Gruppe 13 – B, Al, Ga, In, Th

https://www.schulz.chemie.uni-rostock.de/lehre/vorlesungen-bachelor/anorganische-chemie-iv-ch17/

Leibniz-Institut für Katalyse e.V.

LIKAT Rostock

Übersicht

- 5. Metall/Elementorganische Verbindungen der Hauptgruppenelemente

  » Erdmetalle
  - Bororganyle (Synthese, Struktur, Bindung)
  - Aluminiumorganyle
  - Ga/In/Th-organyle

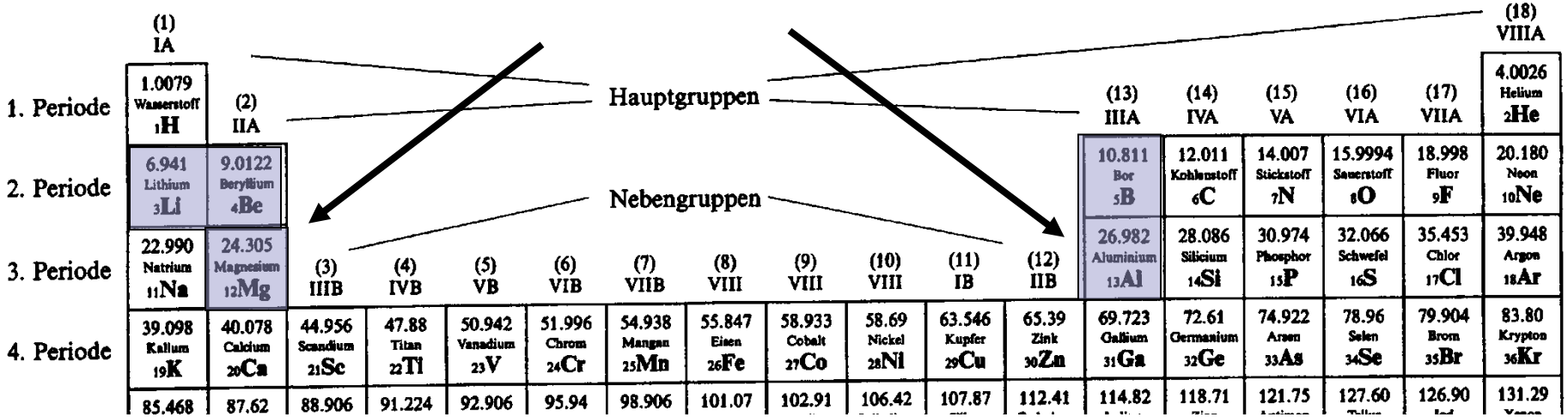
B	**C**
2.0	2.55
Al	
1.6	
Ga	
1.8	
In	
1.8	
Tl	
1.6	

Wirtschaftliche Bedeutung groß

B und Al-Chemie dominieren

Organyle der Erdmetalle/Borgruppe

"Kovalente" Mehrzentrenbindungen



	(1) IA	(2) IIA	(3) IIIB	(4) IVB	(5) VB	(6) VIB	(7) VIIB	(8) VIII	(9) VIII	(10) VIII	(11) IB	(12) IIB	(13) IIIA	(14) IVA	(15) VA	(16) VIA	(17) VIIA	(18) VIIIA
1. Periode	1.0079 Wasserstoff $_1$H																	4.0026 Helium $_2$He
2. Periode	6.941 Lithium $_3$Li	9.0122 Beryllium $_4$Be											10.811 Bor $_5$B	12.011 Kohlenstoff $_6$C	14.007 Stickstoff $_7$N	15.9994 Sauerstoff $_8$O	18.998 Fluor $_9$F	20.180 Neon $_{10}$Ne
3. Periode	22.990 Natrium $_{11}$Na	24.305 Magnesium $_{12}$Mg											26.982 Aluminium $_{13}$Al	28.086 Silicium $_{14}$Si	30.974 Phosphor $_{15}$P	32.066 Schwefel $_{16}$S	35.453 Chlor $_{17}$Cl	39.948 Argon $_{18}$Ar
4. Periode	39.098 Kalium $_{19}$K	40.078 Calcium $_{20}$Ca	44.956 Scandium $_{21}$Sc	47.88 Titan $_{22}$Ti	50.942 Vanadium $_{23}$V	51.996 Chrom $_{24}$Cr	54.938 Mangan $_{25}$Mn	55.847 Eisen $_{26}$Fe	58.933 Cobalt $_{27}$Co	58.69 Nickel $_{28}$Ni	63.546 Kupfer $_{29}$Cu	65.39 Zink $_{30}$Zn	69.723 Gallium $_{31}$Ga	72.61 Germanium $_{32}$Ge	74.922 Arsen $_{33}$As	78.96 Selen $_{34}$Se	79.904 Brom $_{35}$Br	83.80 Krypton $_{36}$Kr
	85.468	87.62	88.906	91.224	92.906	95.94	98.906	101.07	102.91	106.42	107.87	112.41	114.82	118.71	121.75	127.60	126.90	131.29

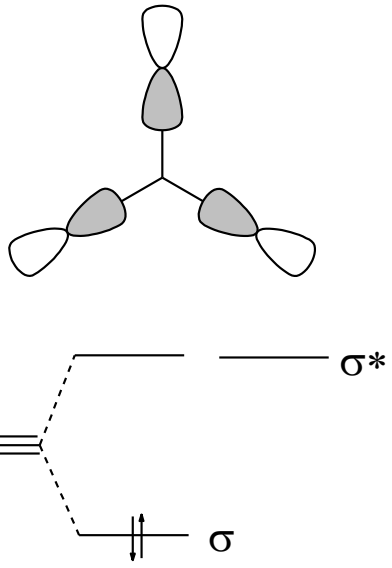
- Es besteht eine enge Verknüpfung zur Chemie der Borhydride

- B-N-Verbindungen isoelektronisch zu C-C-Verbindungen

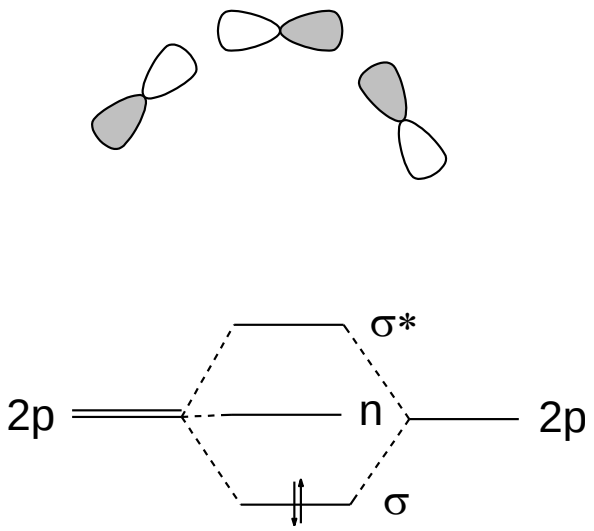
- Aluminiumorganyle dienen als Carbanionenüberträger (unschlagbar billig) und spielen eine Schlüsselrolle in großtechnischen Verfahren

Bindungsverhältnisse

- neben der "klassischen" 2-Zentren-2-Elektronenbindung gibt es:



geschlossene 3-Zentren-2-Elektronenbindung
D_{3h}-Symmetrie

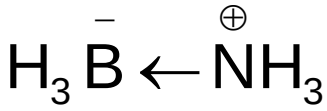


offene 3-Zentren-2-Elektronenbindung
C_{2v}-Symmetrie

Zum Vergleich: Bor-Stickstoff-Verbindungen

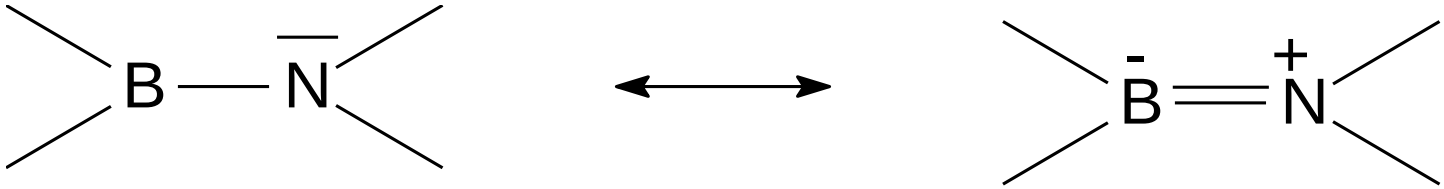
Bor-Amin-Addukte: Lewis-Säure verbunden mit Lewis-Base

Problem: **Formalladung *vs.* Partialladung**



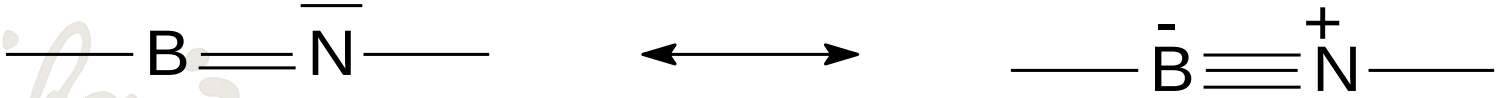
$H_3C\text{-}CH_3$
(d_{CC} = 154 pm, d_{BN} = 167 pm)

Aminoborane:



$H_2C{=}CH_2$

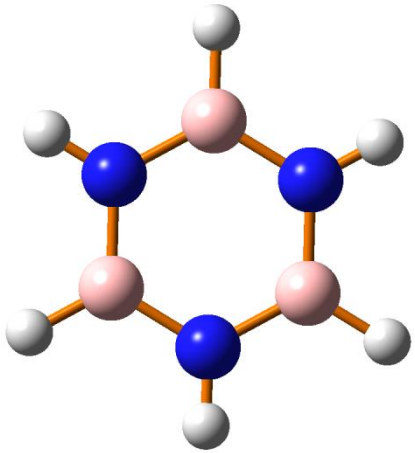
Iminoborane:



Borazol (Borazin)

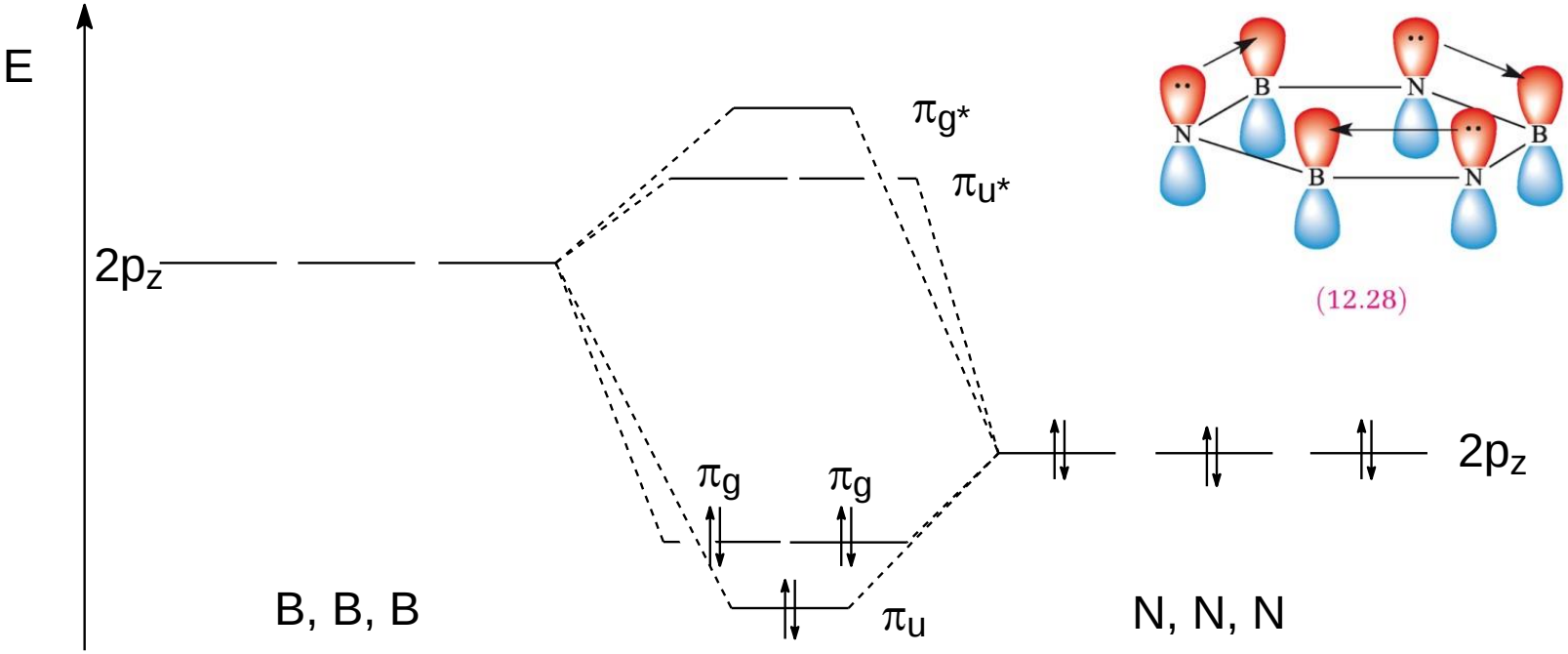
HB=NH ist unbeständig und oligomerisiert zum cyclischen $(HBNH)_3$

$$3\,BCl_3 + 3\,NH_4Cl \xrightarrow{150°C} B_3N_3H_3Cl_3 \xrightarrow{NaBH_4} B_3N_3H_6$$



- farblose Flüssigkeit, aromatischer Geruch,
- D_{3h}, <NBN = 117° und <BNB = 123°,
- stark polare Bindungen, im Gegensatz zu Benzol reaktiver: quasi-aromatisch
- Hydrolyse: NH_3 und $B(OH)_3$

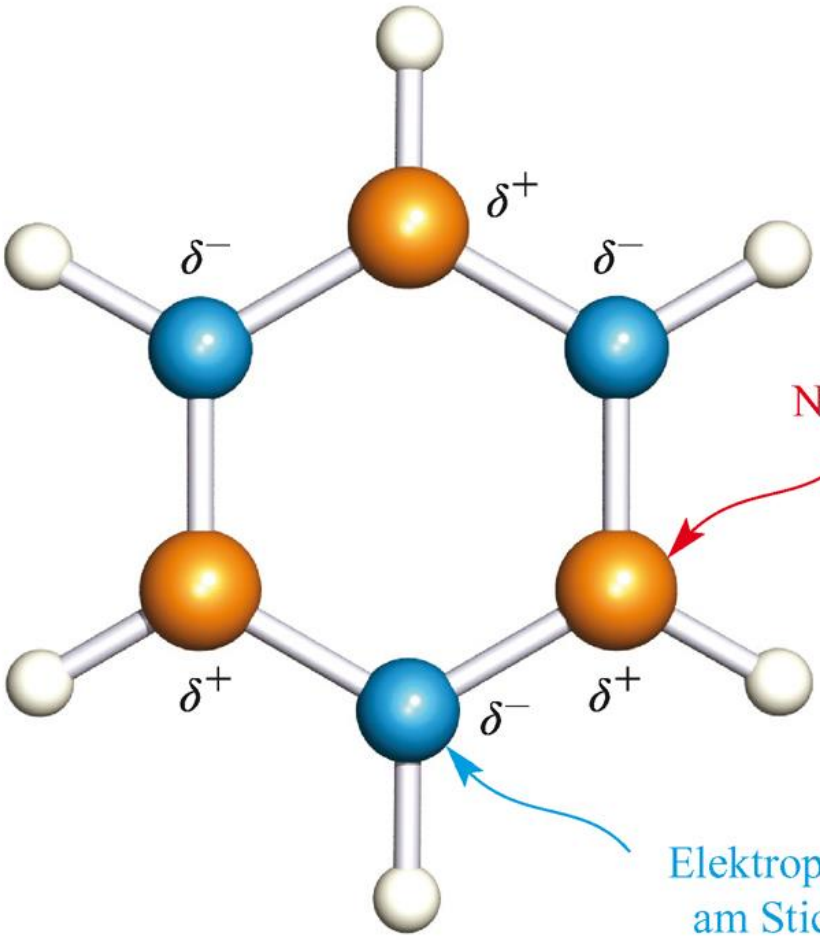
Energieniveaudiagramm für die MO's, die aus 3 $2p_z$ am Bor und entstehen.

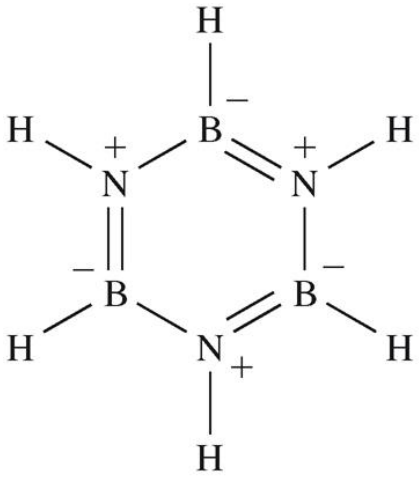


Sandwich wie beim Benzol:

$$B_3N_3Me_6 + Cr(CO)_3(CH_3CN)_3 \longrightarrow [Cr(\eta^6 - B_3N_3Me_6(CO)_3] + 3CH_3CN$$

Hydrolyse: Formal- vs. Partialladung

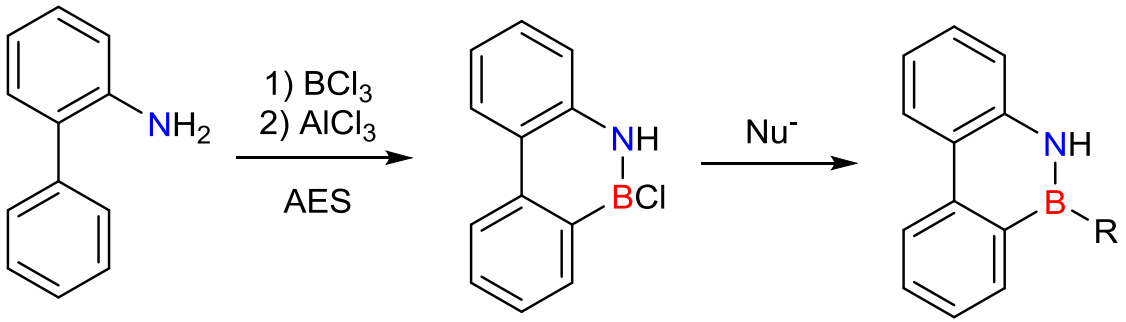




(12.27)

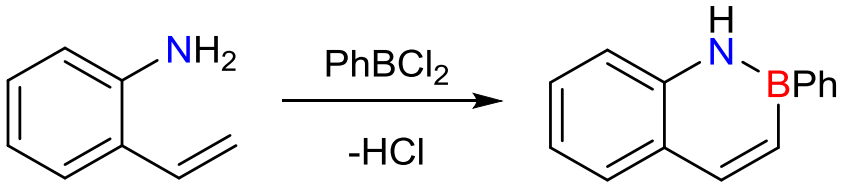
Hybride Organisch/Anorganische Benzol-Derivate

- Erster Bericht eines aromatischen Systems mit 1,2-BN Einheit 1958: 9,10-Azaboraphenatren, Dewar et al.



