity and σ -donation



Chem. Eur. J. 2016, 22, 17169.

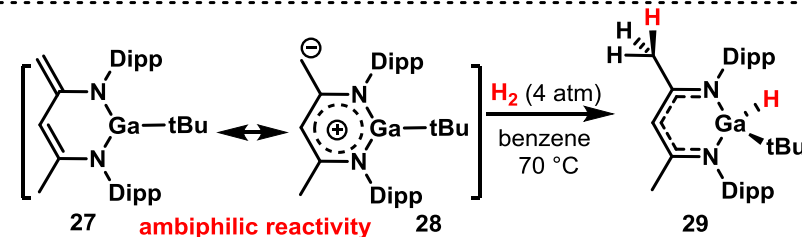
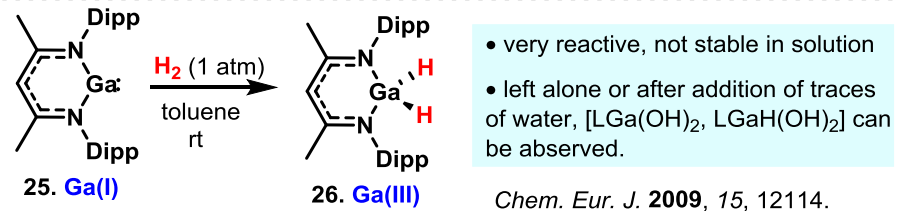
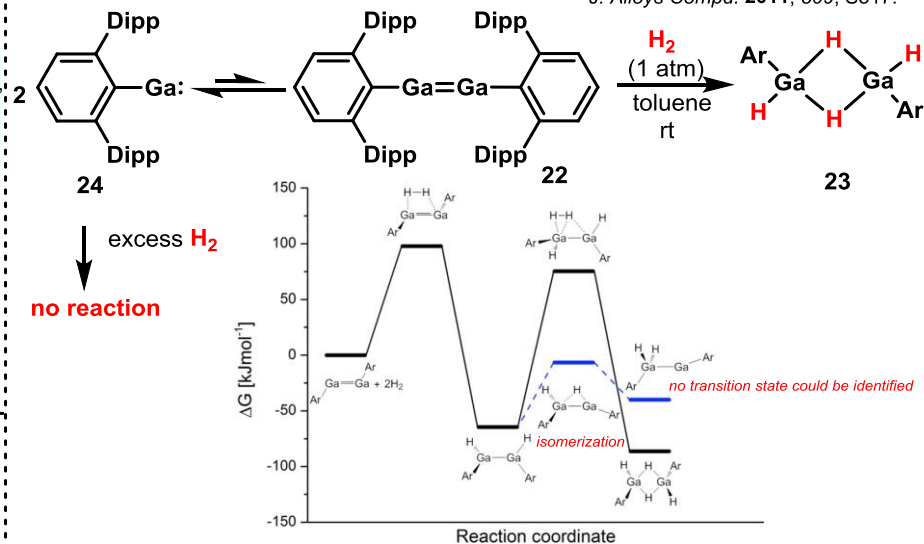




Aluminium hydride: a reversible material for hydrogen storage

- high energy density
- release hydrogen easily
- can be recharged

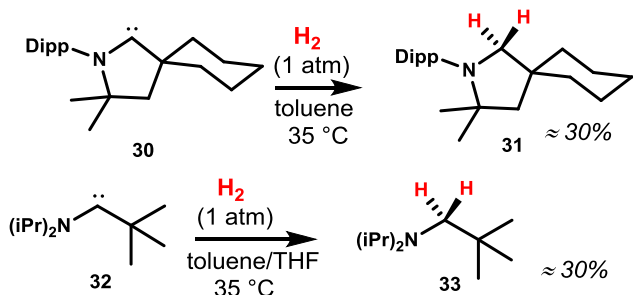
Further reading: *Chem. Commun.* **2009**, 3717.
J. Alloys Compd. **2011**, 509, S517.



