**Hydrogenation with Main Group Compounds**

In industry:

- 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.

**Representative paper:**


- Recently, earth abundant metals can perform hydrogenation.  
  *(Fe, Co)*  

- From 2005, *main group elements*.  

**Frustrated Lewis Pairs (FLPs)**  
(Not covered in this review)  
(Focus on this review)

- Like an "encounter complex" stabilized by noncovalent interactions and dispersion forces that create an electric field in the pocket.
- This electric field polarizes H₂, leading to cleavage of the H-H bond.

**Asymmetric Hydrogenation**

**Stoichiometric Reaction**

**Group 13 Compounds** *(B, Al, Ga, )*

- **H₂** (1 atm)  
  
  **CD₂Cl₂, rt**  
  
  **H₂**  
  
  **B**  
  
  **Ar**  
  
  **H**  
  
  **trans-3 (2.1)**  
  
  **trans-4 (4.3)**  
  
  **cis-3 (1.0)**  
  
  **cis-4 (1.0)**  
  
  **Ar = C₆F₅**:  
  
  **Ar = C₆H₅**:  
  
  **1**  
  
  **2**  
  
  **Ar = C₆F₅**:  
  
  **cis-3 (1.0)**  
  
  **trans-3 (2.1)**  
  
  **trans-4 (4.3)**  
  
  **cis-4 (1.0)**  
  
  **See reviews:**  
  
  
  JACS, 2013, 135, 941.
**Hydrogenation with Main Group Compounds**

**Dipp**

- Linear allenic geometry
- Singlet carbone–borolene adduct
- Bent structure

**1,2-Hydride Migration**

- Dipp = 2,6-disopropylphenyl
- \( \text{H}_2 \) (4 atm) toluene, rt

**Reversible Dihydrogen Activation**

- **9**
- **10** = 2:1, 8 days, 100 °C

**Inreversible Dihydrogen Activation**

- **11**
- **12**
- **13**
- **14**
- **15**

**Quantum-chemical calculations** suggest a concerted, homolytic addition of \( \text{H}_2 \) across both boron atoms.

**FLP-type**

- 9,10-addition
- 1,2-addition
- [1,3]-H migration

**DFT calculations** showed an overall exothermic (\( \Delta G = 19.4 \text{ kcalmol}^{-1} \)) two-step asynchronous \( \text{H}_2 \) addition mechanism proceeding via a bridging hydride intermediate.

**Chem. Eur. J. 2016, 22, 17169.**
Feng Wang

hydrogenation with main group compounds

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**Aluminium hydride:** a reversible material for hydrogen storage
- high energy density
- release hydrogen easily
- can be recharged


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**Reaction coordinate**

JACS, 2017, 139, 2593.

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**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.

![Chemical structures and reactions](image)

- first experimentally observed activation of H₂ by a silylene;
- single-site activation of dihydrogen by a well-defined Main Group compound below room temperature (even at 0 °C);
- Thermodynamically, this H₂ activation reaction is calculated to be strongly exergonic (ΔG = -122.2 kJ mol⁻¹), in line with the experimental observation of irreversibility;
- Mechanistically, a concerted bimolecular process is suggested not only by DFT calculations, but also by the analogous reaction with HD, which yields H₂(NDipp)₂(N(NDipp)SiMe₃) as the sole product.

**References**

- Science, 2007, 316, 439
- JACS, 2012, 134, 6500
- ACIE, 2013, 52, 568
- JACS, 2017, 139, 8134.
hydrogenation with main group compounds

\[
\begin{align*}
\text{A} & \quad R_1 = \text{Si}(\text{TMS})_3 \\
\text{B} & \quad R_1 = \text{Si}(\text{TMS})_3, R_2 = \text{Nil-Bu} \\
\text{C} & \quad R_1 = \text{Si}(\text{TMS})_3, R_2 = \text{Nil-Bu} \\
\text{D} & \quad R_1 = \text{Si}(\text{TMS})_3, R_2 = \text{Nil-Bu}
\end{align*}
\]

**Disilenes:**

- **Syn-addition**
  - \( \text{lit.} 90-110 \text{ kcal mol}^{-1} \)
- **Stepwise-addition**
  - \( 38.2 \text{ kcal mol}^{-1} \)
- **Anti-addition**
  - \( 15.6 \text{ kcal mol}^{-1} \)

**Synthesis of 41:**

\[
\text{1'}\text{BuN} = \begin{array}{c}
\text{N} \\
\text{N} \\
\text{Bu}
\end{array}
\]

- **Disilene:**
  - \( x = 1, 43:44:45:46 = 60:21:10:9 \)
  - \( x = 2, 44:45:46 = 2:85:13 \)
  - \( x = 3, 45:46 = 65:35 \)

**JACS, 2005, 127, 12232.**

- The digerme 44 exists in equilibrium with either monomeric.
- Possible singlet diradical character of the Ge-Ge bonding of 43.