R = OH, Me, Ph, H

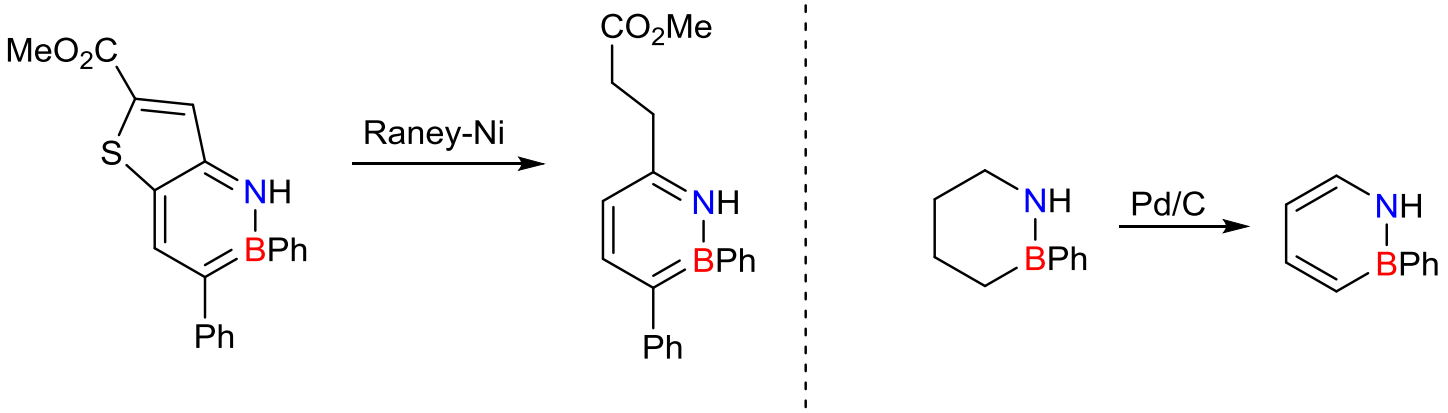
- 1959 dann das erste BN-Naphtalen:



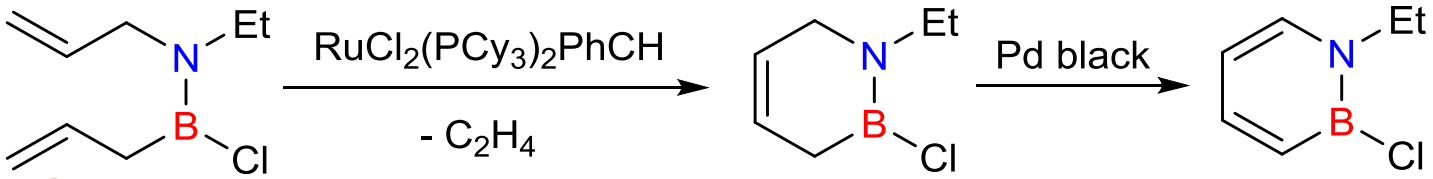
a) M. J. S. Dewar, V. P. Kubba, R. Pettit, *J. Chem. Soc.* **1958**, 3073; b) M. J. S. Dewar, *Tetrahedron* **1959**, *7*, 213

Hybride Organisch/Anorganische Benzol-Derivate

- 1962 dann das erste 1,2-Azaborin durch Dewar und White



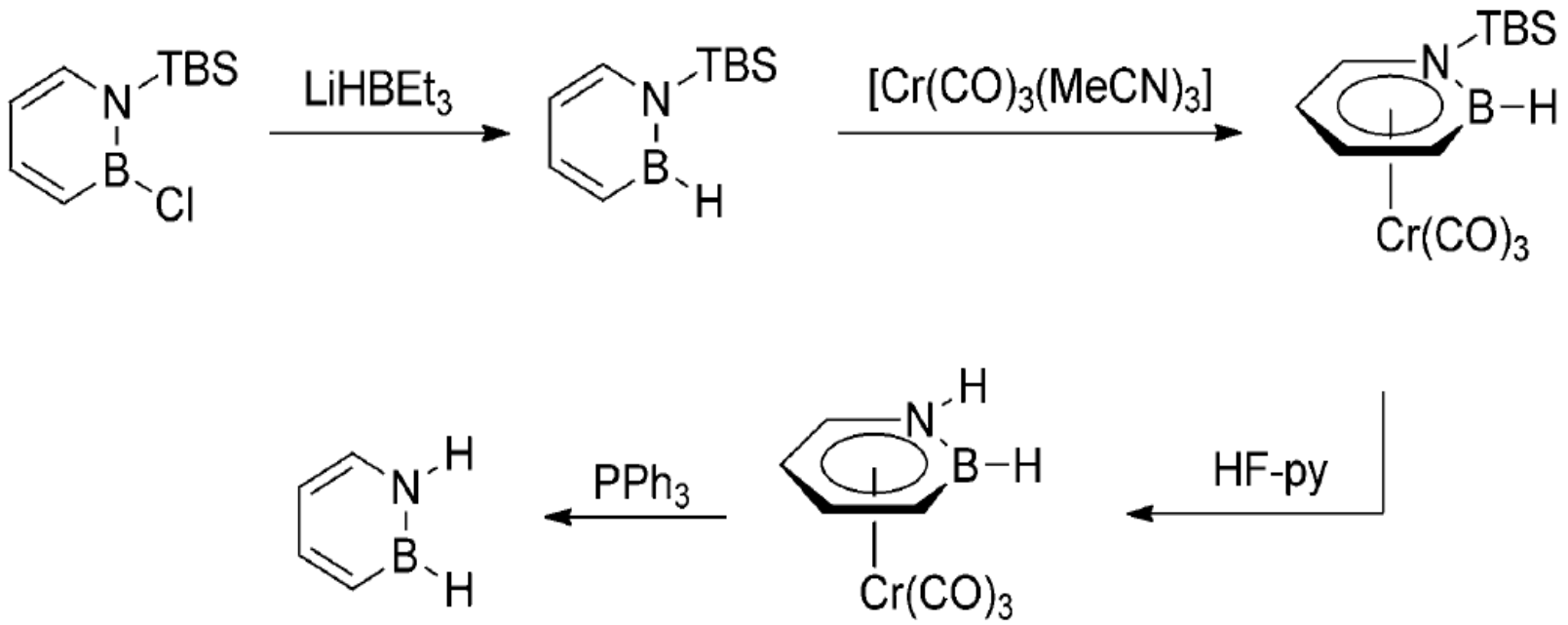
- Liu et al. nutzen ROMP zur Darstellung von funktionalisierten 1,2-Azaborinen



a) M. J. S. Dewar, P. A. Marr, *J. Am. Chem. Soc.* **1962**, *84*, 3782; b) A. J. V. Marwitz, E. R. Abbey, J. T. Jenkins, L. N. Zakharov, S.-Y. Liu, *Org. Lett.* **2007**, *9*, 4905

Das 1,2-Dihydro-1,2-Azaborin

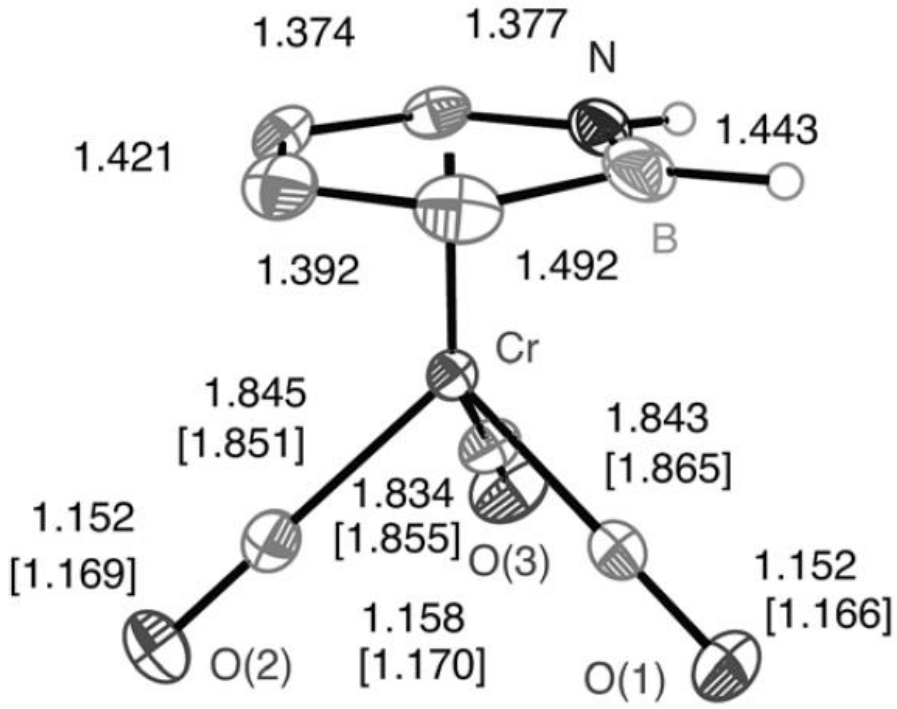
- 2009 Synthese des „Stamm“ 1,2-Dihydro-1,2-Azaborins



A. J. V. Marwitz, M. H. Matus, L. N. Zakharov, D. A. Dixon, S.-Y. Liu, *Angew. Chem. Int. Ed.* **2009**, *48*, 973.

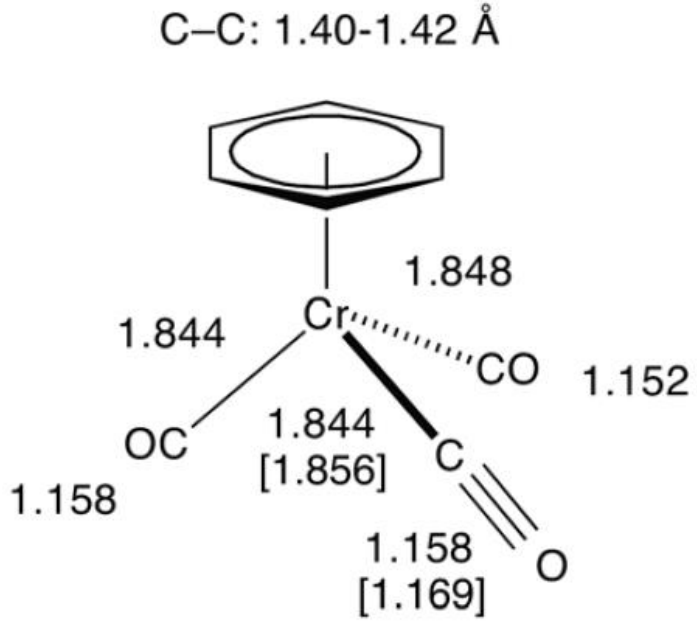
Das 1,2-Dihydro-1,2-Azaborin

ν(CO) = 1898,1975 cm^{-1}



81

ν(CO) = 1892,1972 cm^{-1}

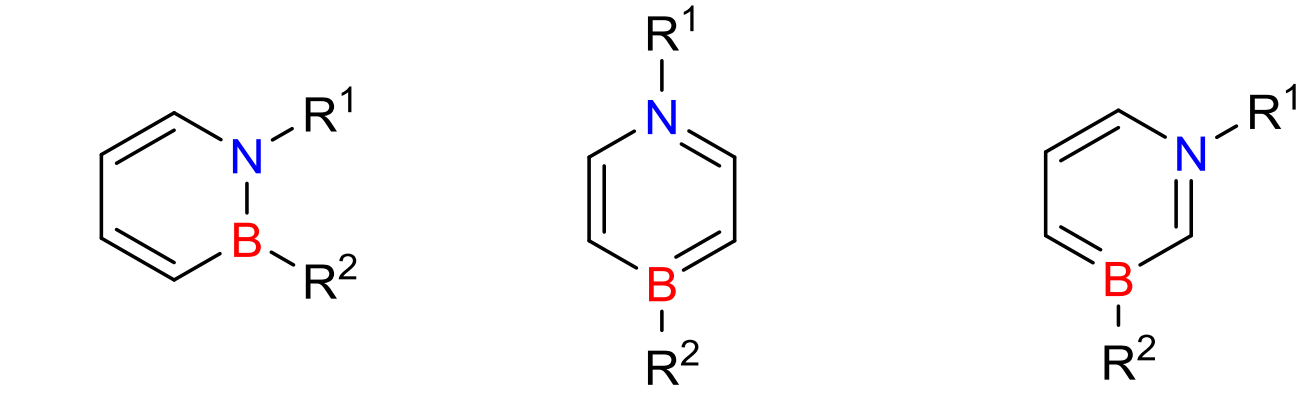


$[Cr(CO)_3(C_6H_6)]$

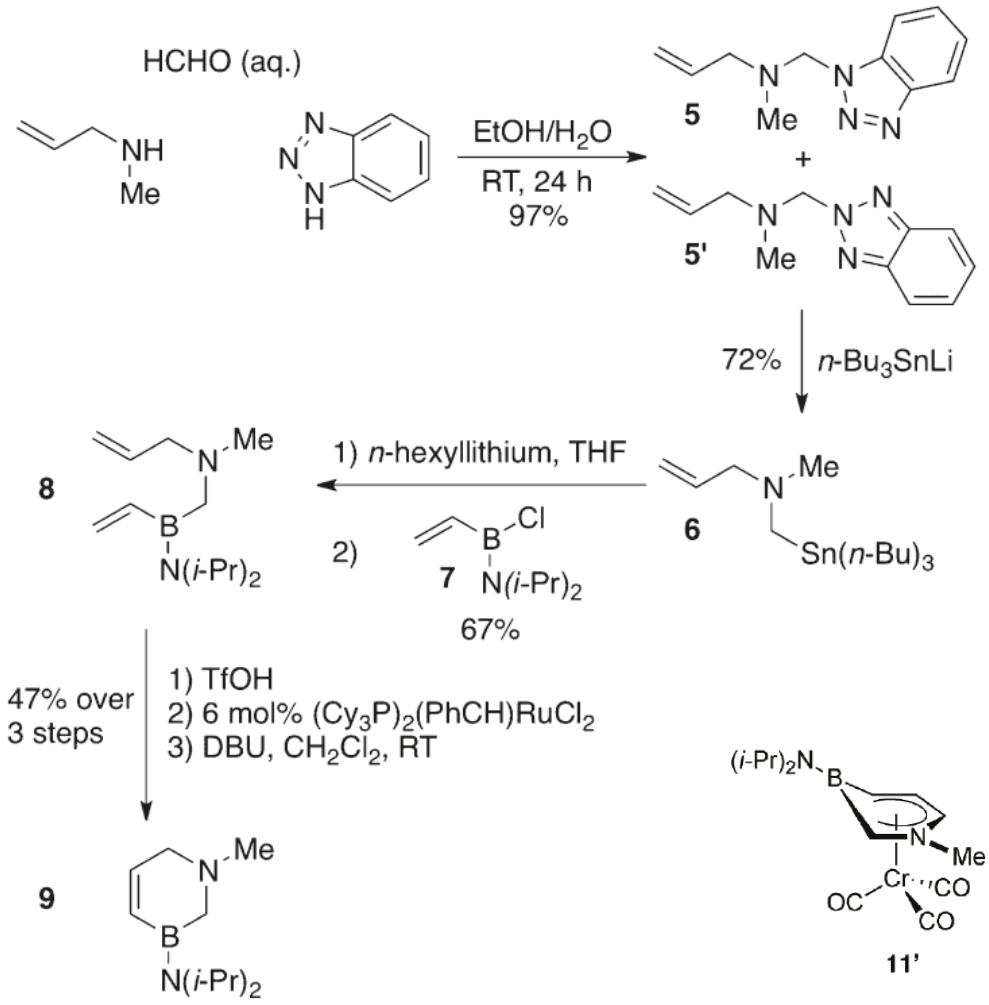
A. J. V. Marwitz, M. H. Matus, L. N. Zakharov, D. A. Dixon, S.-Y. Liu, *Angew. Chem. Int. Ed.* **2009**, *48*, 973.

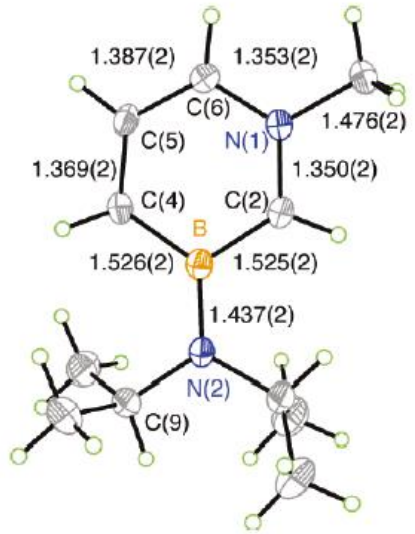
Konstitutionsisomere des Azaborins

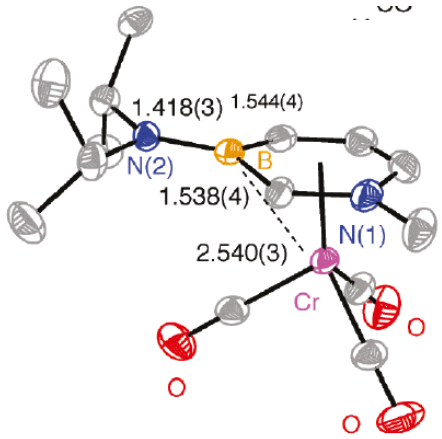
- 1,2-Isomer thermodynamisch am stabilsten
- 1,2 > 1,4 > 1,3



Das 1,3-Azaborin



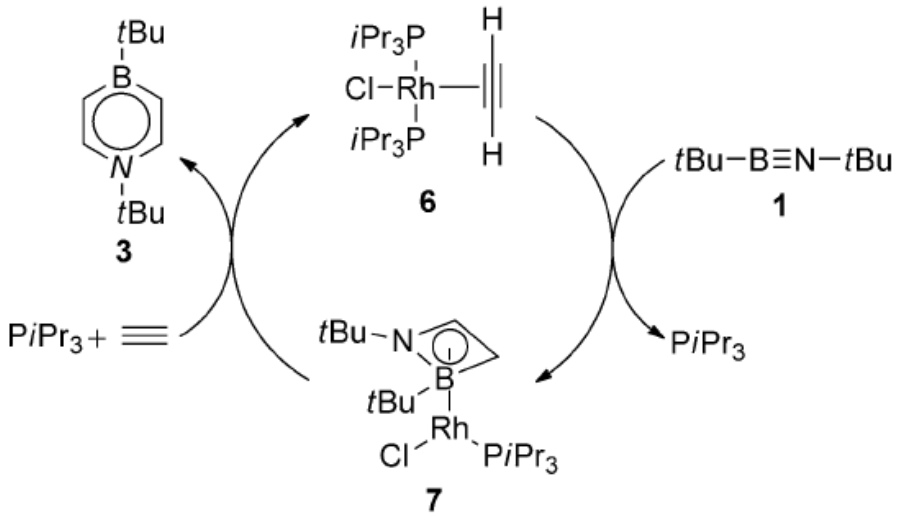


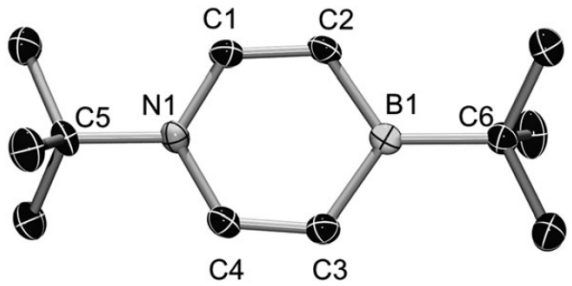


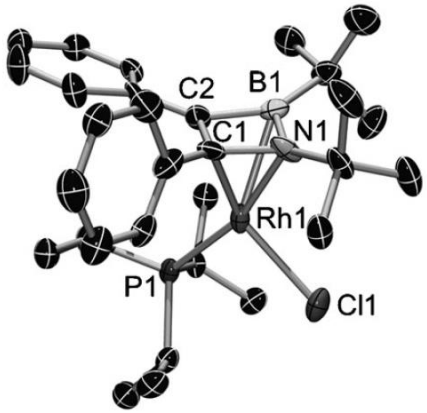
S. Xu, L. N. Zakharov, S.-Y. Liu, *J. Am. Chem. Soc.* **2011**, *133*, 20152

Das 1,4-Azaborin

- Braunschweig et al. 2012 – [2+2+2]-Zyklisierung an 14e-Rhodium-Komplexen
- Stabiles Iminoboran ^{t}Bu-NB-^{t}Bu und Acetylen als Edukt





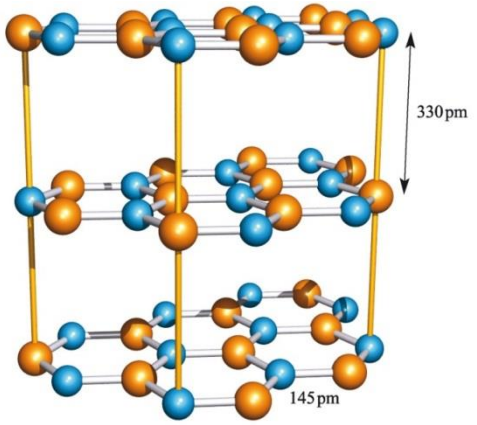


H. Braunschweig, A. Damme, J. O. C. Jimenez-Halla, B. Pfaffinger, K. Radacki, J. Wolf, *Angew. Chem.* **2012**, *124*, 10177.

Weitere Analogien - Bornitrid

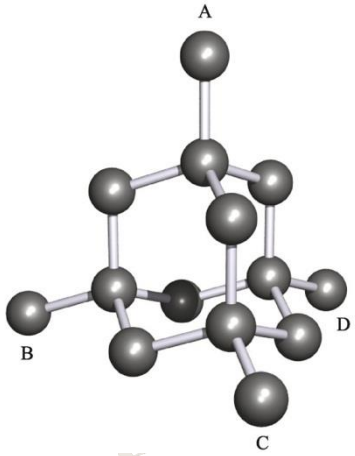
Bornitrid (**Graphit** analog):

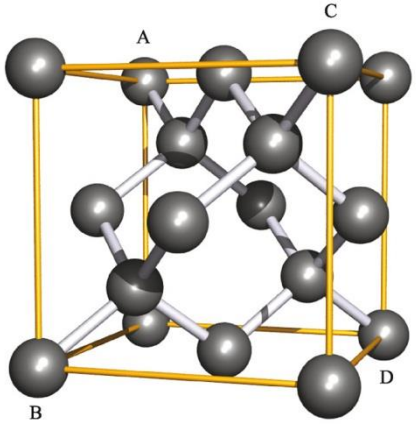
$$B_2O_3 + 3C + N_2 \xrightarrow{1850^\circ C} 2/x(BN)_x + 3CO$$

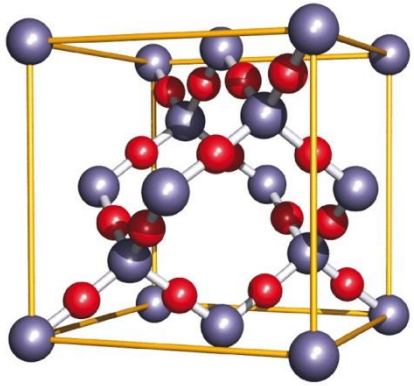


Graphit/Diamant Analogie:

$(BN)_x$ hexagonal $\xrightarrow{60-90x10^8\,Ps,\,1500-2000^\circ C}$ ***anorganischer Diamant***

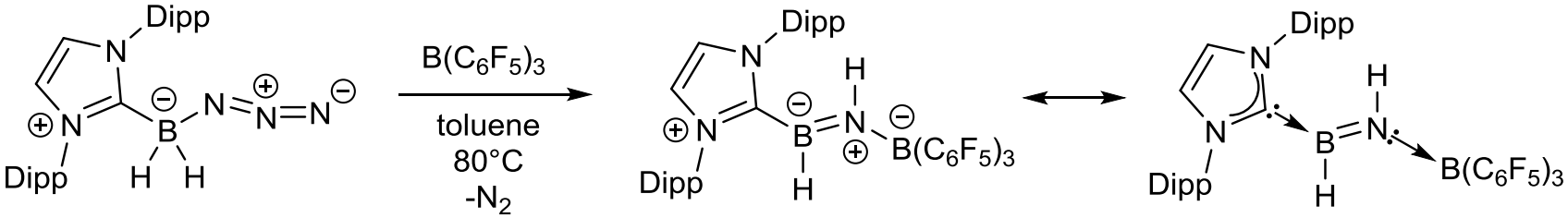


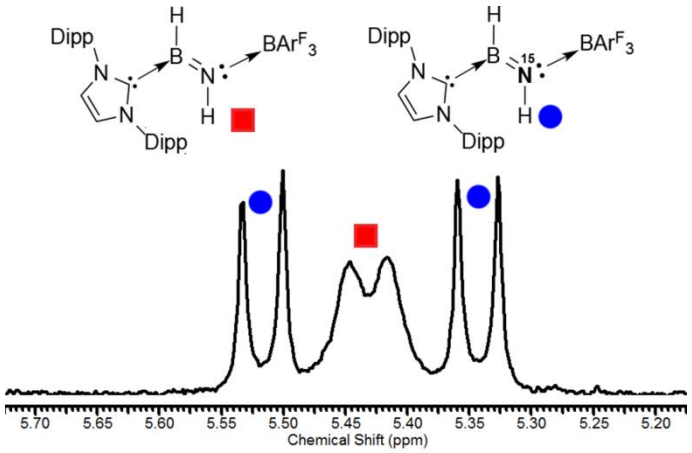




Molekulare Prekusoren für BN?