DFT calculations revealed the HOMO resides primarily on the terminal carbon of the exocyclic alkene moiety, the LUMO is dominated by the Ga 4p character

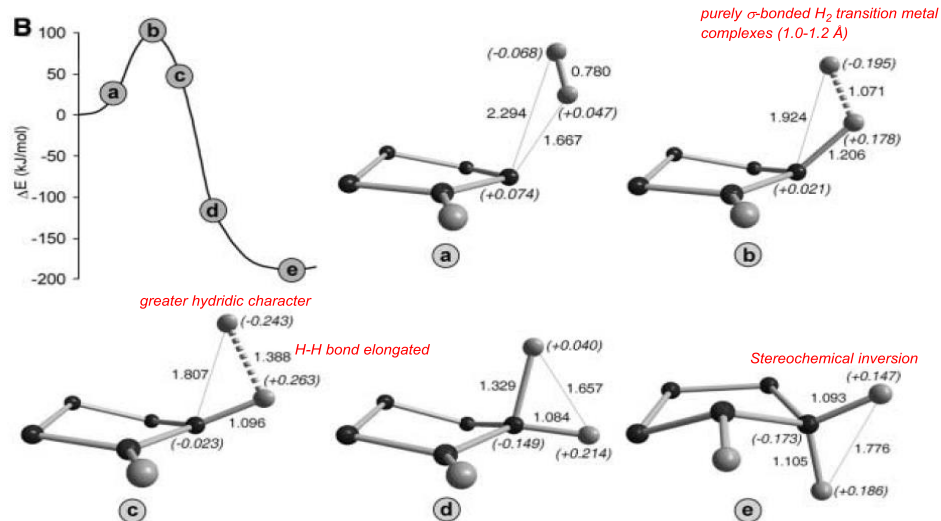
ACIE, 2015, 54, 5098.

Group 14 Compounds (C, Si, Ge, Sn)

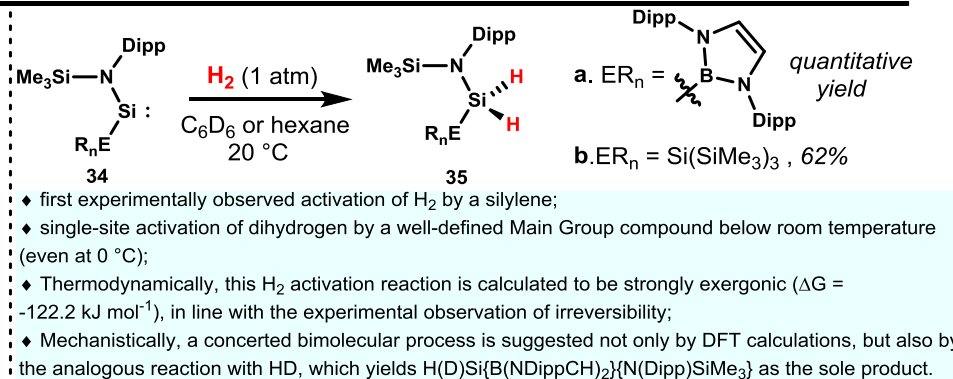


♦ a singlet carbene has a vacant orbital and a filled nonbonding orbital and in that respect resembles transition metal centers.

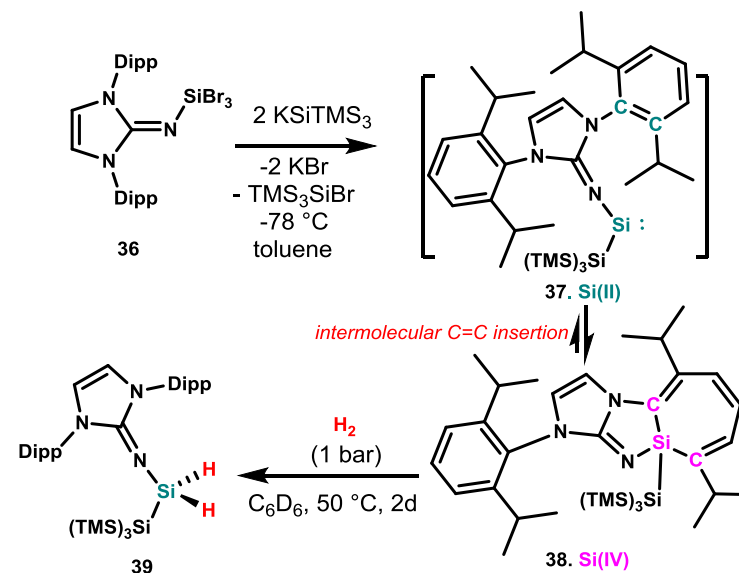
♦ in contrast to transition metals that act as electrophiles toward dihydrogen, these carbenes primarily behave as nucleophiles, creating a hydride-like hydrogen, which then attacks the positively polarized carbon center.