**Reactivity:**

- In solution: \(-10^\circ\text{C}\), solid state: \(20^\circ\text{C} (\geq 95\% \text{ yield}, 1 \text{h})\)
- Unlike 43, compound 47 did not further react with \( \text{H}_2 \) even at elevated temperatures (up to \(100^\circ\text{C}\)).
- Addition of \( \text{H}_2 \) to 47 gave the singly bridged species \( \text{L}^1\text{Ge}(\text{u-H})\text{GeH}_3 \), which then rearranged via a low activation pathway to the symmetrically hydrogenated compound \( \text{L}^1\text{HGe-GeH}_3 \) followed by rearrangement to the most stable isomer 48.
- The second addition of \( \text{H}_2 \) would result in cleavage of the Ge-Ge bond, giving \( \text{L}^1\text{GeH} \) and \( \text{L}^1\text{GeH}_3 \).
- However, this reaction was calculated to be thermodynamically unfavorable, consistent with the observed reactivity.

**JACS, 2011, 133, 18622.**
reaction of 49 and 51 with $\text{H}_2$ likely proceeded via interaction of the $\sigma$ orbital of $\text{H}_2$ with the empty 4p orbital at the germanium atom with concomitant back donation from the germanium lone pair to the $\text{H}_2 \sigma^*$ 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 $\text{Ar}^{\text{Dipp}}$ groups introduced sufficient strain such that the preferred pathway is elimination of $\text{HAr}^{\text{Dipp}}$ along with production of monomeric $\text{GeHAr}^{\text{Dipp}}$, which then reacted with $\text{H}_2$ to give the final product 46.  

\textit{JACS. 2009, 131, 16272.}

Why the Mechanisms of Digermyne and Distannyne Reactions with $\text{H}_2$ Differ So Greatly?

Further Reading: JACS, 2012, 134, 8856.
**Group 15 Compounds (P)**  
**Reversible Activation of H₂**

1,4-addition  
P inversion  
suprafacial hydride shift

**Catalytic Reaction**

alkaline metals

\[ \text{Ph} \quad \text{Ph} \quad \text{H₂} \quad (20 \text{ bar), THF/HMPA} \]

\[ \text{cat 1 (2.5 mol%)} \]

\[ \text{JACS, 1964, 86, 3750.} \quad \text{JACS, 2002, 124, 8693.} \]

\[ \text{>99% conv.} \]

**Conversion rates increase with metal size:**  
\[ \text{Mg < Ca < Sr < Ba} \]  
(for Ba, quantitative conversion is reached within 15 min).

ACIE. 2016, 55, 12214
hydrogenation with main group compounds

**Correction:** ACIE, 2017, 56, 9266.

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**65a.** Ar = C₆H₄-4-IBu  
**65b.** = C₆H₃-3,5-Me₂  
**66a.** Ar = C₆H₄-4-IBu  
**66b.** = C₆H₃-3,5-Me₂

\[
\text{H}_2 + \text{D}_2 \xrightarrow{\text{rt}, 5 \text{ min}} 2 \text{ HD}
\]

\[
\begin{align*}
\text{65b} \ (5 \text{ mol\%)} & \quad \text{H}_2 \ (1 \text{ bar}), \ d_{6}-\text{THF}, 25-80 \ ^\circ\text{C} \\
\text{65a or 66a} \ (2.5-10.0 \text{ mol\%)} & \quad 15 \text{ examples} \\
& \quad 0-98\% \text{ conv.}
\end{align*}
\]

**ACIE, 2012, 51, 4452.**  
**ACIE, 2016, 55, 4794.**  
**ACIE, 2017, 56, 12367.**

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**Acenine compound**

\[
\begin{align*}
\text{Cat 1} (5-20 \text{ mol\%}) & \quad \text{H}_2 \ (50 \text{ bar}), \ \text{LiHMDS} \ (0.3-1.0 \text{ eq.}) \\
& \quad \text{toluene}, 50-80 \ ^\circ\text{C}
\end{align*}
\]

69-100% yield

**ACIE, 2015, 54, 9542.**

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**Important!!!**

blank reaction (2.25 equiv. LiHMDS, without catalyst) cannot work!!!

**ACIE, 2015, 54, 9542.**
b. Stepwise mechanism

\[ \text{LiH} + \text{R}^2-\text{N}-\text{R}^1 \rightarrow \text{R}^2-\text{N}-\text{R}^1 + \text{H}\ ] \rightarrow \text{R}^2-\text{N}-\text{R}^1 \]

(1)

(2)


Fullerene, UV light

\[ \text{H}_2 \text{ (1 atm), rt} \]

4-6 MPa H\text{2}, 140-160 °C

JACS, 2009, 131, 16380.