- Stabilisierung von anorganischem Acetylen (HNBH) zwischen Carben (IPr) und LS $B(C_6F_5)_3$





A. K. Swarnakar, C. Hering-Junghans, K. Nagata, M. J. Ferguson, R. McDonald, N. Tokitoh, E. Rivard, *Angew. Chem. Int. Ed.* **2015**, *54*, 10666.

Borane B_nH_m, Hydroborat-Anionen (Boranate), Carbaborane und Carbaborat-Anionen (BH^- ersetzt durch CH)

Begründer: Alfred Stock (1912-1936)

Bindungseigenschaften: W. N. Lipscomb 1976 Nobelpreis

Literatur:

L. Muetterties, *Boron Hydrogen Chemistry*, Academic Press, London, New York, 1975

R. Köster, M. A. Grassberger, *Angew. Chemie*, **1967**, *79*, 197.

W. N. Lipscomb, *Angew. Chemie*, **1977**, *89*, 685.

4 allgemeine Bruttoformel:

B_nH_{n+2}	B_nH_{n+4}	B_nH_{n+6}	B_nH_{n+8}
closo	**nido**	**arachno**	**hypho**
Käfig	-1 Ecke	-2 Ecken	-3 Ecken

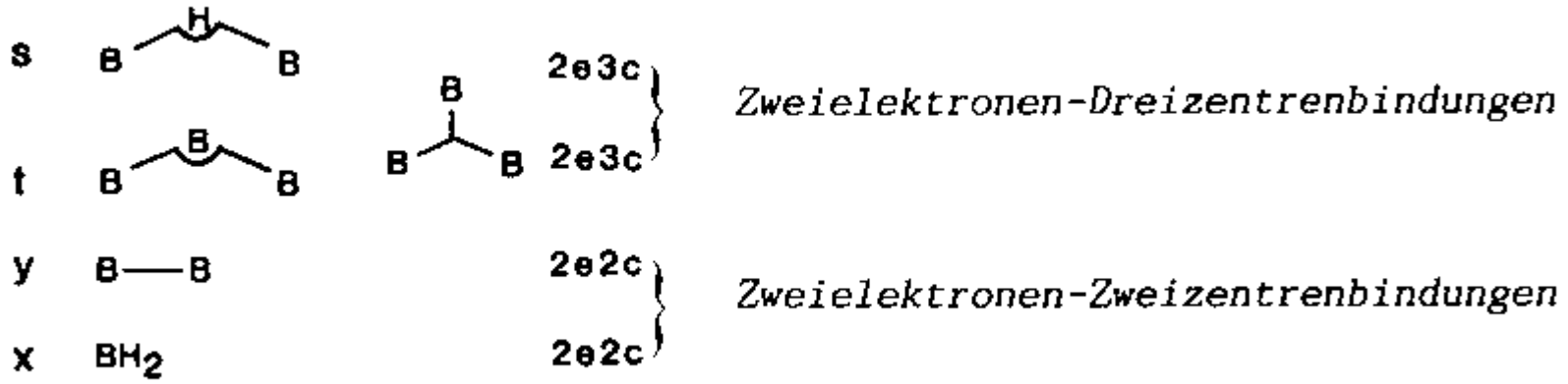
Beispiel für B_nH_{n+4}:	B_2H_6, B_4H_8,	...	$B_{18}H_{22}$
Beispiel für B_nH_{n+6}:	B_4H_{10}, B_5H_{11}	...	$B_{20}H_{26}$

- elektronen Mangelverbindungen
- stark endotherme Verbindungen: $B_2H_6 + 3\ O_2 \rightarrow B_2O_3 + 3\ H_2O$ $D\mathit{H}°(298) = -2138$ KJ/mol

- Nomenklatur: BH_3: Boran (3); B_2H_6: Diboran (6); B_4H_{10}: Tetraboran (10)

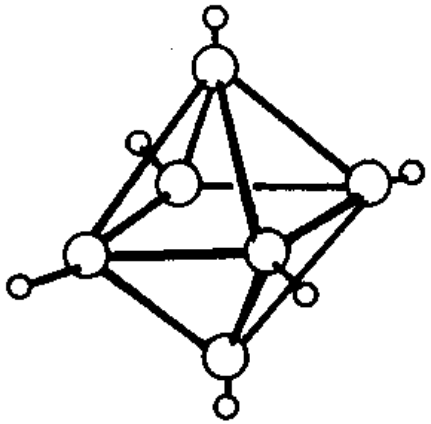
Mehrzentrenbindungen in Boranen

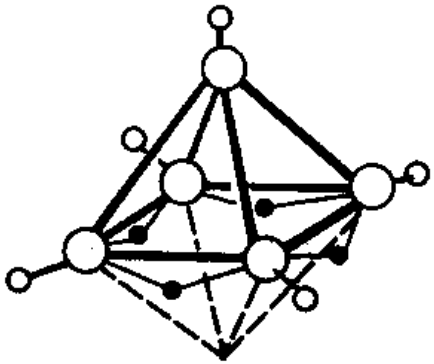
- In Boranen (auch C-substitutierten) liegen immer mehr Gerüstverbindungslinien als Elektronenpaare vor (LIPSCOMB)
- Styx - Code

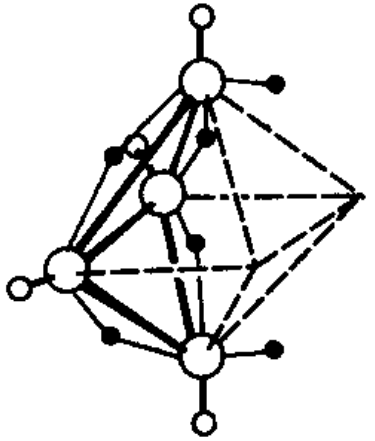


z.B. B_2H_6 styx code = 2002

Borhydride – Eine Wiederholung







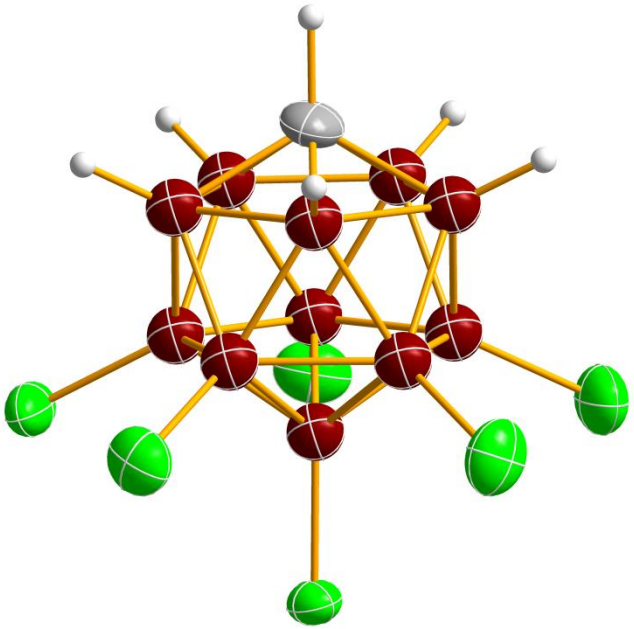
$2n+2$ $2n+4$ $2n+6$ Gerüstelektronen

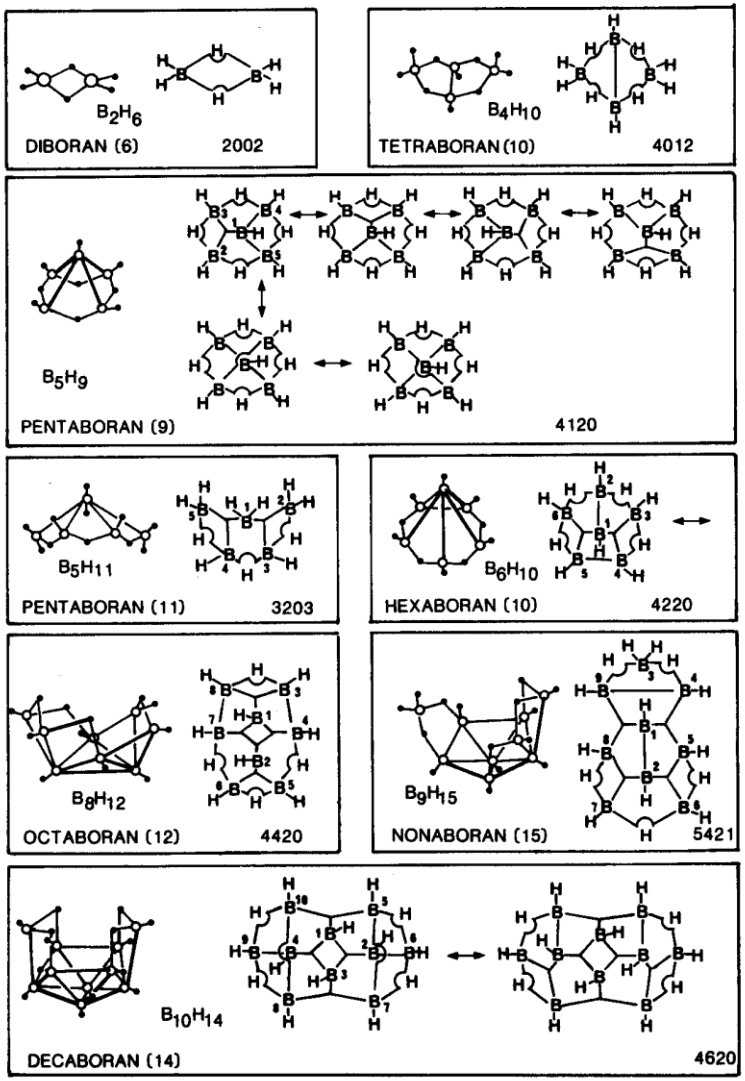
closo ($B_6H_6^{2-}$) ***nido*** (B_5H_9) ***arachno*** (B_4H_{10})

- Erste Ergebnisse von A. Stock (1876-1946)
- WADE´schen Regeln: Anzahl der Gerüstelektronen = Summe der Valenzelektronen der (Bor-)Gerüstatome + Valenzelektronen der H-Atome + Anzahl der Elektronenladungen - zwei Elektronen pro Hauptgruppen-Gerüstatom bzw. zwölf pro Nebengruppen-Gerüstatom.

Borhydride – Eine Wiederholung

Sehr gute schwachkoordinierende Anionen! Z.B. $[HCB_{11}H_5Cl_6]^-$





Synthese

$$4BCl_3 + 3LiAlH_4 \xrightarrow{\text{Ether}} 2B_2H_6 \uparrow + 3LiCl + AlCl_3$$

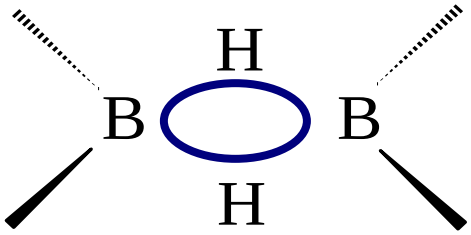
$$4BF_3 + 3NaBH_4 \xrightarrow[25°C]{\text{Ether}} 2B_2H_6 \uparrow + 3NaBF_4$$

$$2NaBH_4 + I_2 \longrightarrow B_2H_6 \uparrow + 2NaI + H_2$$

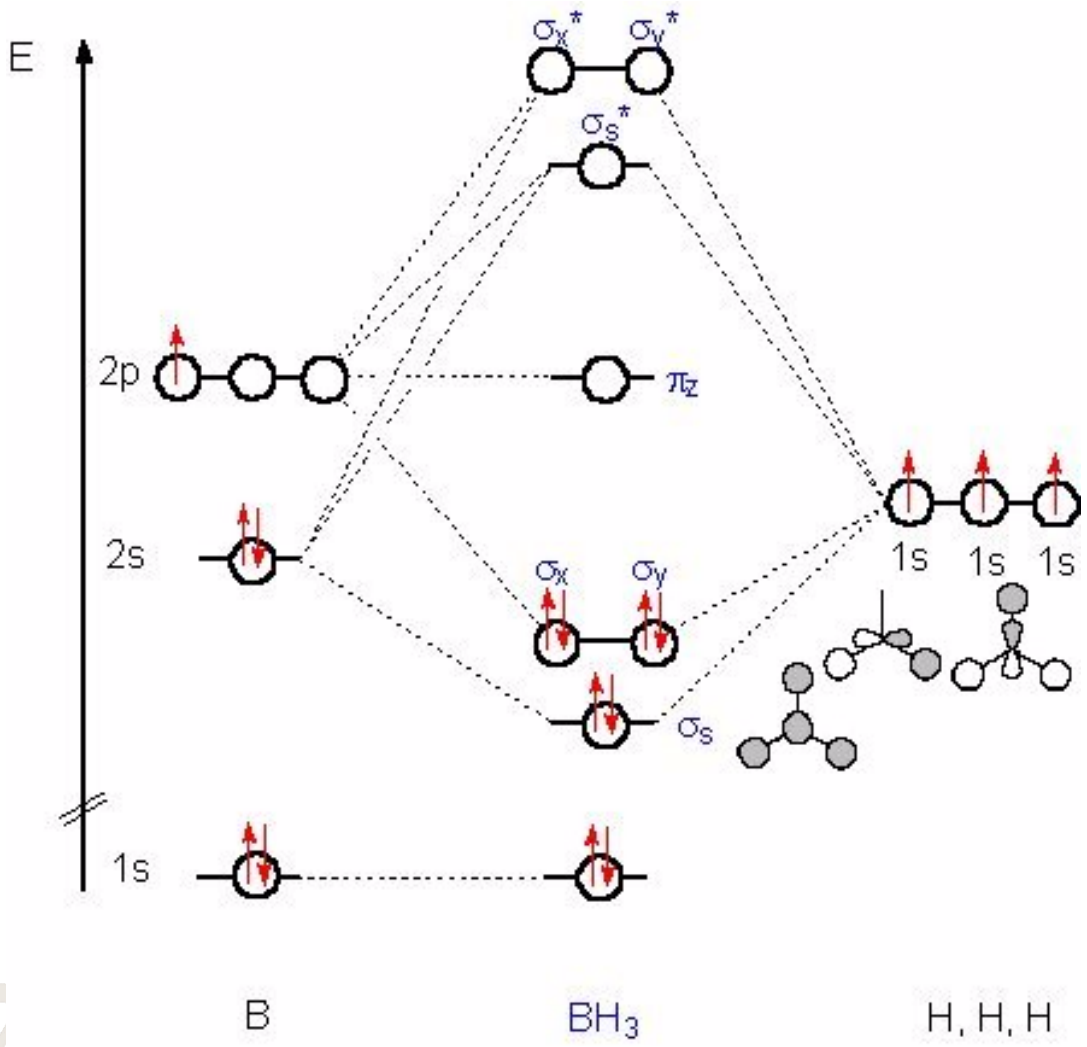
Gleichgewicht:

$$B_2H_6 \rightleftharpoons 2\,BH_3$$

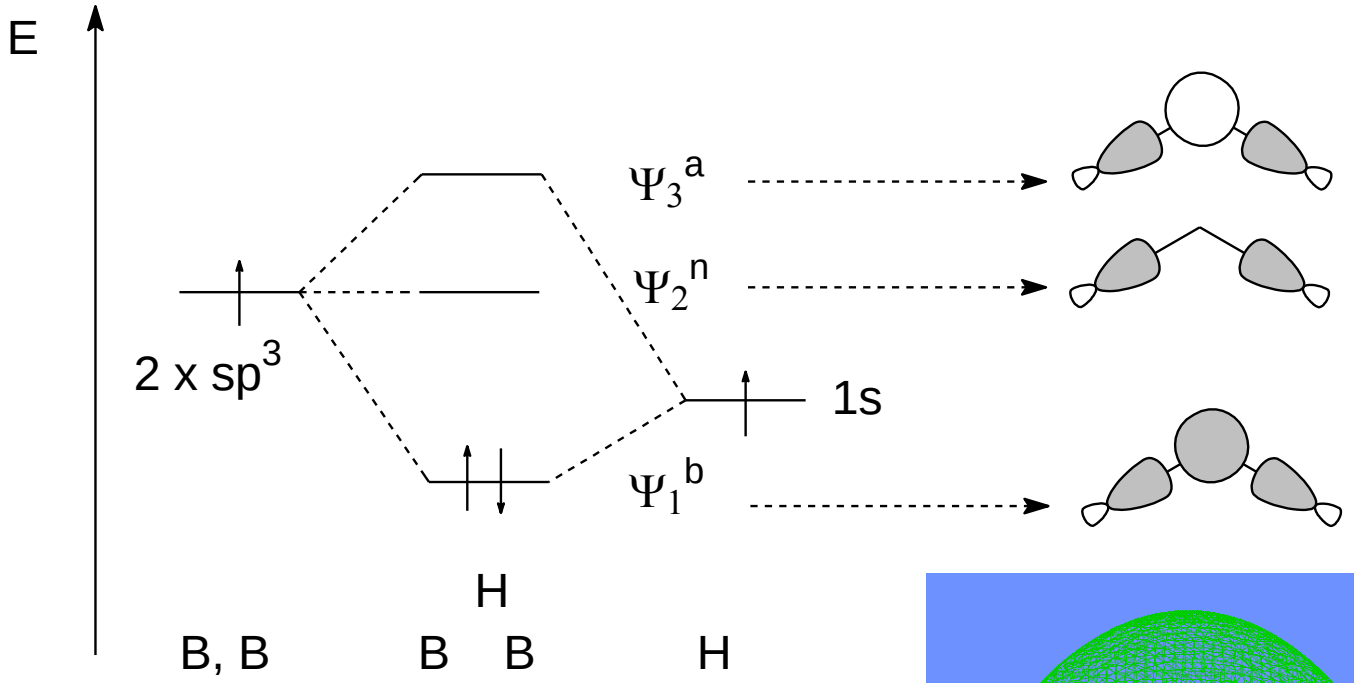
$\Delta H_{Diss.}(298) = 150$ kJ/mol

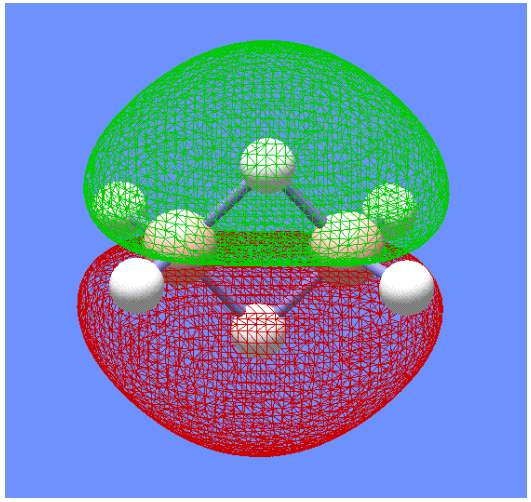


MO-Diagramm unter Verwendung delokalisierter MO's



Die Dreizentrenbindung im Diboran





MO-Darstellung

B-C Verbindungen: Synthese

BR_3

E_{Diss}(B-F) = 646 kJ/mol
E_{Diss}(B-O) = 526 kJ/mol
E_{Diss}(B-N) = 500 kJ/mol
E_{Diss}(B-H) = 372 kJ/mol
E_{Diss}(B-C) = 352 kJ/mol
E_{Diss}(C-C) = 345 kJ/mol
E_{Diss}(B-B) = 310 kJ/mol