Science, 2007, 316, 439

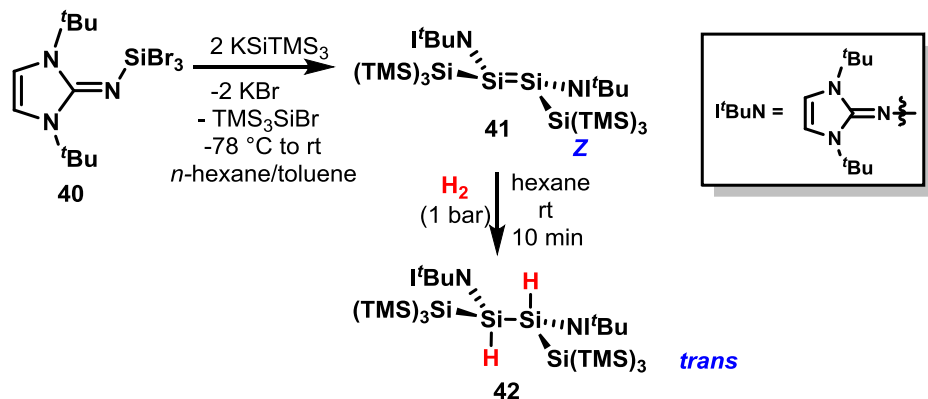


JACS, 2012, 134, 6500 ACIE, 2013, 52, 568

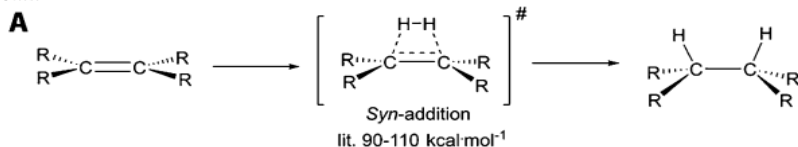
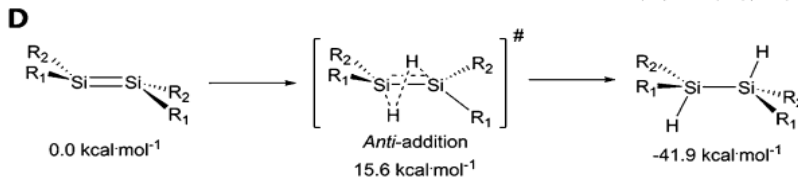
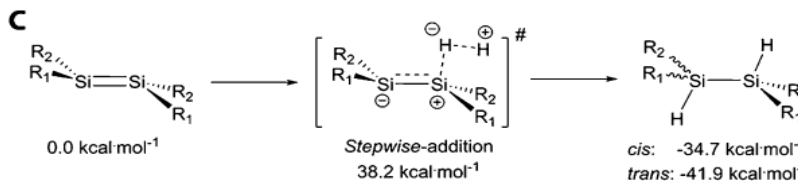
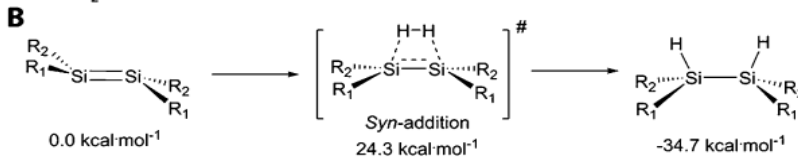


amido-type ligand and a donating main-group substituent (silyl), resulting in a decreased HOMO-LUMO gap sufficient for the activation of strong bonds.

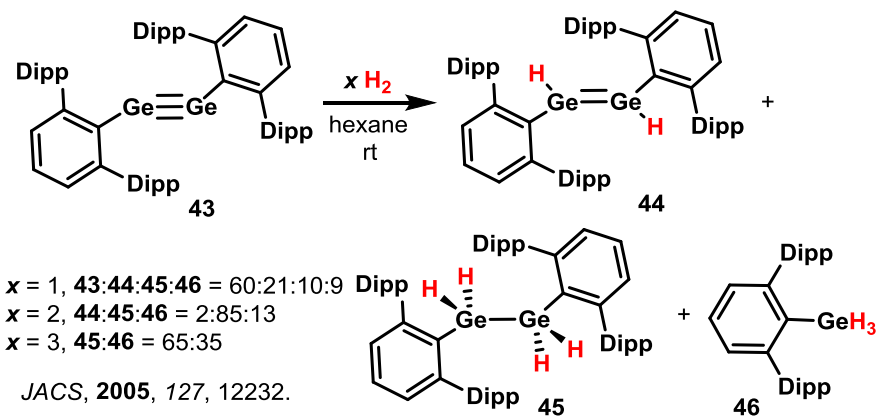
JACS, 2017, 139, 8134.



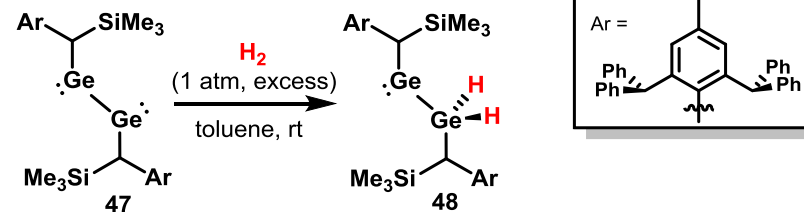
Olefin:

Disilene: R₁ = SiTMS₃
R₂ = Niⁱ-Bu

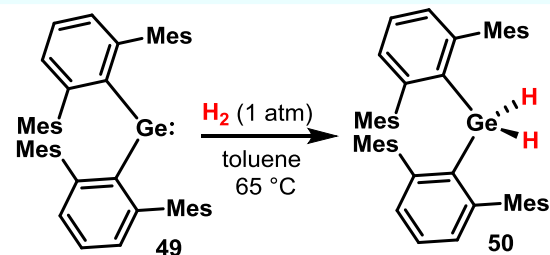
JACS, 2017, 139, 9156.

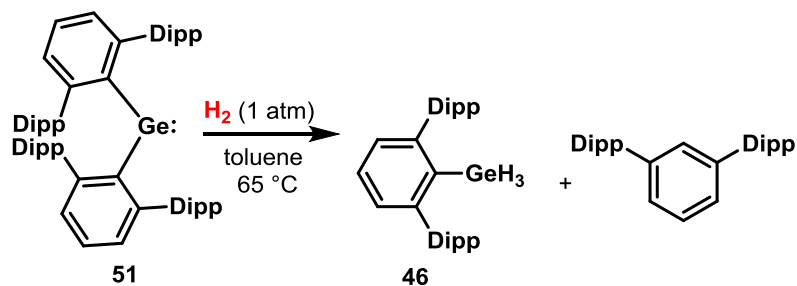


- the digermene 44 exists in equilibrium with either monomeric
- possible singlet diradical character of the Ge-Ge bonding of 43.



- In solution: -10 °C, solid state: 20 °C (>95% yield, 1h)
 - Unlike 43, compound 47 did not further react with H₂ even at elevated temperatures (up to 100 °C).
 - addition of H₂ to 47 gave the singly bridged species L¹Ge(μ-H)GeHL¹, which then rearranged via a low activation pathway to the symmetrically hydrogenated compound L¹HGe-GeHL¹ followed by rearrangement to the most stable isomer 48
 - the second addition of H₂ would result in cleavage of the Ge-Ge bond, giving L¹GeH and L¹GeH₃.
- However, this reaction was calculated to be thermodynamically unfavorable, consistent with the observed reactivity.
- JACS, 2011, 133, 18622.



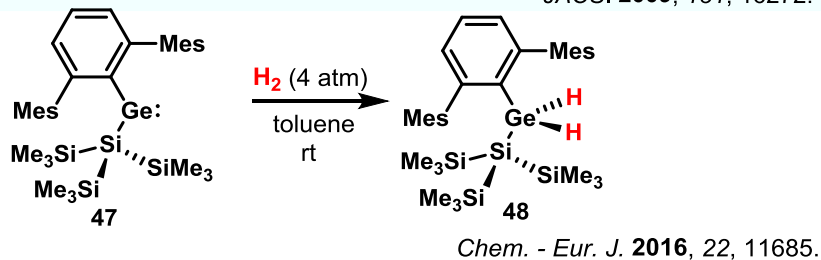


• reaction of **49** and **51** with H_2 likely proceeded via interaction of the σ orbital of H_2 with the empty 4p orbital at the germanium atom with concomitant back donation from the germanium lone pair to the H_2 σ^* orbital.