Synthese

1.) Metathese

$$BF_3(OEt_2) + 3\ Li\text{-}R \longrightarrow 3\ Li\text{-}F + BR_3 + Et_2O$$

$$BR_3 \xrightarrow{+Li\text{-}R} LiBR_4$$

Darstellung

besser:

$$BCl_3 + 3\ Li\text{-}R \longrightarrow 3\ Li\text{-}Cl + BR_3$$

R = -Alkyl, -Aryl, $-C_6F_5$

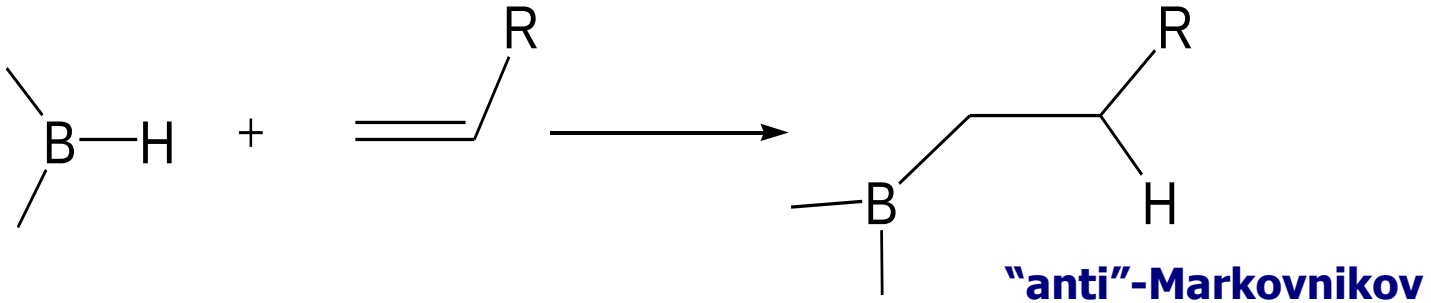
Auf genaue Stöchiometrie achten, da sonst "at"-Bildung

im Gegensatz:

$$B(OEt)_3 + Al_2R_6 \longrightarrow Al(OEt)_3 + BR_3$$

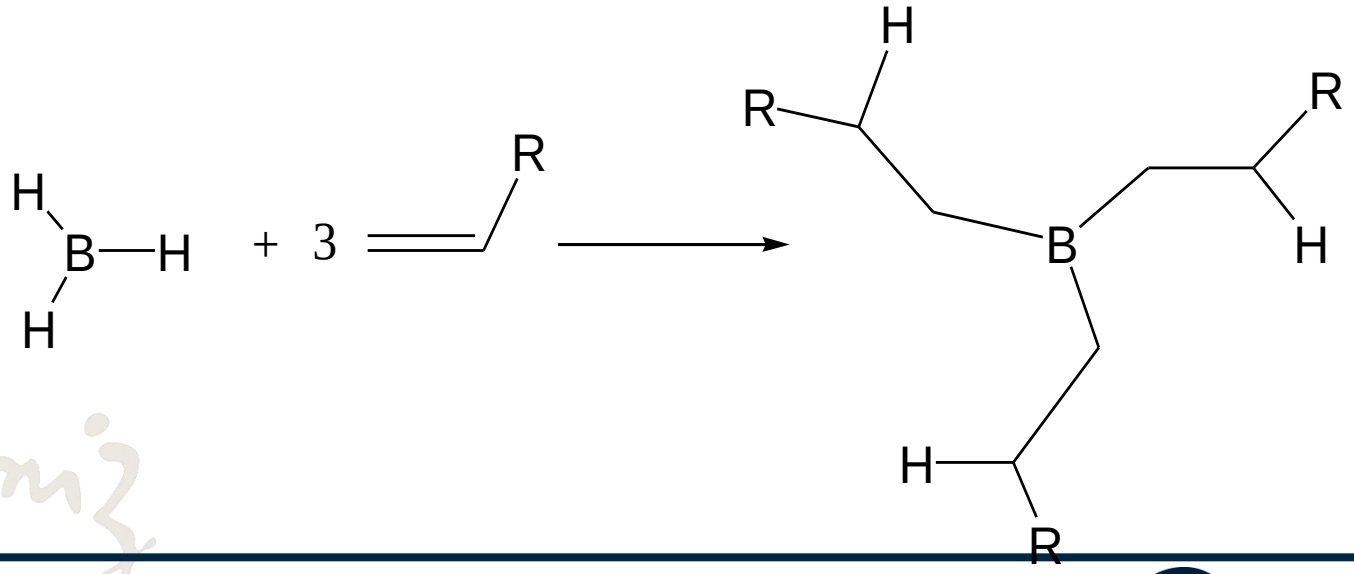
Darstellung

2.) Hydroborierung (H. C. Brown, Nobelpreis 1979 (mit Wittig))

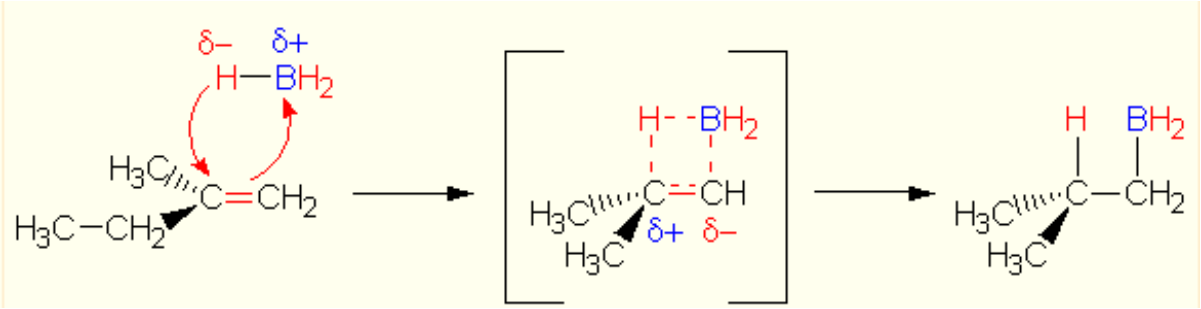


"anti"-Markovnikov

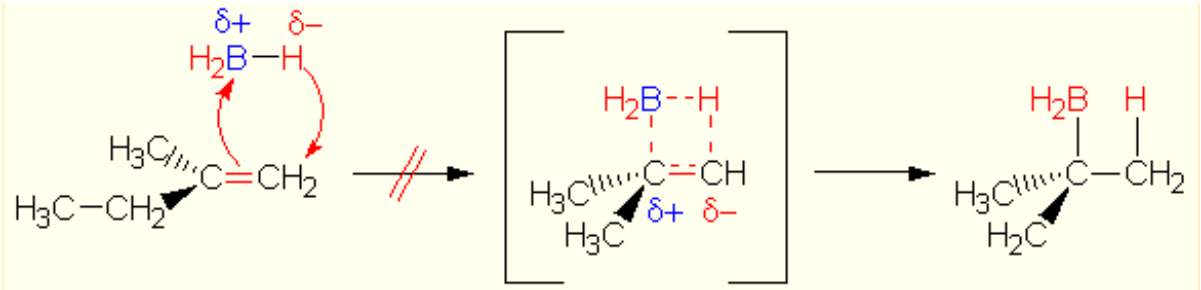
oder 3-fach



anti-Markovnikov



Beobachtetes Produkt



Nicht beobachtetes Produkt

Darstellung binärer Verbindungen

3.) Darstellung mittels Grignard

Binäre Verbindungen

$$(Et_2O)BF_3 + 3\ R\text{-}Mg\text{-}X \longrightarrow R_3B + 3\ MgXF + Et_2O$$

$$2\ B(OEt)_3 + Al_2R_6 \longrightarrow 2\ R_3B + 2\ Al(OEt)_3$$

Metathese

$$R_2B\text{-}X + X\text{-}Mg\text{-}R' \longrightarrow R_2B\text{-}R' + MgX_2$$

$$B(OR)_3 + n\ Li\text{-}R \longrightarrow R_nB(OR)_{3-n}$$

$RB(OR)_2$ Boronsäureester
$R_2B(OR)$ Borinsäureester

Eigenschaften

BR_3 ist relativ robust gegen Wasser

aber BMe_3 ist an Luft pyrophor !!

BR_3	R=Me	Gas bei 298 K
	R=Et	Sdp. 95 °C
	R=*n*Bu	Sdp. 208 °C

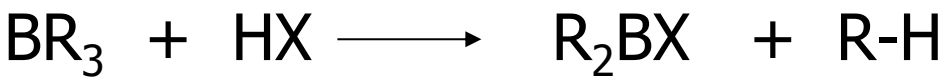
EN(B) = 2.0
EN(C) = 2.5 ⟶ Kovalente Bindung

Lewis-saurer Charakter von Boranen

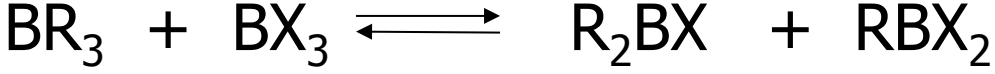
- Bildung von Addukten

Darstellung von Halogen-Boranen R-BX_2

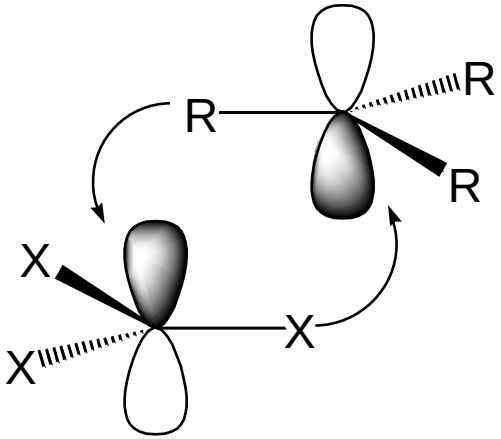
a) Nucleophiler Angriff



b) Kommutierung



Postulierter Mechanismus - Kommutierung



Analog 3-Zentren-4-Elektronenbindung

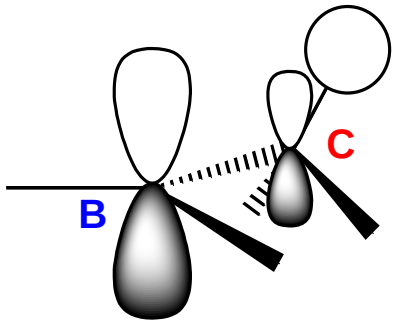
Strukturen und Reaktivität

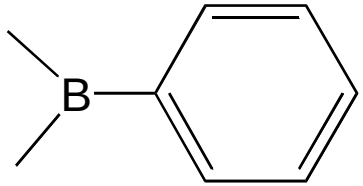
trigonal planar = hohe Lewis Acidität!!

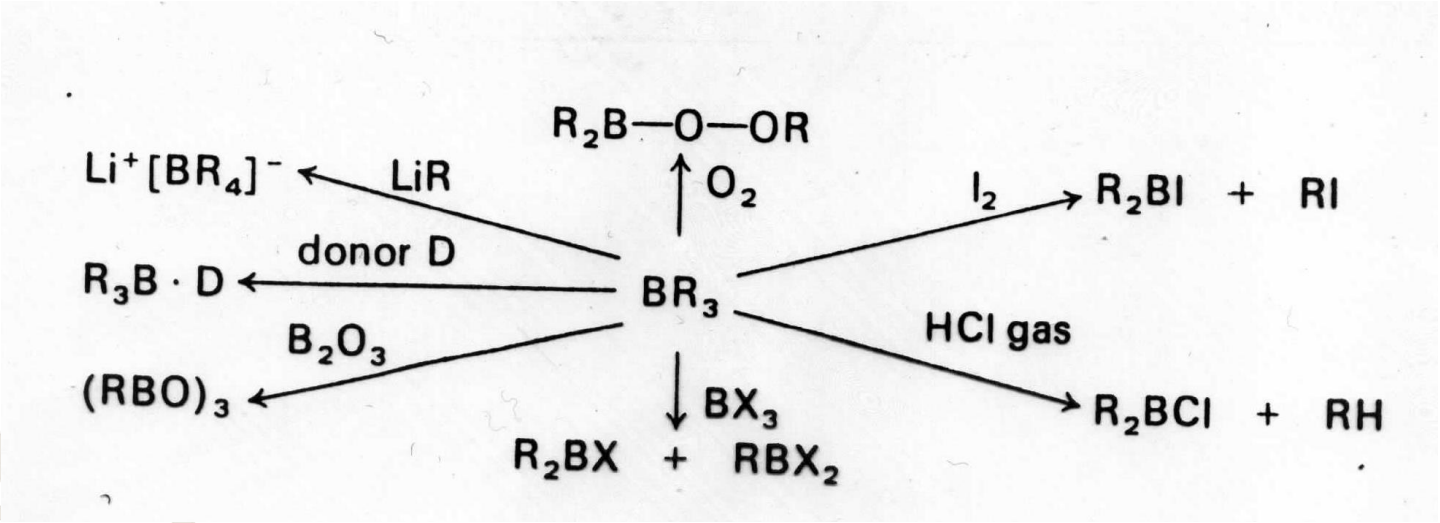
Stabilisierung durch

a) Hyperkonjugation

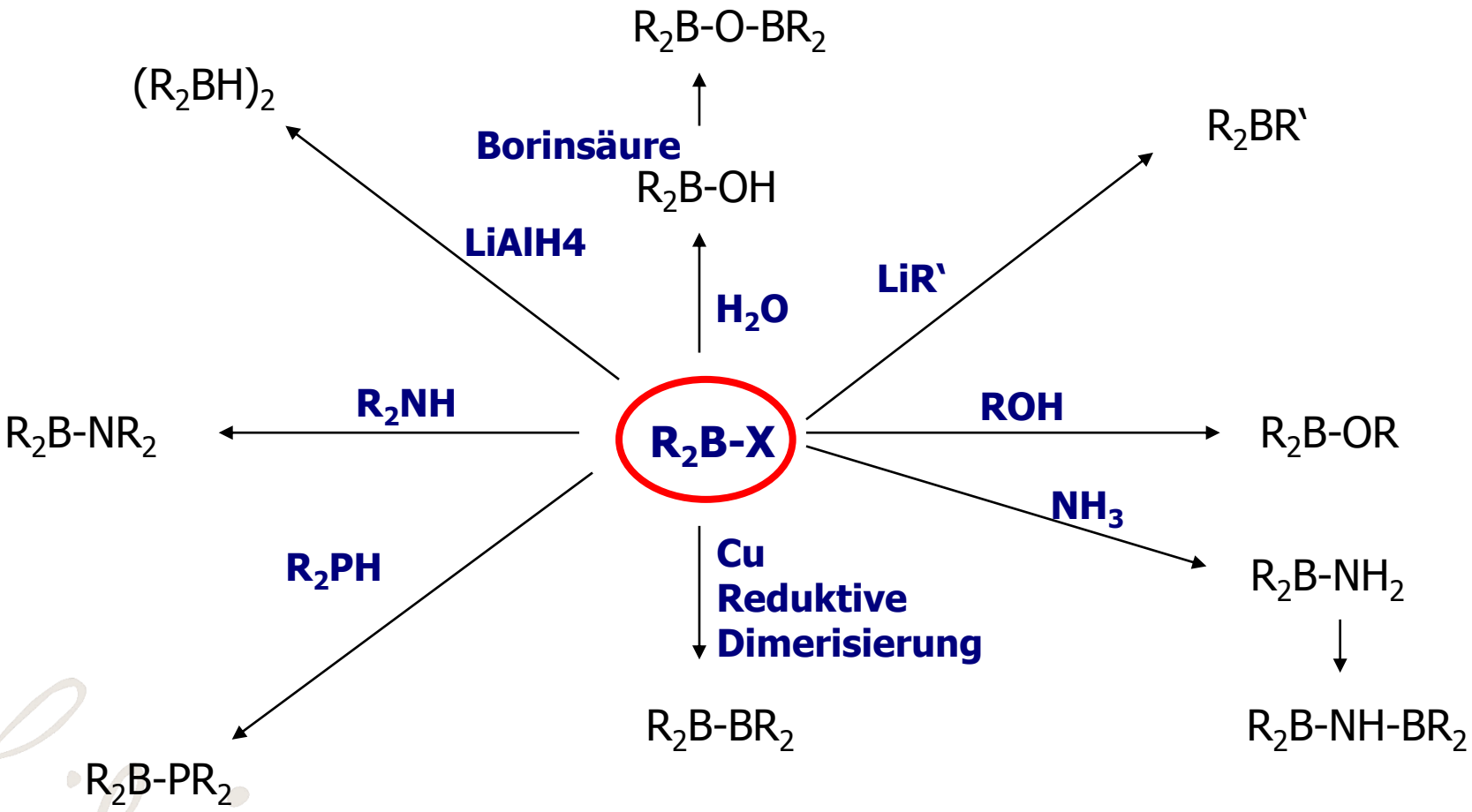
b) Resonanzstabilisierung







Reaktivität von Haloboranen



Tetraorganoborate

- Tetraorganoboranate $[BR_4]^-$

- analytische Anwendung – **Kalignost** (Kalium erkennend)

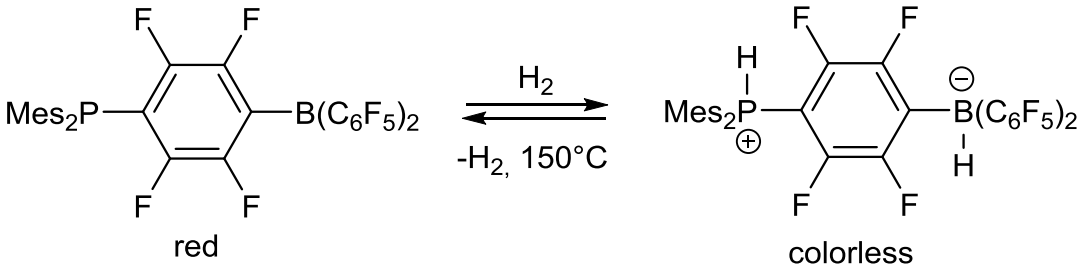
$$NaBF_4 + 4\ PhMgBr \longrightarrow NaBPh_4 + 4\ MgBrF$$

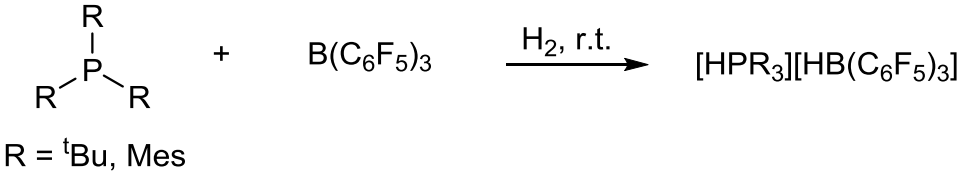
- Bildet schwerlösliche Salze mit Kalium, Rubidium, Caesium und Thallium(I)

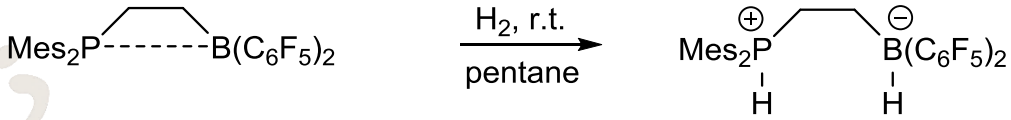
$$K^+_{(aq)} + [B(C_6H_5)_4]^-_{(aq)} \rightleftharpoons K[B(C_6H_5)_4]_{(s)}\downarrow$$

FLP's – Frustrierte Lewis-Säure-Base-Paare

Die Kombination sterisch gehinderter Lewis-Säuren und -Basen führt nicht zur üblichen Neutralisationsreaktion unter Bildung der „klassischen" Lewis-Säure/Base-Addukte. Stattdessen stehen die Lewis-Acidität und -Basizität solcher „frustrierten Lewis-Paare" (**FLP**s) gemeinsam für die Durchführung ungewöhnlicher Reaktionen, wie **H-H-, N-H-, C-H, CO_2, ... -Aktivierung** zur Verfügung.