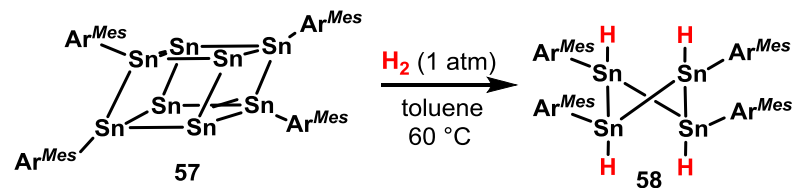
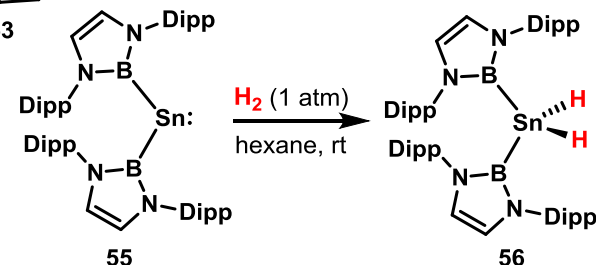
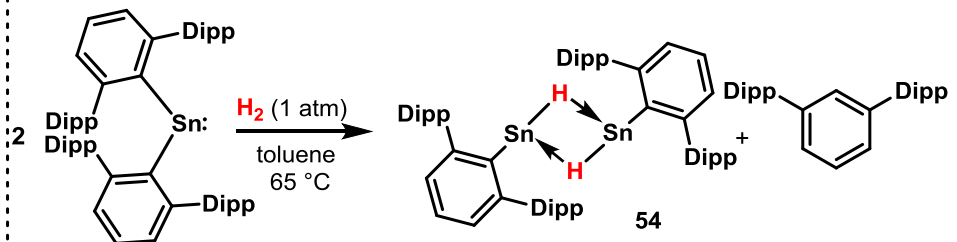
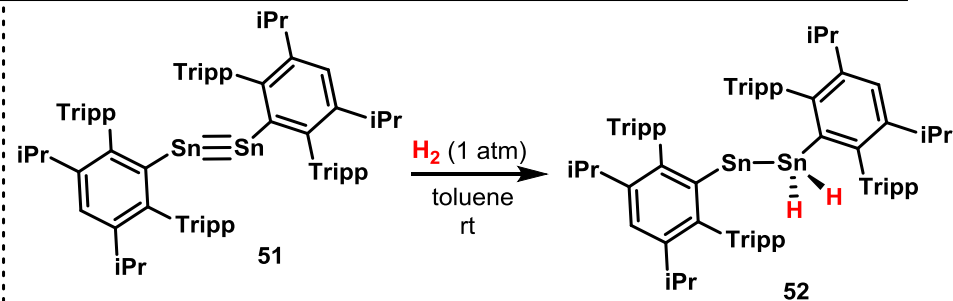
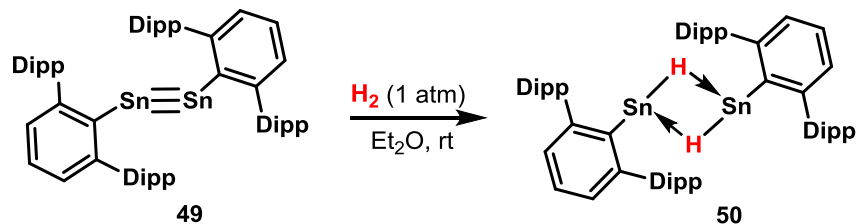
• With **49**, H-H bond cleavage gave the energetically favored product **50**.

• In the case of **51**, the initial steps are identical; however, the bulky Ar^{Dipp} groups introduced sufficient strain such that the preferred pathway is elimination of HAr^{Dipp} along with production of monomeric $:\text{GeHAr}^{\text{Dipp}}$, which then reacted with H_2 to give the final product **46**.

JACS. 2009, 131, 16272.



Chem. - Eur. J. 2016, 22, 11685.



Chem. Commun. 2008, 6042.

JACS. 2008, 130, 12268.

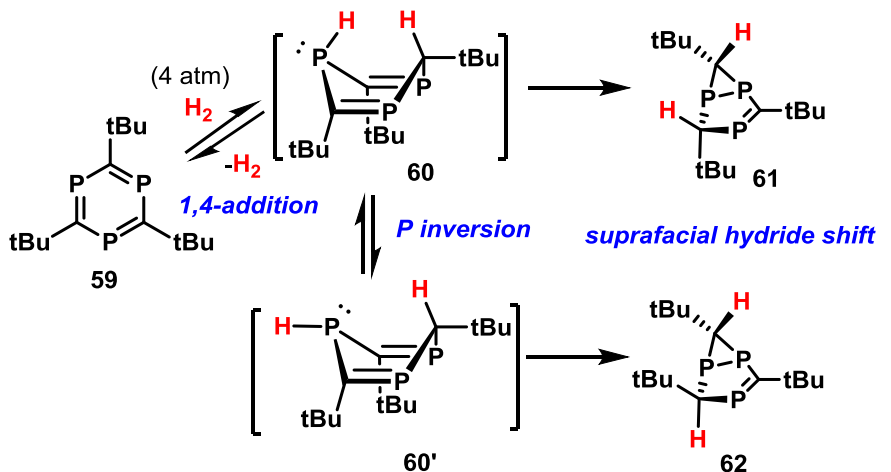
JACS, 2016, 138, 4555

ACIE, 2015, 54, 3802.

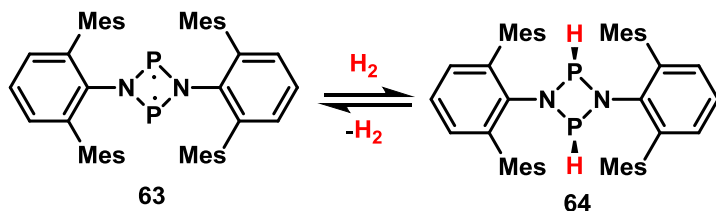


Why the Mechanisms of Digermene and Distannyne Reactions with H_2 Differ So Greatly?

Further Reading: JACS, 2012, 134, 8856.

Group 15 Compounds (P) Reversible Activation of H₂

JACS. 2014, 136, 13453.



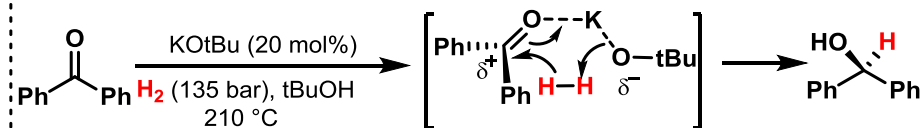
- 64 was not stable, slowly releasing H₂ to regenerate 63 (6 months, 90% 64 and 10% 63, by ³¹P NMR)

- The rate of dihydrogen elimination can be increased by heating a solution of 64 above 60 °C
- DFT calculations: The activation barrier of H₂ addition step: 17.9 kcalmol⁻¹, the reverse reaction: 25.7 kcal mol⁻¹.

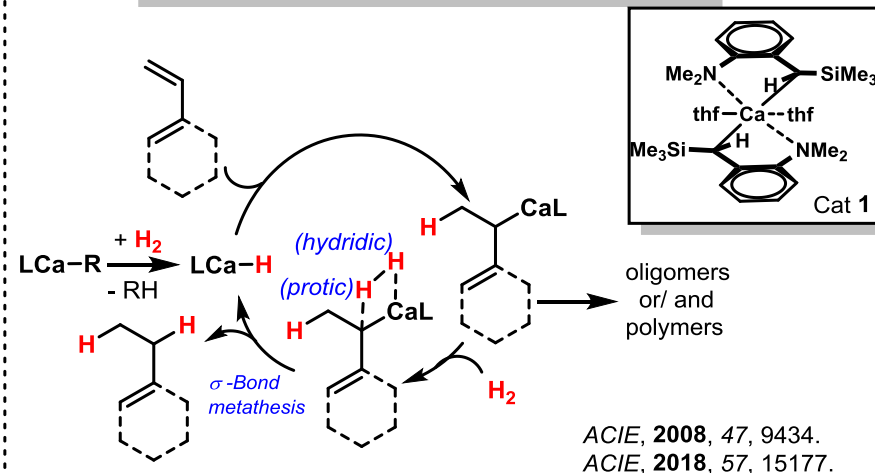
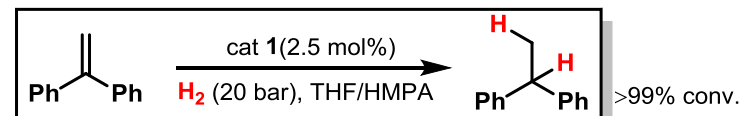
ACIE. 2016, 55, 12214