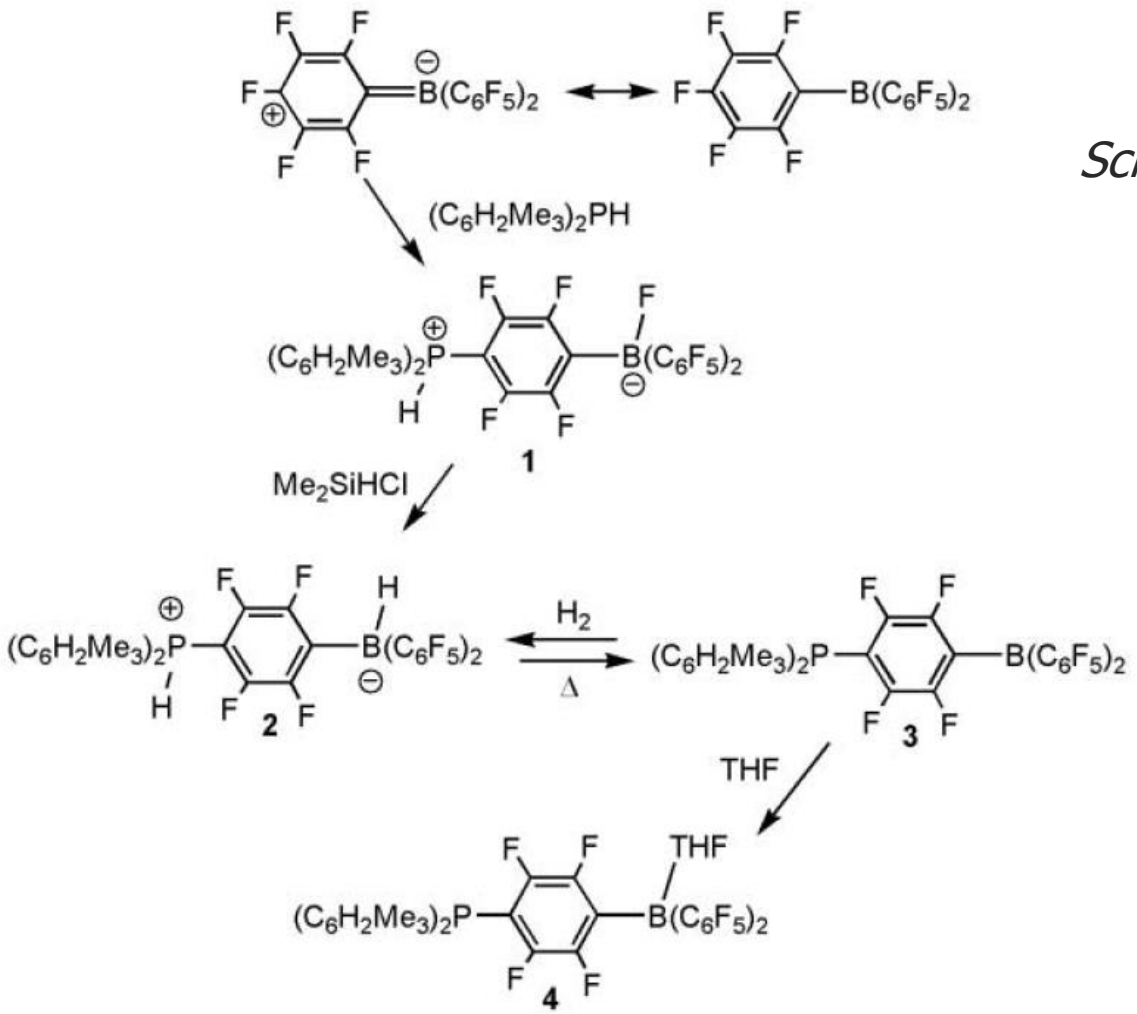




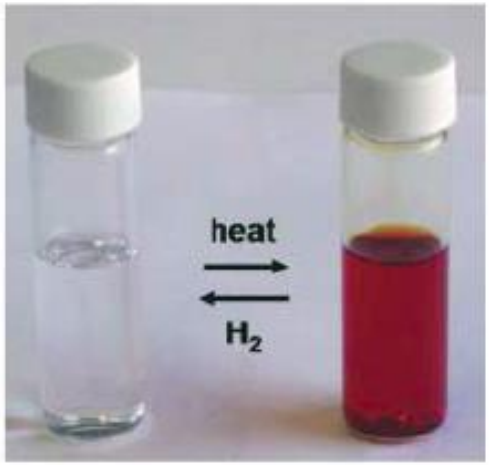


D. Stephan, G. Erker, *Angew. Chem.* Int. Ed. **2015**, *54*, 6400.

Highlights: H_2-Speicher ohne Metall



Science **2006**, *314*, 1124

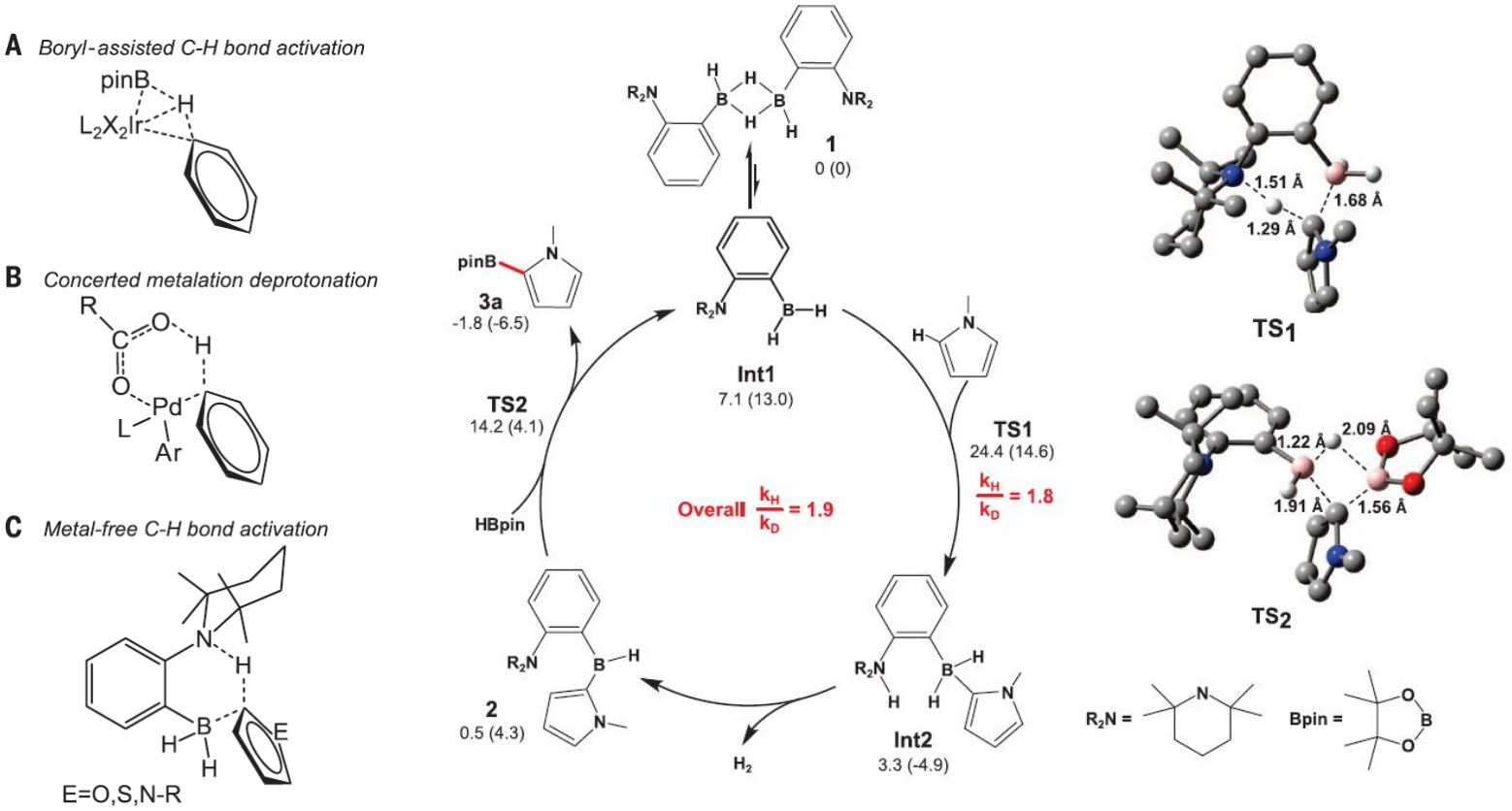


Highlights: Aktivierung kleiner Moleküle

- Aktivierung von CO_2, N_2O und SO_2

Highlights: Metallfreie *CH*-Aktivierung

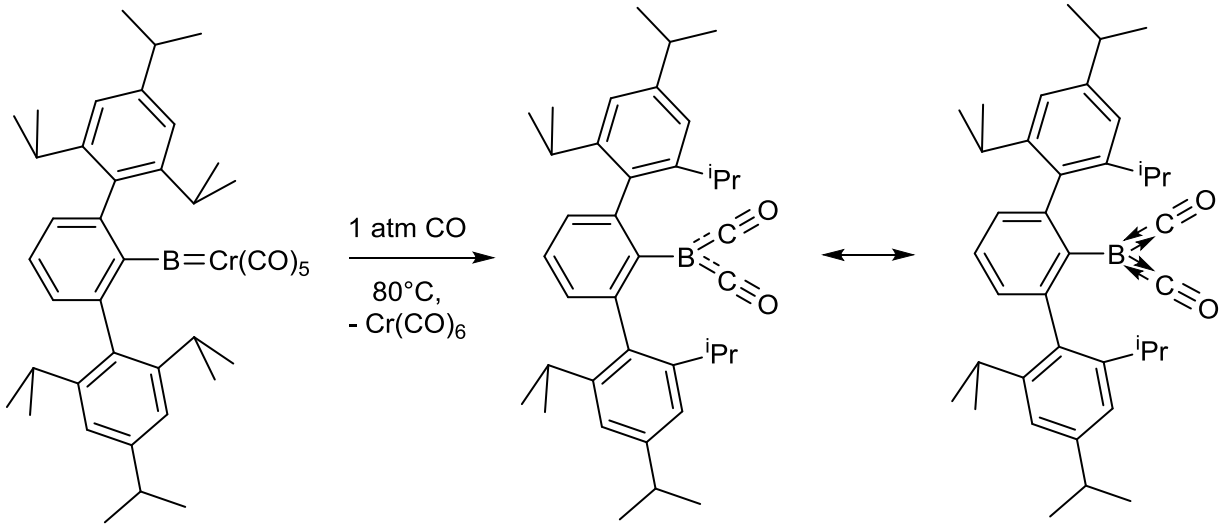
- Rationales Design eines B/N-FLP's zur CH-Aktivierung von C_{sp2}-H Bindungen (Fontaine et al.)



M.-A. Légaré, M.-A. Courtemanche, É. Rochette, F.-G. Fontaine, *Science* **2015**, *349*, 513.

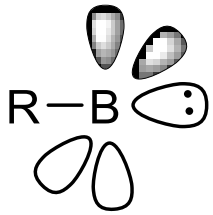
Highlights: CO-Komplexe

- Terminale Borylen-Komplexe $(CO)_5M{=}B\text{-}Tip$ als Quelle für hoch reaktives Borylen R-B → zeigt ÜM-ähnliches Verhalten



Gelb
$\delta(^{11}B)$ = 155 ppm

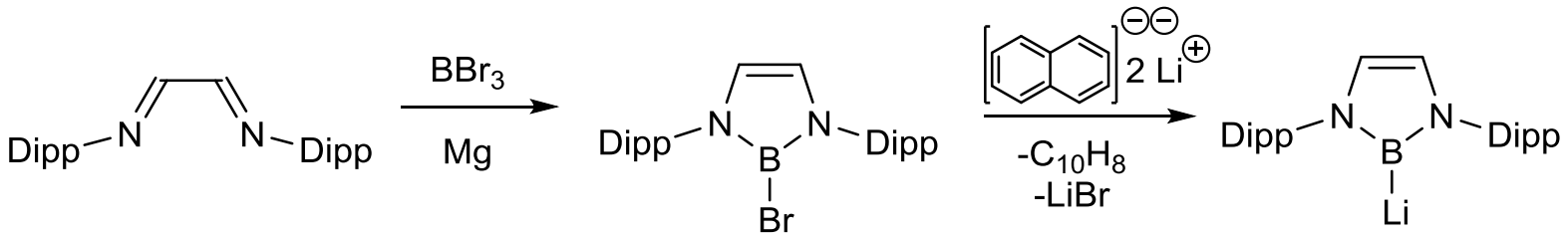
Blau
$\delta(^{11}B)$ = -32ppm
ν (IR) = 1942, 2060 cm^{-1}



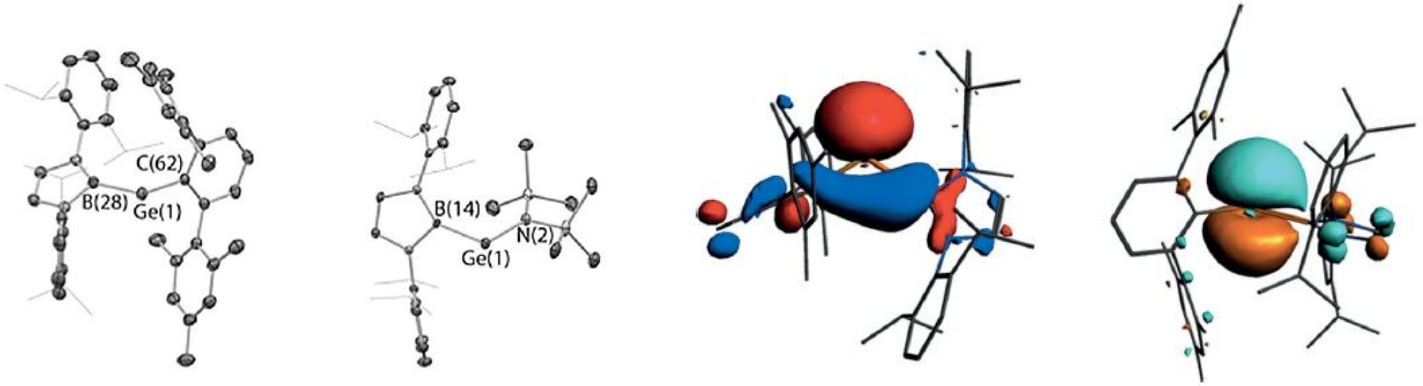
H. Braunschweig, R. D. Dewhurst, F. Hupp, M. Nutz, K. Radacki, C. W. Tate, A. Vargas, Q. Ye, *Nature* **2015**, *522*, 327.

Bor: Jetzt auch Nucleophil

- *N*-heterozyklische Boryl-Anionen (Yamashita et al.)



- Boryl-Lithium zur Stabilisierung niedervalenter Ge-Verbdg.

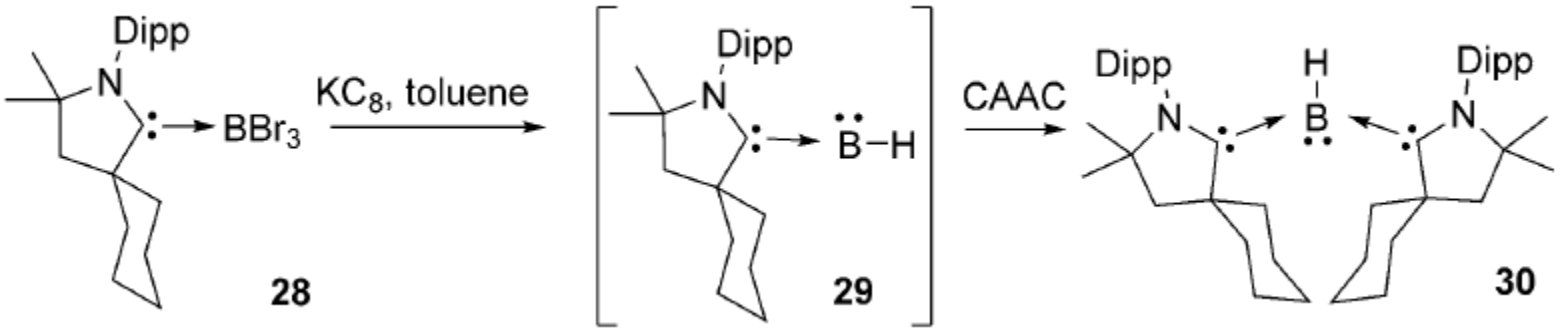


- Sind gute π-Akzeptor-Liganden → Tuning der HOMO-LUMO-Lücke

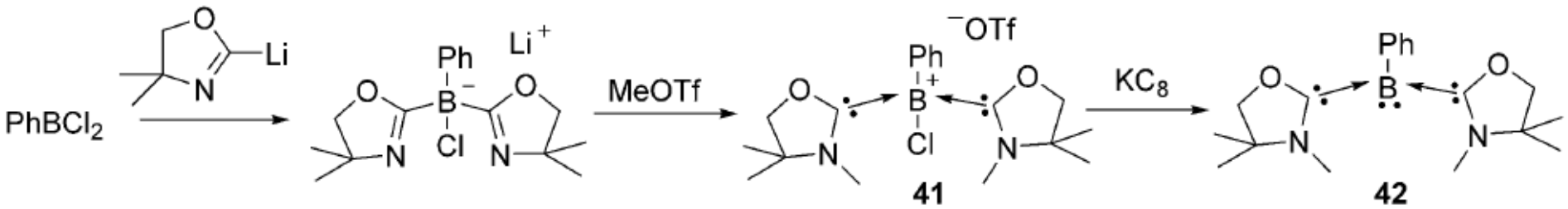
Y. Segawa, M. Yamashita, K. Nozaki, *Science* **2006**, *314*, 113

Bor: Jetzt auch Nucleophil

- Stufenweise Synthese eines Bis-Donor-Stabilisierten Borylenes



- Alternative Route konnte durch Kinjo et al. gezeigt werden



R. Kinjo, B. Donnadieu, M. A. Celik, G. Frenking, G. Bertrand, Science 2011, 333, 610; b) L. Kong, Y. Li, R. Ganguly, D. Vidovic, R. Kinjo, Angew. Chem. Int. Ed. 2014, 53, 9280.

Aluminiumorganyle

technisch wichtigste Organometallverbindungen

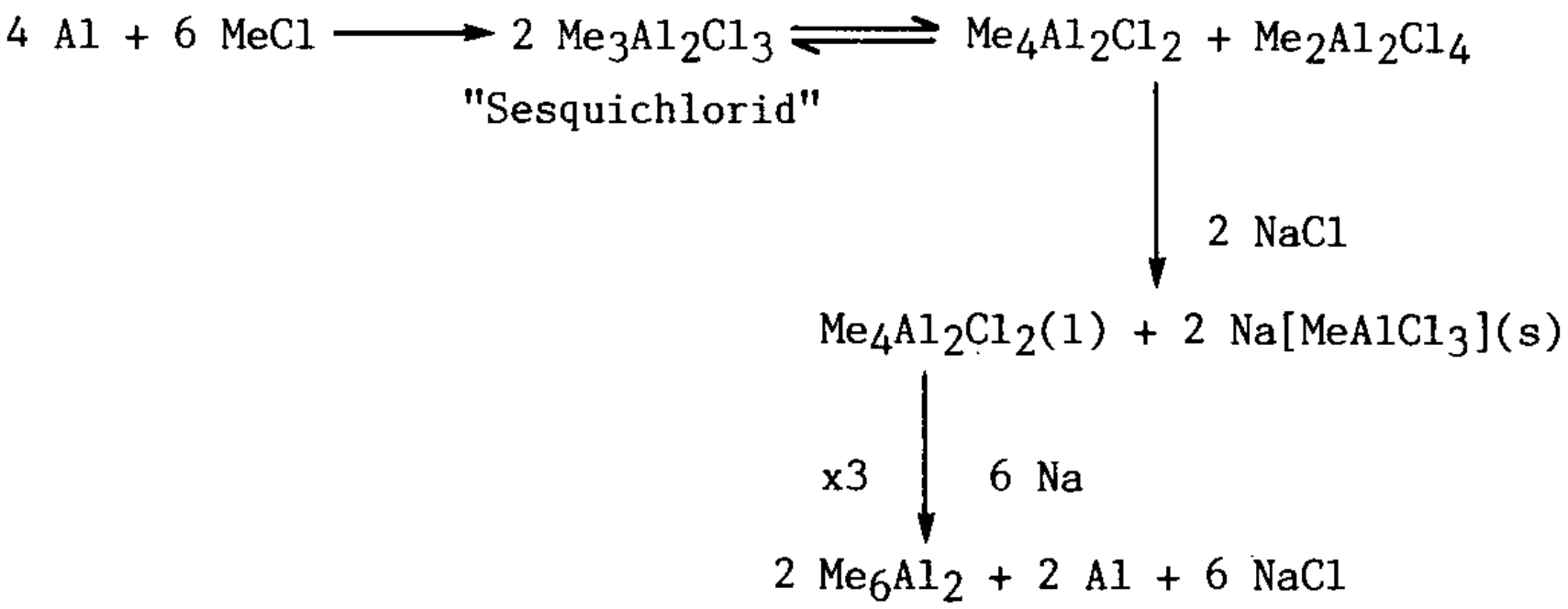
> 50000 t/a

WICHTIG: Ziegler-Natta Polymerisation 1952

- K. ZIEGLER, G. NATTA in den 50ern
- früher meist auf das Lösungsmittel Diethylether beschränkt
- addieren bereitwilligst an Alkene und Alkine
- Regio- und Stereoselektiv
- stellen Derivate des billigsten verfügbaren Metalls dar
- kostengünstige Alternative zu den Lithium- und Magnesiumalkylen

R_3Al // R_6Al_2 R_2AlH // $R_4Al_2H_2$ R = Me, Et

Technische Darstellung: $AlMe_3$



ehem. HÜLS AG, ehem. Neue Degussa, dann DEGUSSA jetzt **EVONIK**

Et_3Al Darstellung - Hydroaluminierung

$2\ Al + 3\ H_2 + 4\ Et_3Al \rightarrow 6\ Et_2AlH$

Vermehrung

$3\ Et_2AlH + 3\ H_2C{=}CH_2 \rightarrow 3\ Et_3Al$

Anlagerung

$2\ Al + 3\ H_2 + 6\ H_2C{=}CH_2 \rightarrow 2\ Et_3Al$ ***Summe***

ZIEGLER-Direktverfahren

Auch für andere Alkene $H_2C{=}CR_2$, $H_2C{=}C(H)R$

Darstellung

Direkt:

$$2\ Al + 6\ RX \longrightarrow 2\ Al_2R_3X_3$$

aber:

Metathese:

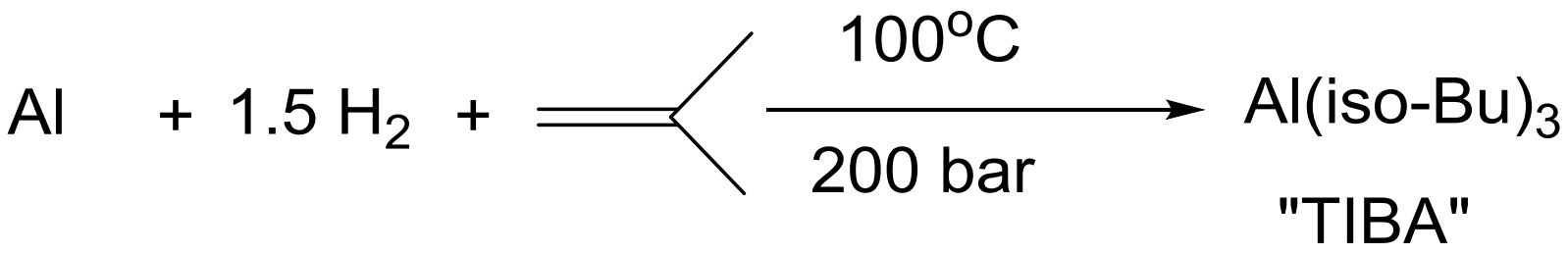
$$AlX_3 + 3\ R\text{-}Mg\text{-}X \xrightarrow{Et_2O} AlR_3{*}Et_2O + 3\ MgX_2$$