Catalytic Reaction

alkaline metals

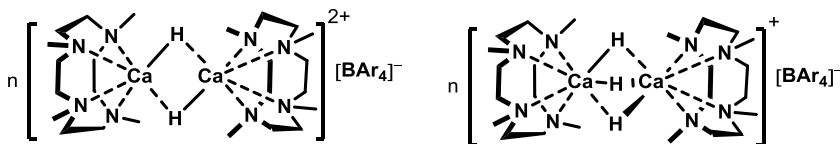
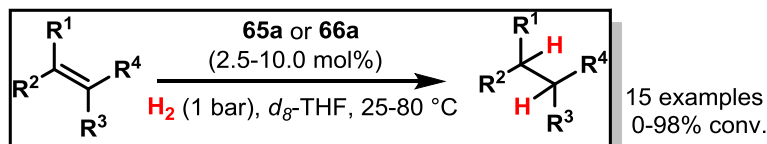
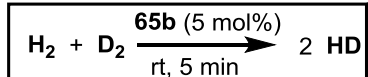


JACS, 1964, 86, 3750. JACS, 2002, 124, 8693.

ACIE, 2008, 47, 9434.
ACIE, 2018, 57, 15177.

Conversion rates increase with metal size:
Mg < Ca < Sr < Ba
(for Ba, quantitative conversion is reached within 15 min).

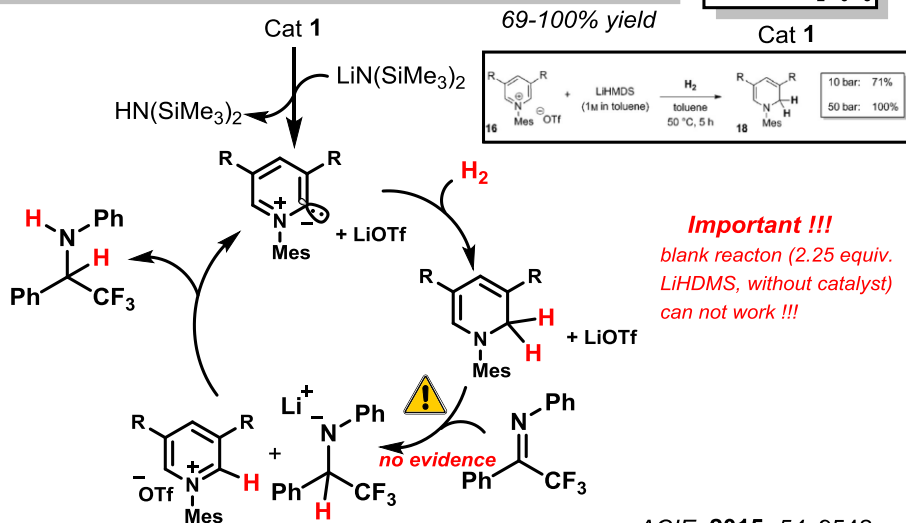
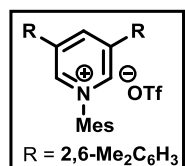
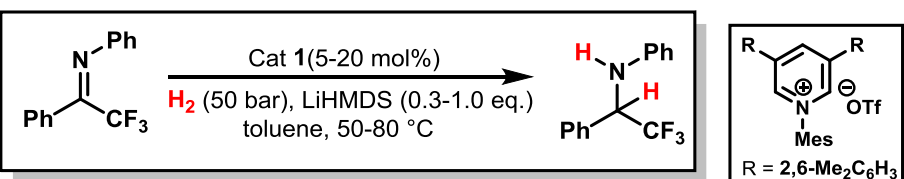
Nat. Catal. 2018, 1, 40.

65a. Ar = C₆H₄-4-tBu65b. = C₆H₃-3,5-Me₂66a. Ar = C₆H₄-4-tBu66b. = C₆H₃-3,5-Me₂

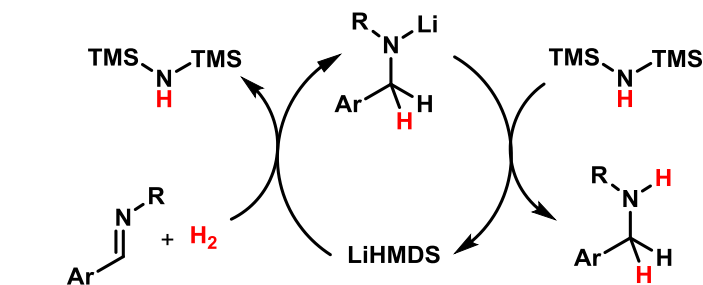
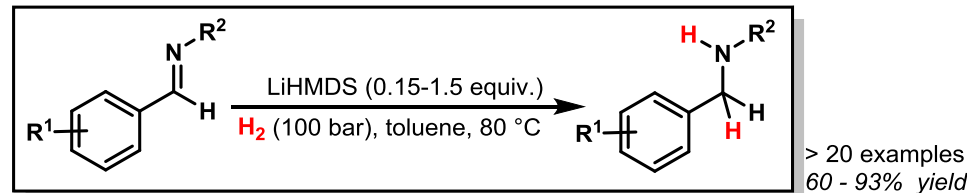
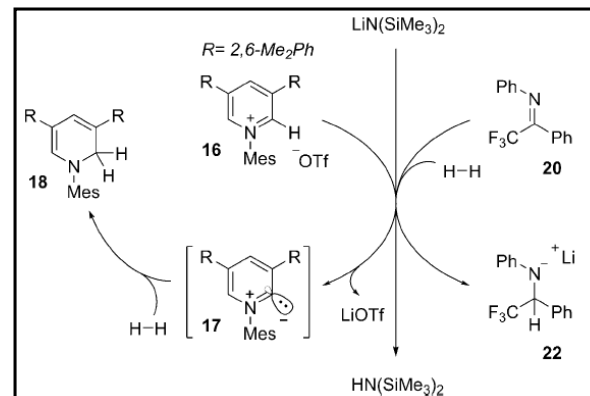
ACIE, 2012, 51, 4452.

ACIE, 2016, 55, 4794.

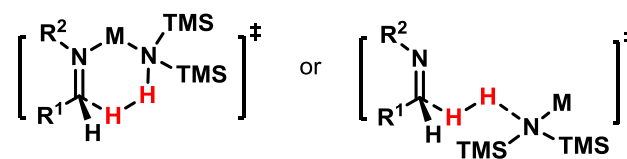
ACIE, 2017, 56, 12367.



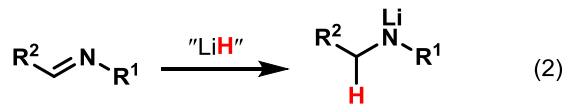
ACIE, 2015, 54, 9542.

can not be reproduced !!!**Correction:** ACIE, 2017, 56, 9266.

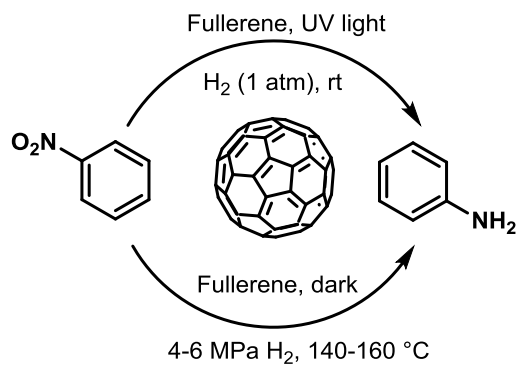
a. Concerted mechanism



b. Stepwise mechanism



Chem. Eur. J. **2019**, *25*, 1.



JACS, **2009**, *131*, 16380.