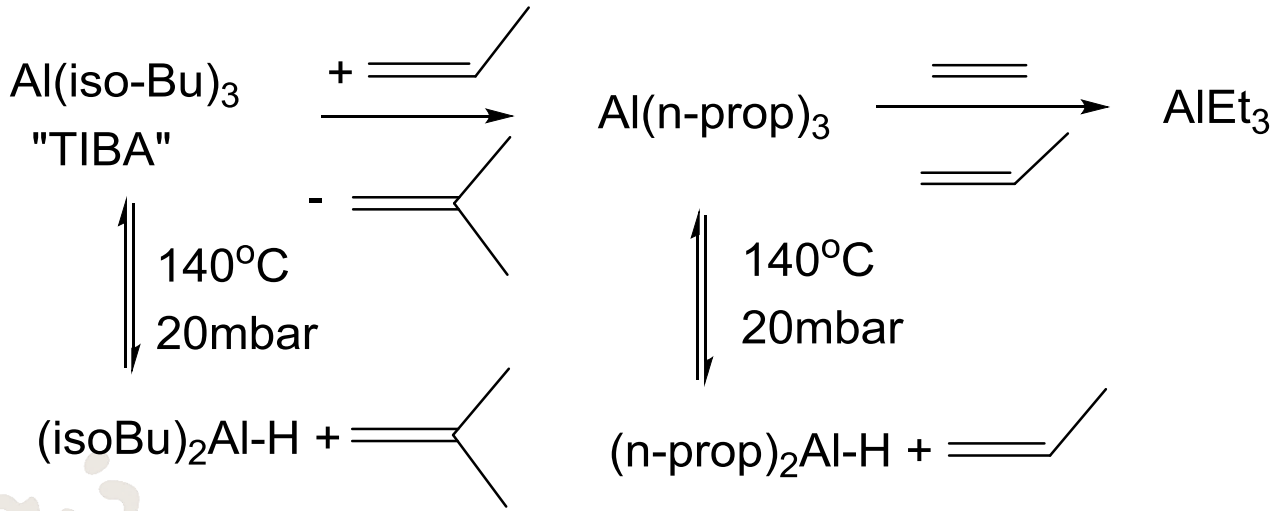
Adduktbildung

Transmetallierung:

$$2\ Al + 3\ HgR_2 \longrightarrow 2\ AlR_3 + 3\ Hg$$

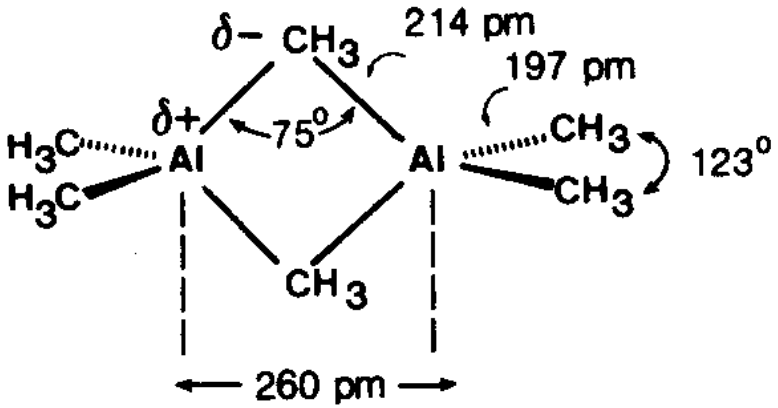
Darstellung



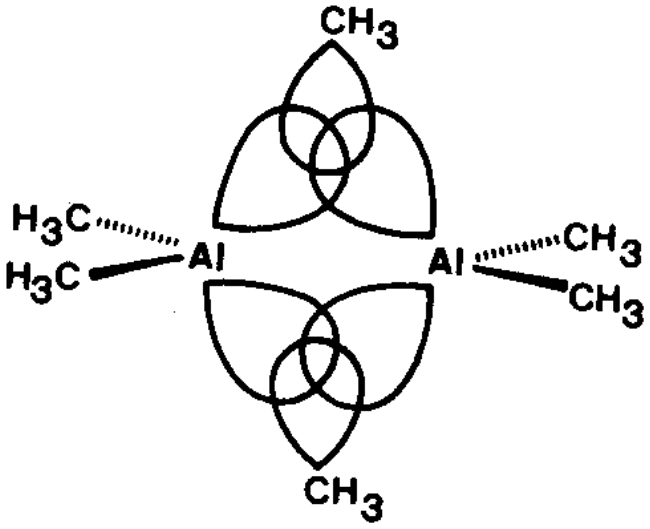


Bindung

Strukturparameter für $Al_2(CH_3)_6$



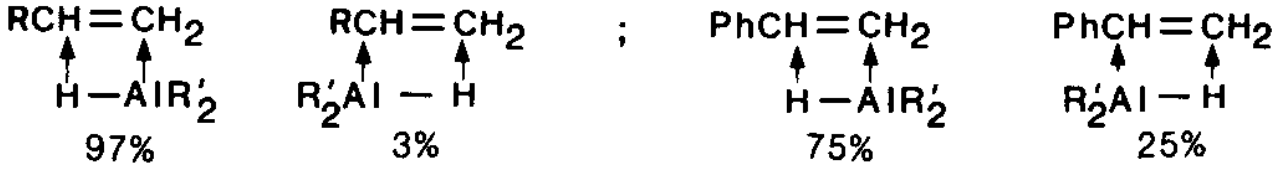
Al–C–Al (2e3c)Bindungen in $Al_2(CH_3)_6$



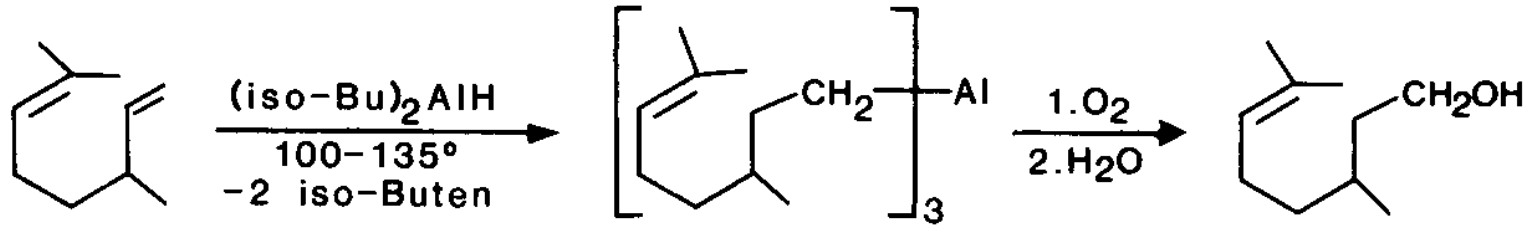
- Tendenz zur Dimerisierung
- große (sperrige) organische Reste wirken dem Entgegen (*i*-Bu_3Al)

Reaktivität

- **Hydroaluminierung**
  stereoselektiv, aber Regioselektivität variiert mit Rest R

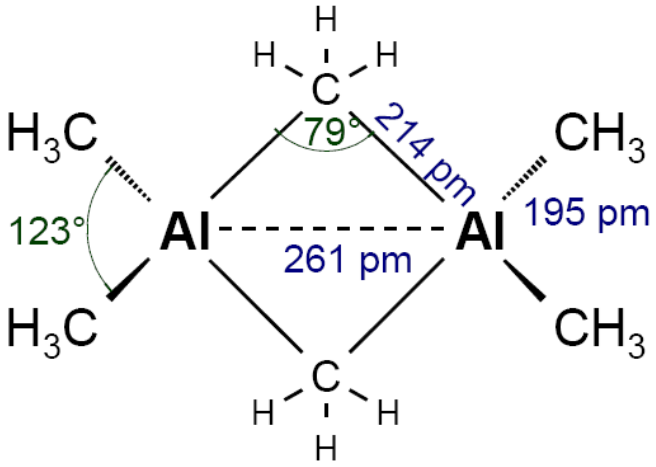


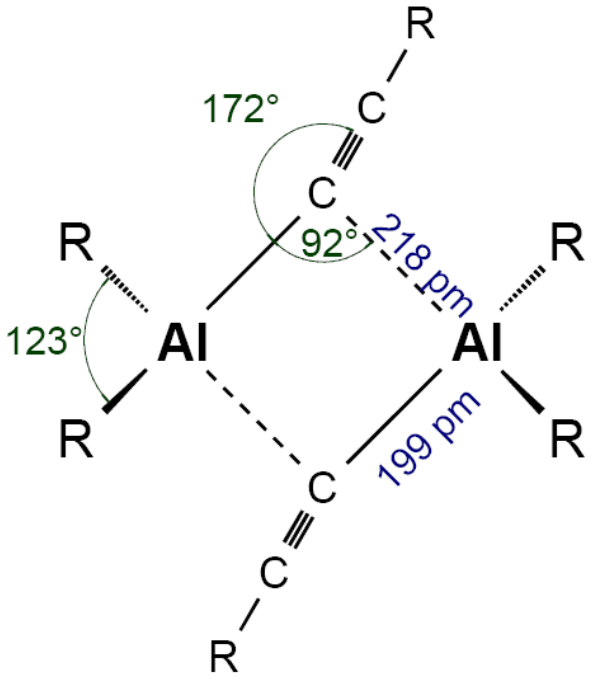
Anwendungsbeispiel:

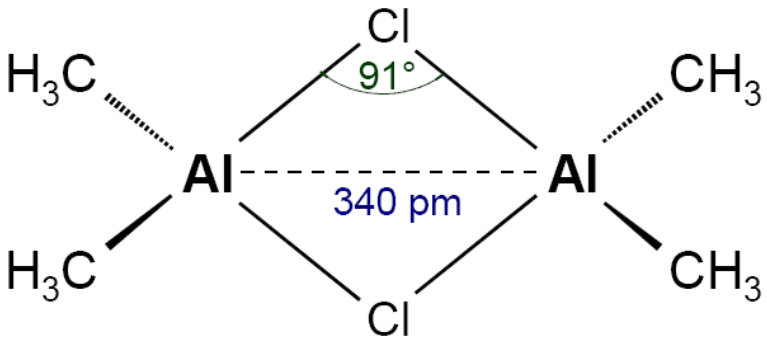


β-Citronellol

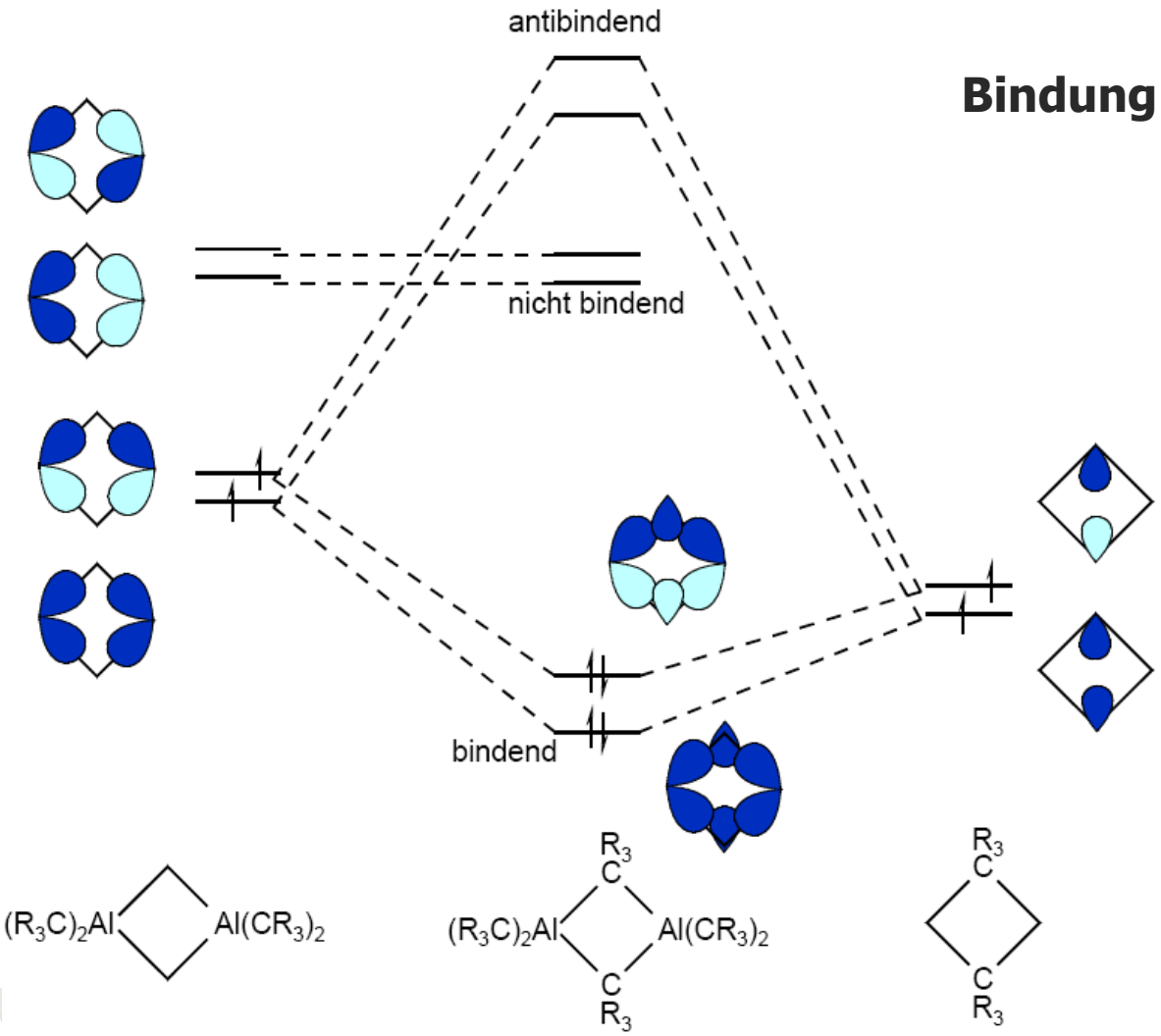
Struktur


H
H
H
C
79°
214 pm
H3C
CH3
123°
Al
261 pm
Al
195 pm
H3C
CH3
C
H
H
H


R
172°
C
C
92°
218 pm
R
R
123°
Al
Al
R
R
199 pm
C
R
C
C
R


Cl
91°
H3C
CH3
Al
Al
340 pm
H3C
CH3
Cl

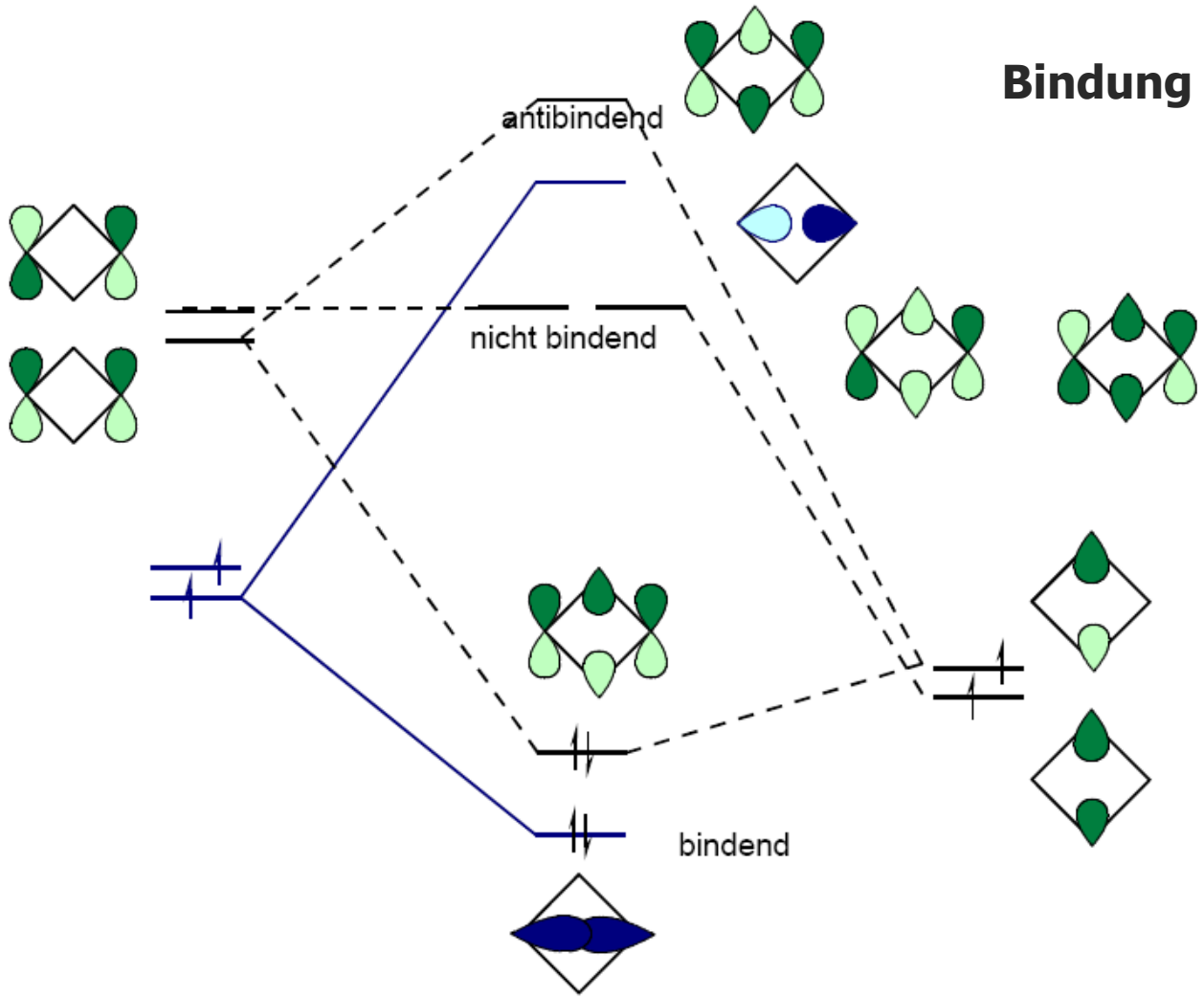
Modell 1: 2 x 2e-3c-Bindung



Bindung im $(Me_3Al)_2$

Modell 2: 1x 2e-2c und 1x 2e-4c Bindung

Bindung im $(Me_3Al)_2$



Eigenschaften

AlR_3 R=Me, Et, Butyl

farblose Flüssigkeiten !

extrem Pyrophor !!!!!
(nur mit speziellem Schutzanzug!)

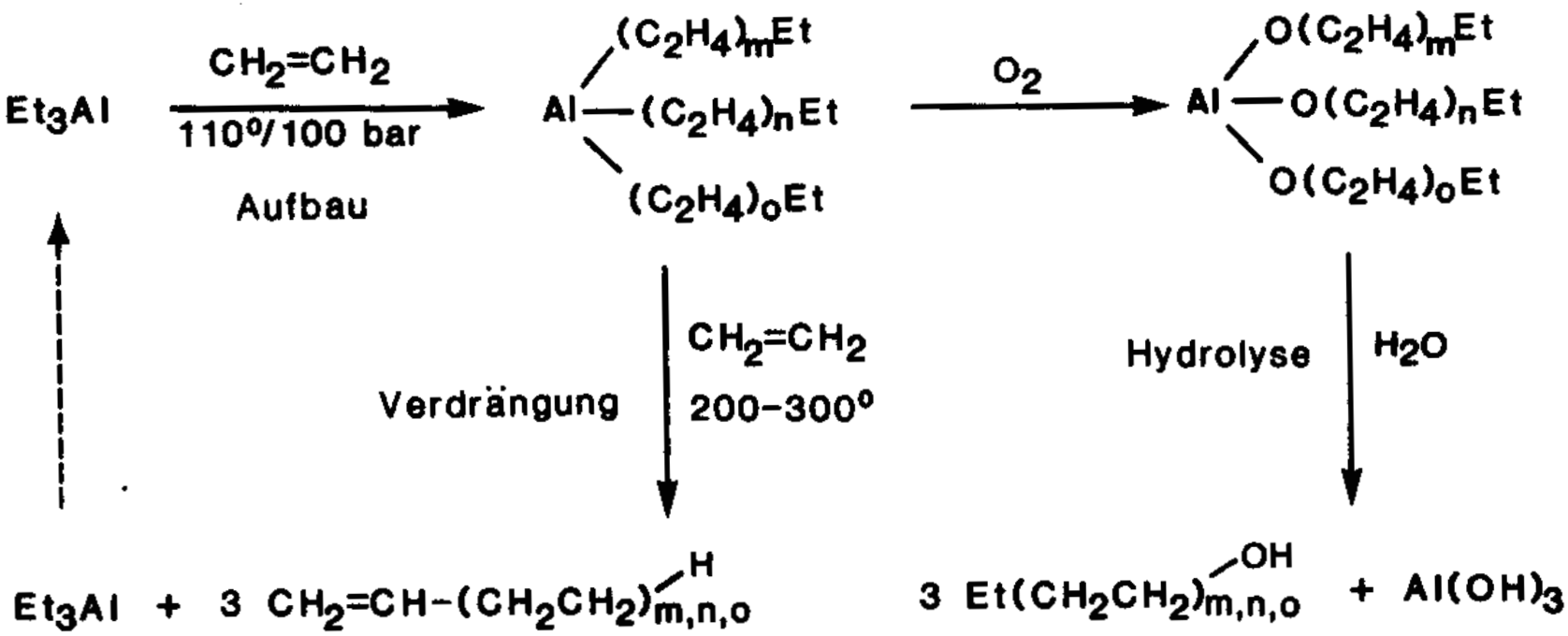
Starke Lewis-Säuren stabilisieren sich durch:

1) AlR_3 + Base $\longrightarrow$ R_3Al-B

2) b-Hydrideliminierung

3) Dimerenbildung

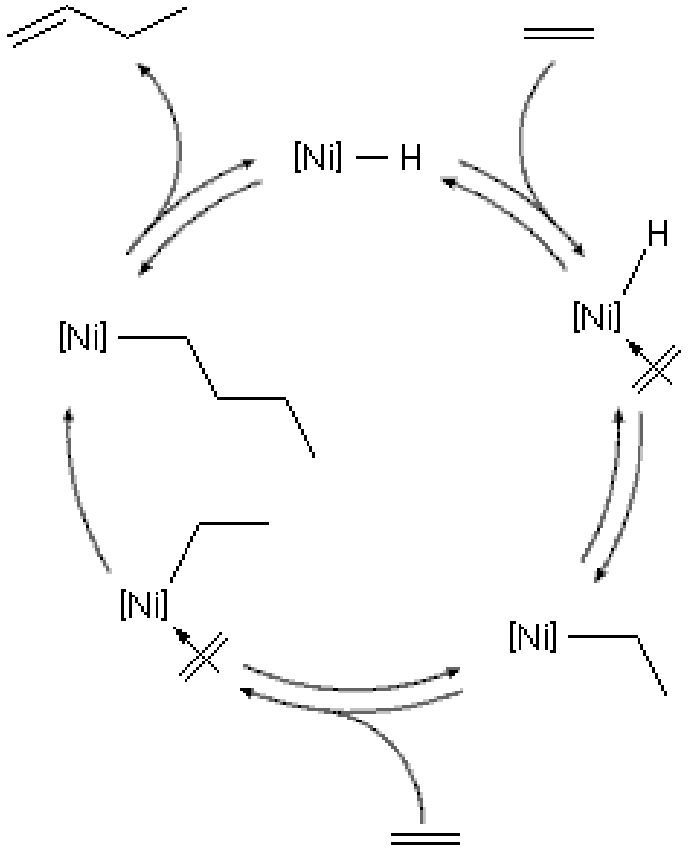
Al-Organyle: Technische Anwendungen



ZIEGLER - Aufbaureaktion

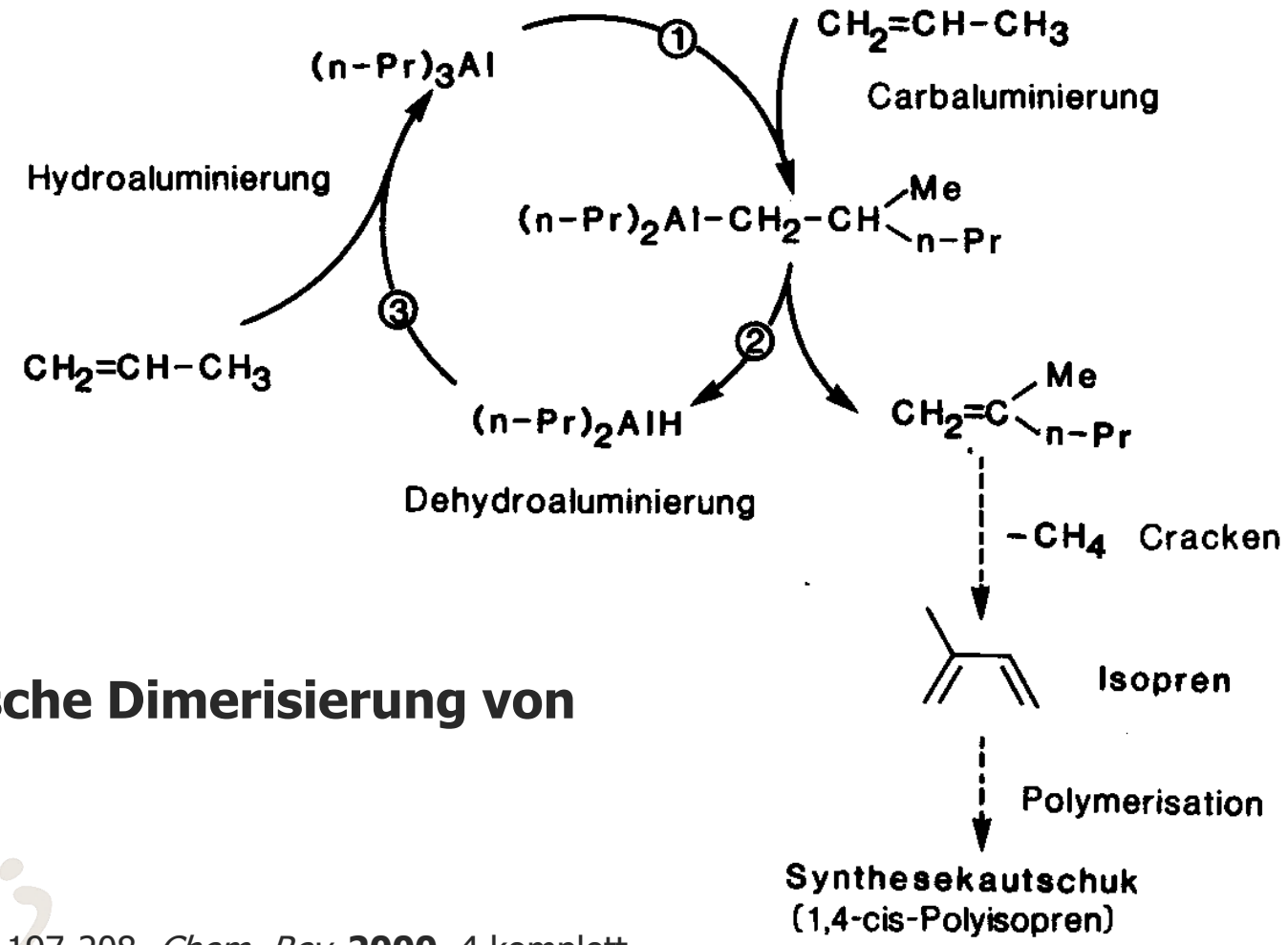
- Dient zum **Aufbau von 1-Alkenen** und **unverzweigten Alkoholen**
- letztere dienen zum **Aufbau von Fettsäuren**

Der Nickeleffekt



Bei Untersuchungen zur Aufbaureaktion (1953) mit Et_3Al hatten sich anstelle langkettiger Alkylaluminiumverbindungen nur Butene gebildet.

Katalytische Dimerisierung von Propylen

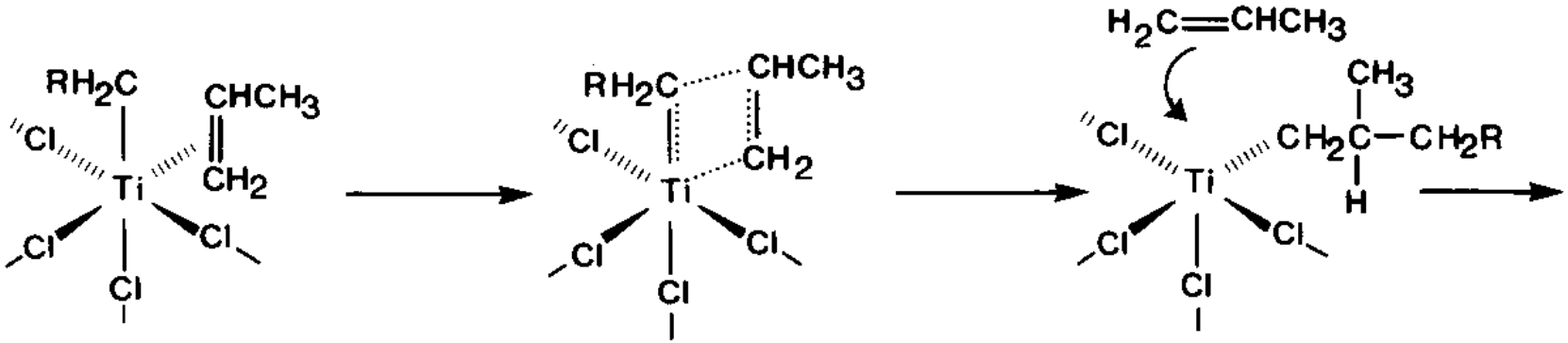


Katalytische Dimerisierung von Propen

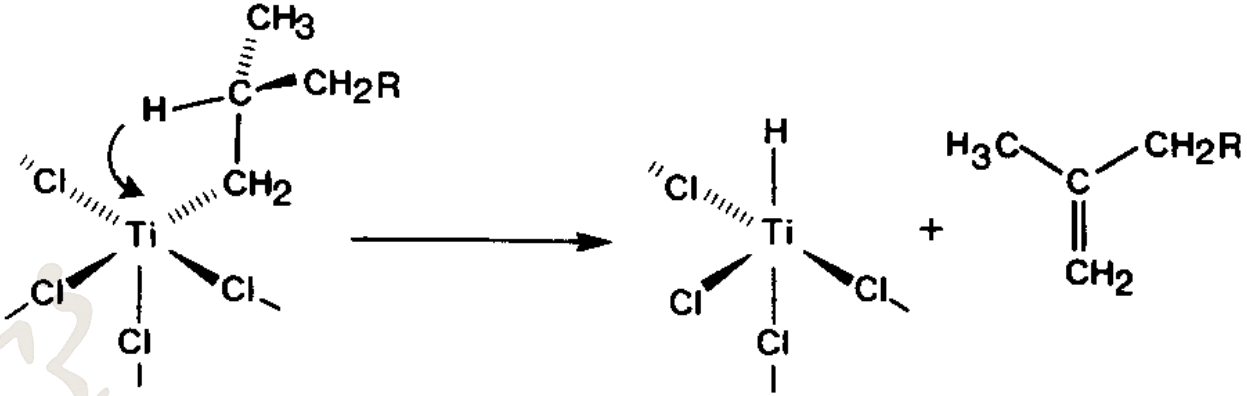
Literatur
CHIUZ **1994**, *28*, 197-208, *Chem. Rev.* **2000**, 4 komplett

Al-Organyle: Technische Anwendungen

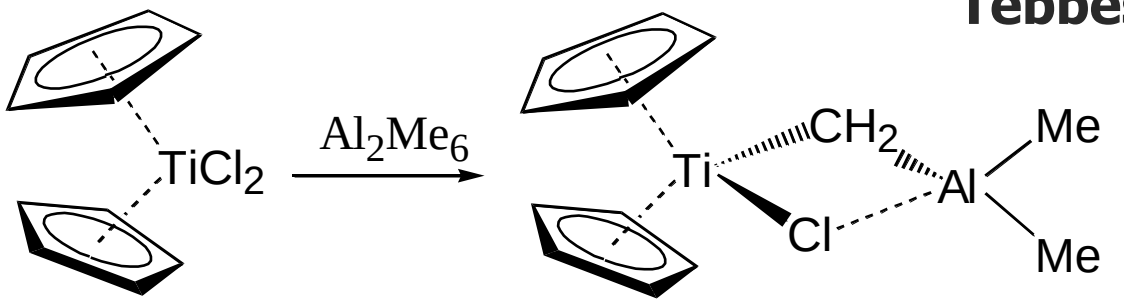
ZIEGLER-NATTA-Niederdruckverfahren mittels $Et_3Al/TiCl_4$

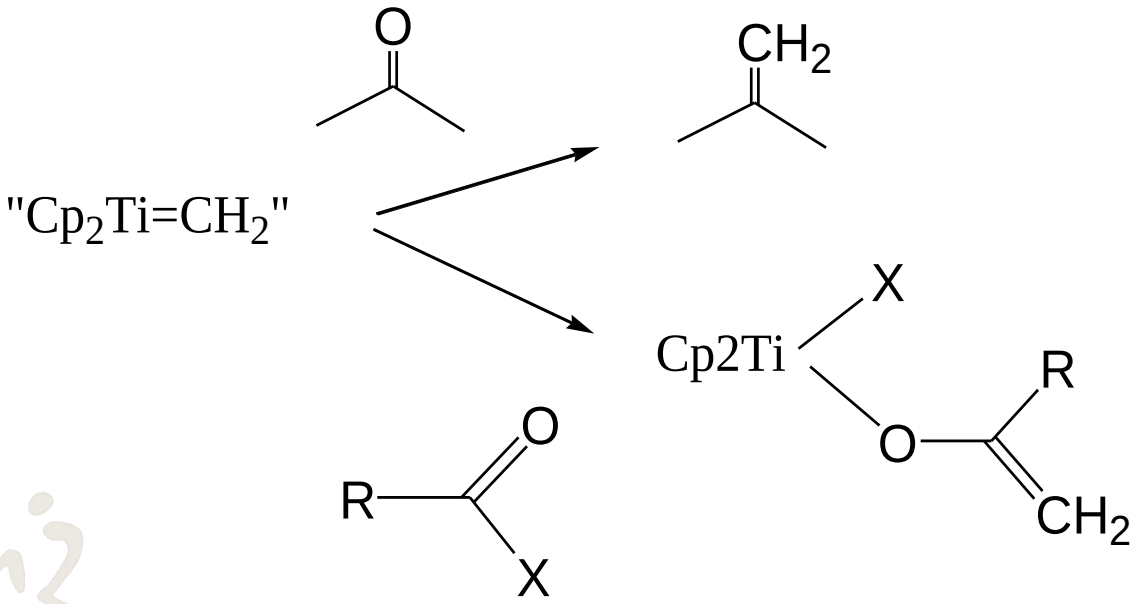


Kettenabbruch:



Tebbes Reagenz



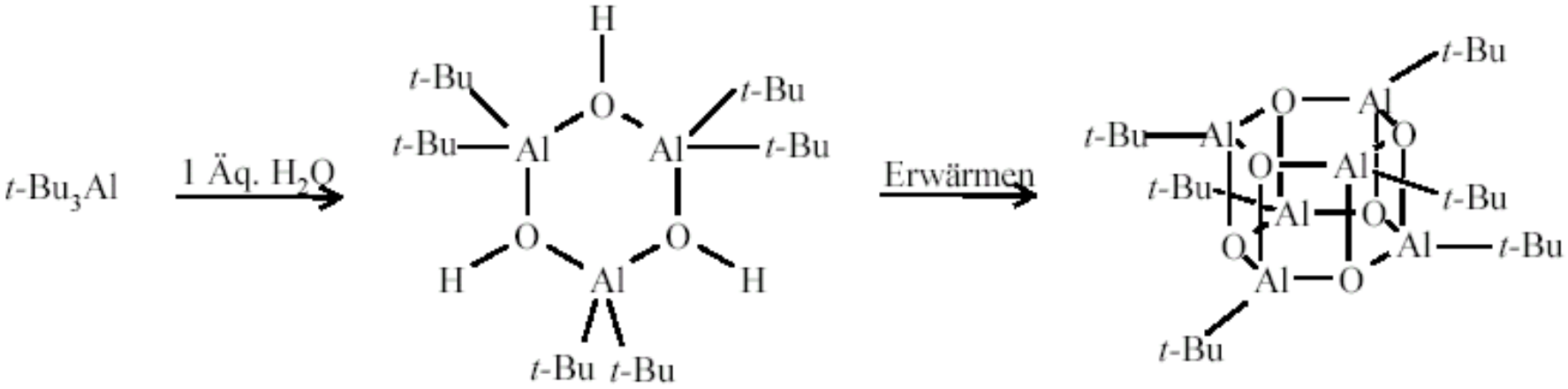


Anwendung: MAO

JACS **1993**, *115*, 4971

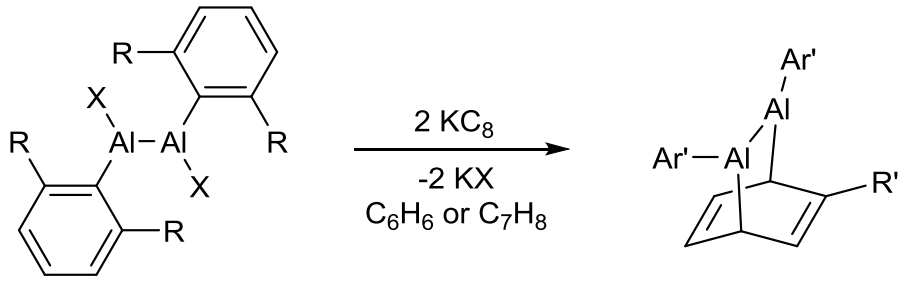
MAO
Methylalumoxan

$$Al_2Me_6 + H_2O \longrightarrow [MeAlO]_x$$



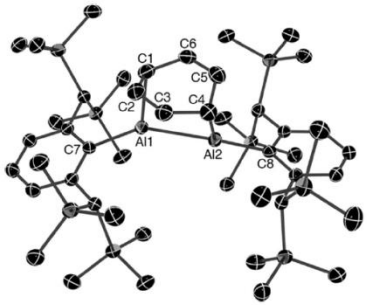
Moderne Alumiumorganyle

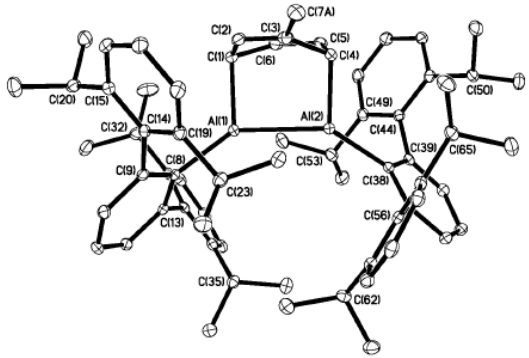
- Bereits 2002 erste „Synthone" für Diallumene, formal Al=Al Doppelbindung → trans-bent Struktur
- Stabilisierung über [4+2]-Cycloadditionen mit LM



R = $CH(SiMe_3)_2$ (Bbp), X=Br
R = 2,6-$^{i}Pr_2C_6H_3$ ($Ar^{\#}$), X=I

Ar' = Bbp (R=H), $Ar^{\#}$ (R=Me)

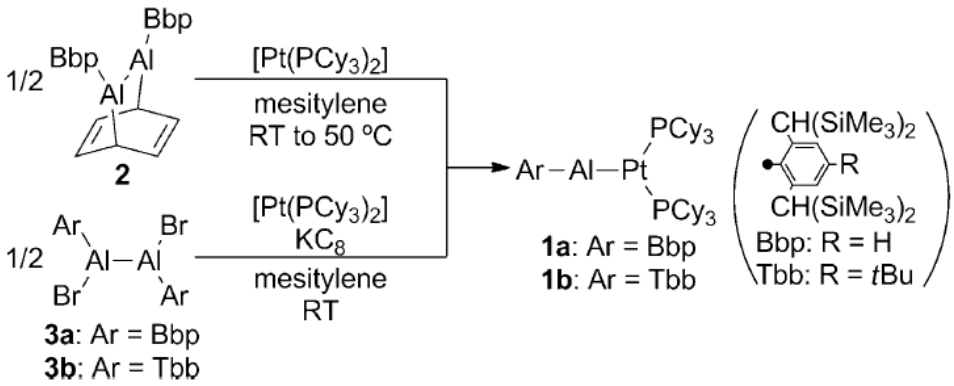


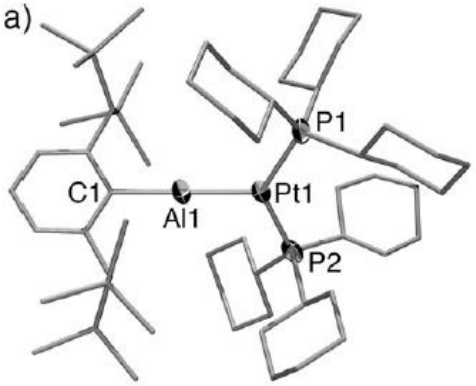


a) Wright, A. D. Phillips, P. P. Power, *J. Am. Chem. Soc.* **2003**, *125*, 10784; b) T. Agou, K. Nagata, N. Tokitoh, *Angew. Chem. Int. Ed.* **2013**, *52*, 10818.

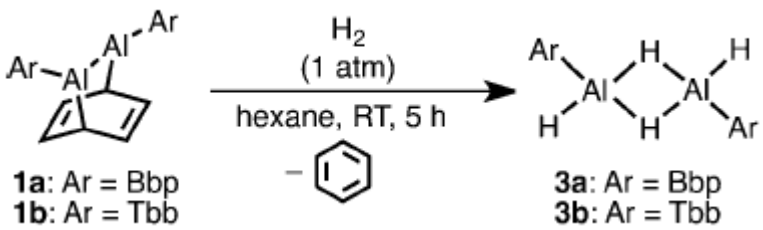
Moderne Alumiumorganyle

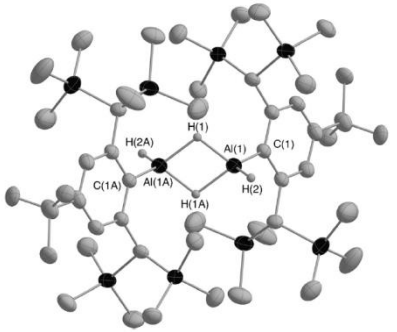
- $(Bbp)_2Al_2(C_6H_6)$ als Synthon für freies R-Al, Alumene





- Diallumene für die Aktivierung kleiner Moleküle

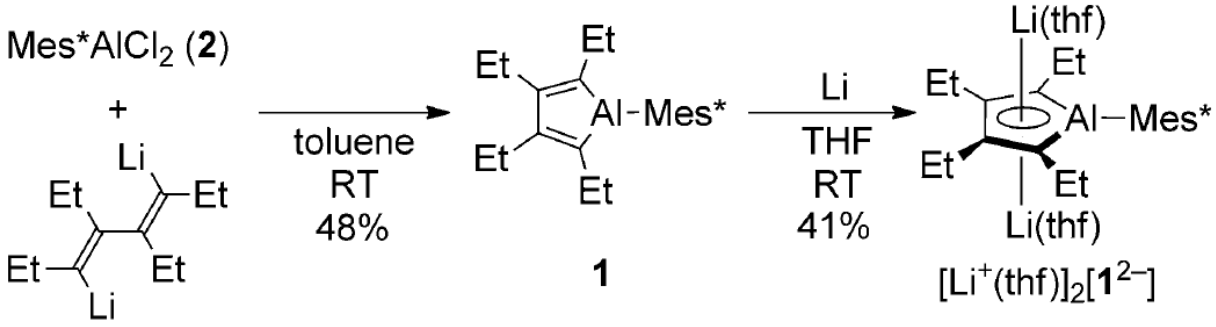


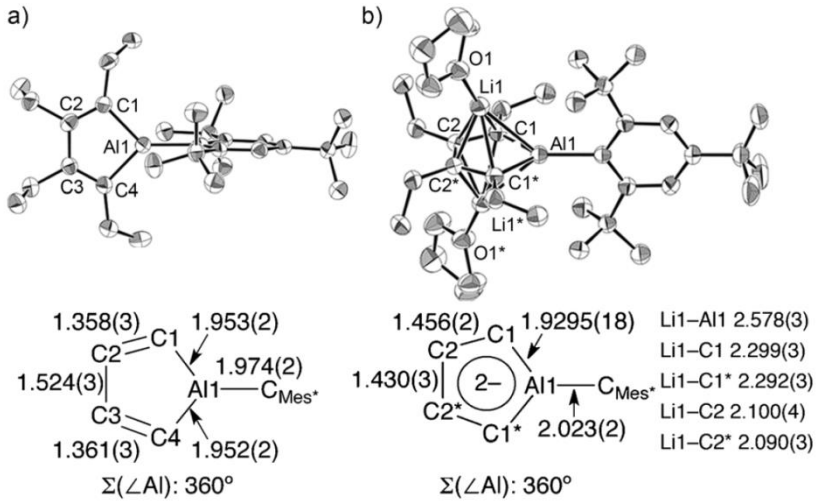


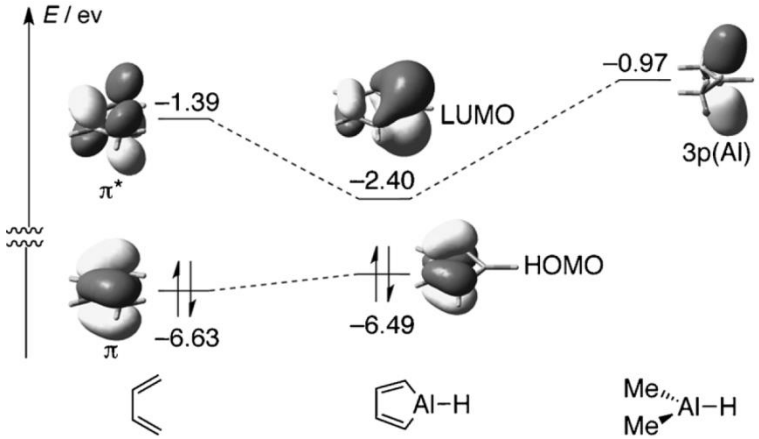
a) K. Nagata, T. Agou, N. Tokitoh, *Angew. Chem. Int. Ed.* **2014**, *53,* 3881; b) K. Nagata, T. Murosaki, T. Sasamori, T. Agou, N. Tokitoh, *Angew. Chem. Int. Ed.* **2016**, *55*, 12877.

Moderne Alumiumorganyle

- 5-gliederige Heterocyclen mit Aluminium → Alumole

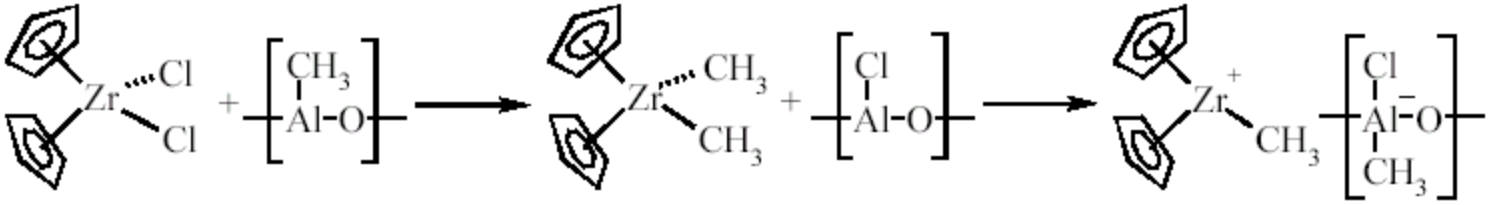






T. Agou, T. Wasano, P. Jin, S. Nagase N. Tokitoh, *Angew. Chem. Int. Ed.* **2013**, *53*, 10031.

Anwendung: MAO



Vergleich:

$$Cp_2ZrCl_2 \underset{}{\overset{Al_2Me_6}{\rightleftharpoons}} \boxed{Cp_2ZrClMe} \underset{}{\overset{Al_2Me_6}{\rightleftharpoons}} Cp_2ZrMe_2$$

Indium-, Gallium- und Thalliumorganyle: Allgemeines

Oxidationsstufen:

Ga, In, Tl

+III: ns^0p^6

+II: ns^1p^0

+I: ns^2p^0

Oxidationsstufe +III

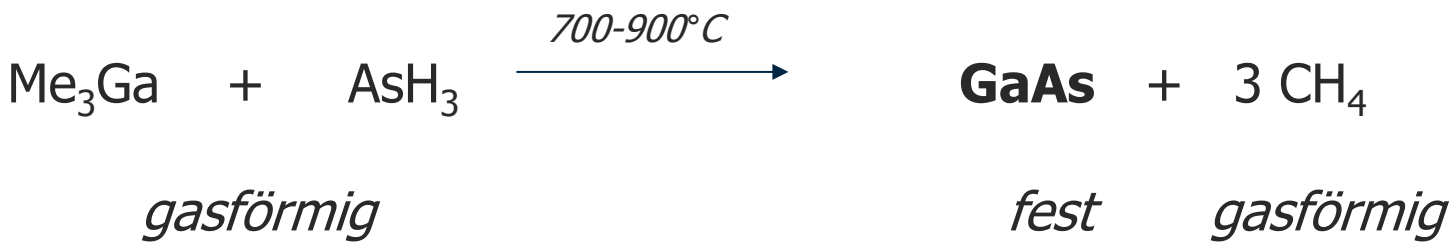
Synthese:

Metathese:

$$MX_3 + LiMe \longrightarrow MMe_3 + 3\,LiX \quad M=Ga, In, Tl$$

Indium-, Gallium- und Thalliumorganyle: Allgemeines

- Sind deutlich weniger von Bedeutung als die B- und Al-Organyle
- Ga/In-Organyle dienen als Dotierungsreagenzien in der **Halbleiter-industrie**



- Tl-Organyle finden trotz ihrer Toxizität Anwendung in der Synthese
- *Ga(III)* und *In(III)* dominieren in der Chemie
- bei Thallium die Tl(I)-Spezies
- im Gegensatz zu B und Al **kaum noch Dimeren/Brückenbildung** daraus resultiert eine noch höhere Ox.-empfindlichkeit
- Stabilisierung erfolgt im Normalfall durch **Komplexbildung**

Eigenschaften

MR_3 (Ga, In , Tl) stark Lewis-Sauer!!

- Säure-Base Addukte

$$MR_3 + \text{Base} \longrightarrow R_3M\text{-Base}$$

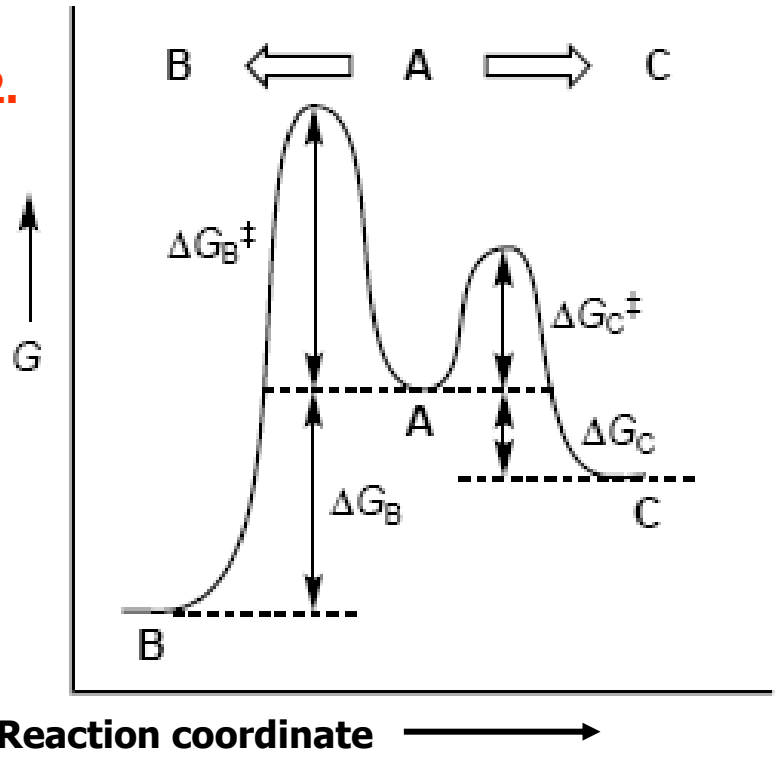
- Metallate

$$MX_3 + 4\ LiR \longrightarrow LiMR_4 + 3\ LiX$$

Dynamische („Kovalente") Chemie

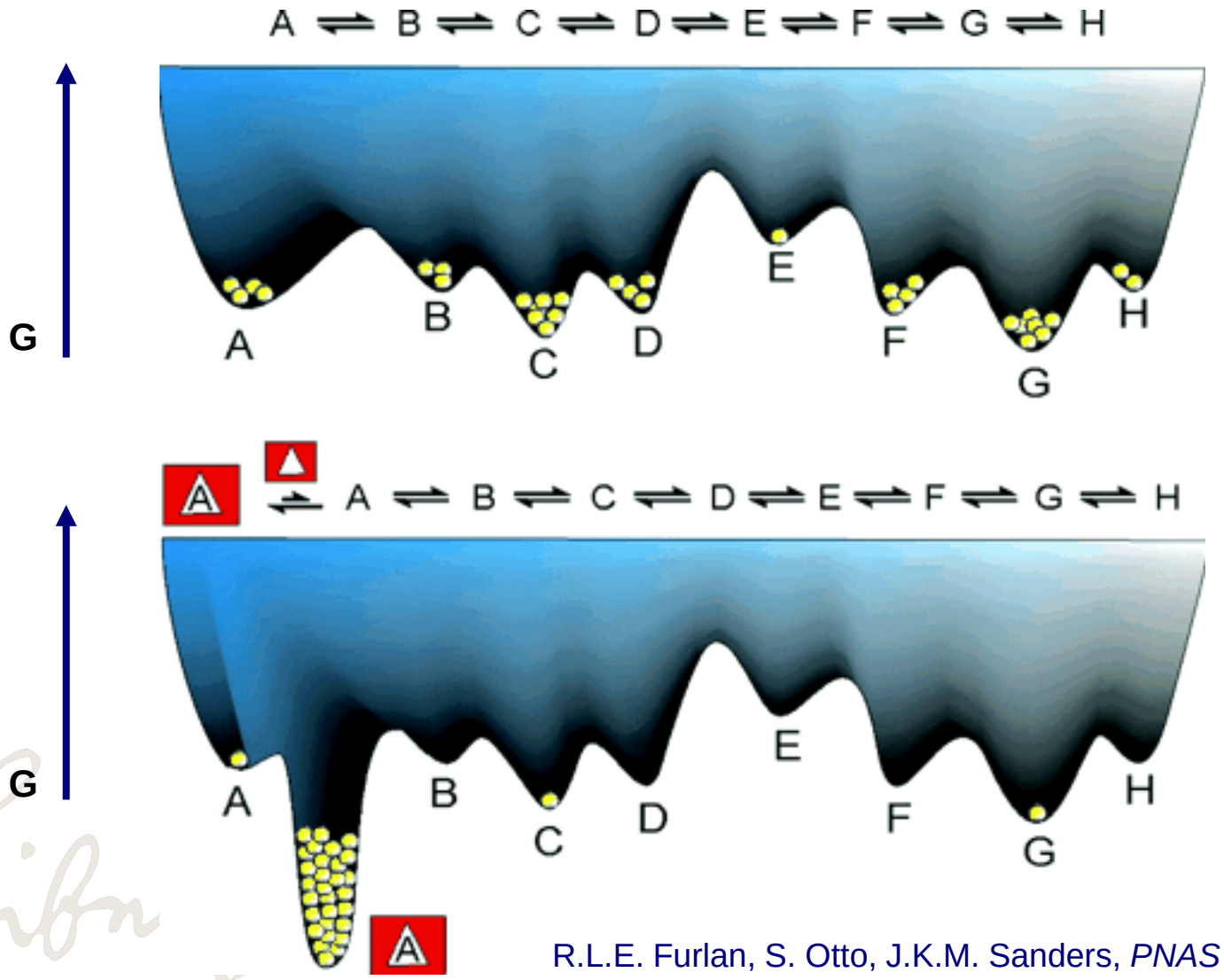
S.J. Rowan, S.J. Cantrill, G.R.L. Cousins, J.K.M. Sanders, J.F. Stoddart,
***Angew. Chem. Int. Ed.* 2002, *41*, 898-952.**

Dynamic Chemistry



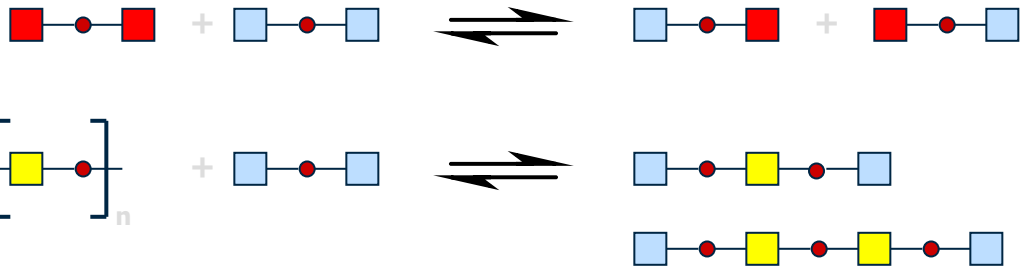
Free energy profile illustrating kinetic (A-C) versus thermodynamic (A-B) control of product distribution. Most covalent chemistry is irreversible and so occurs under kinetic control while most supramolecular and dynamic chemistry is reversible and so occurs under thermodynamic control.

Dynamische („Kovalente“) Chemie



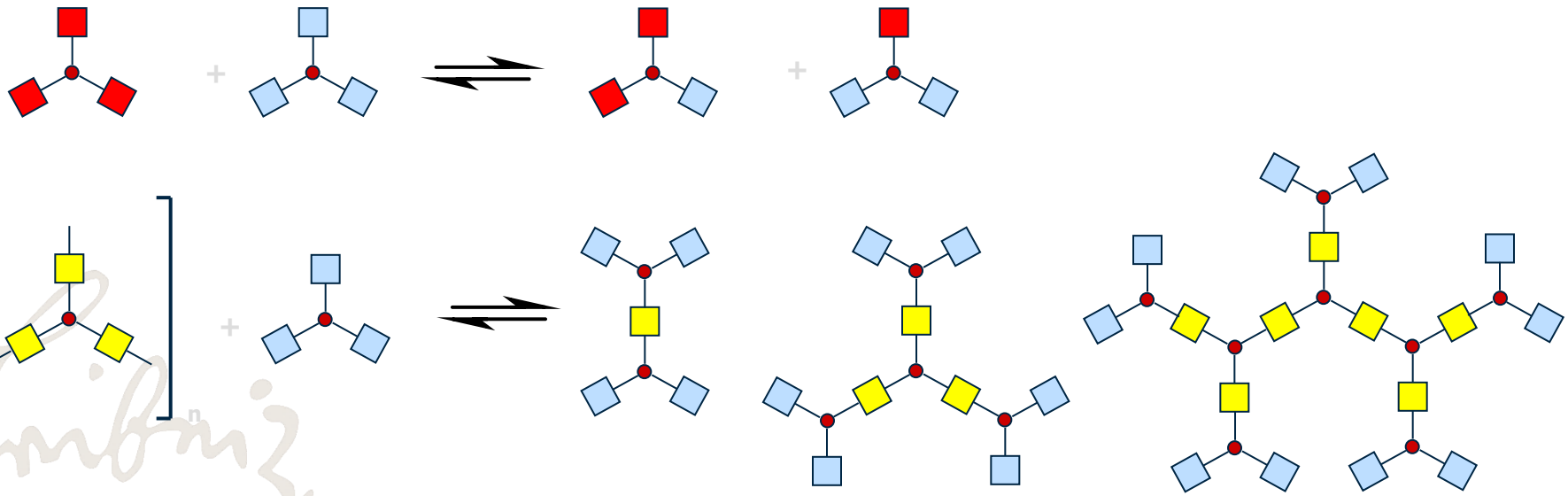
R.L.E. Furlan, S. Otto, J.K.M. Sanders, *PNAS 2002*, *99*, 4801

Dynamische kovalente Organometallchemie



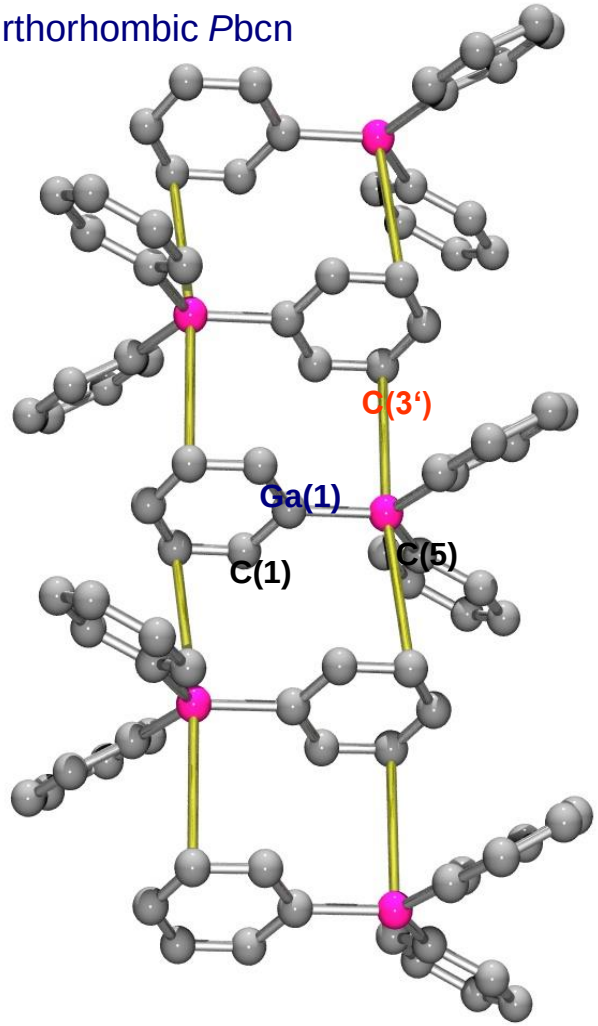
$MR_2 + MR^*_2 \rightleftharpoons 2\ MRR^*$ M: Mg; Zn; Hg

$3\ MR_2R^* \rightleftharpoons 2\ MR_3 + MR^*_3$ M: Al; Ga; In



Festkörperstruktur Ph_3In

Orthorhombic *P*bcn

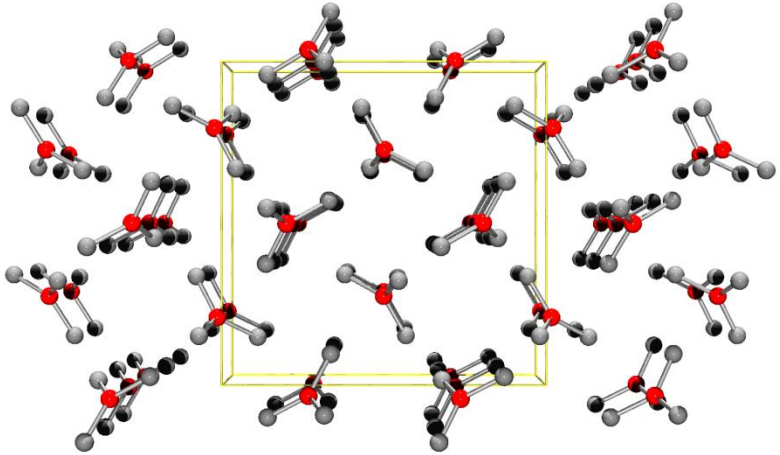


Selected distances [Å]:
Ga(1)-C(1): 1.95
Ga(1)-C(5): 1.97
Ga(1)-C(3’): 3.42

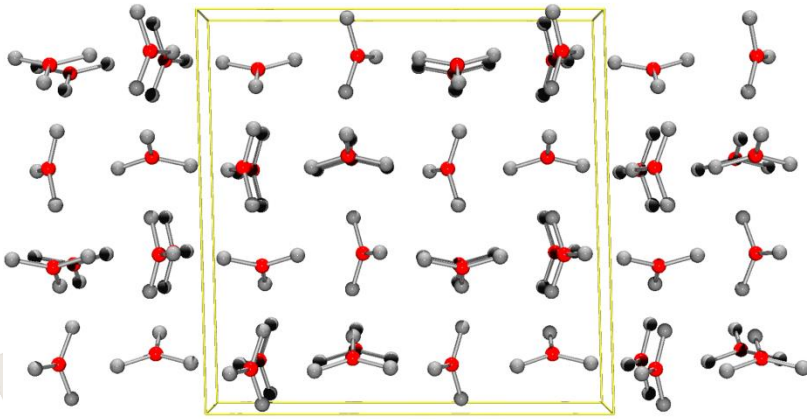
Sum of angles [°]:
at Ga(1): 360

J.F. Malone, W.S. McDonald, *J. Chem. Soc. A* **1970**, 3362.

Festkörperstruktur Me_3Ga

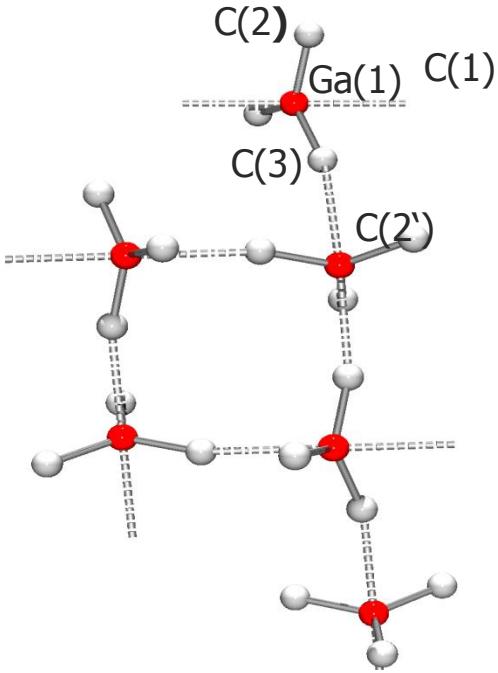


N.W. Mitzel, *Angew. Chem*. **2002**, *114*, 2629.



Monoclinic *C*2/c

R. Boese, *Organometallics* **2003**, *22*, 2450.



Selected distances [Å]:

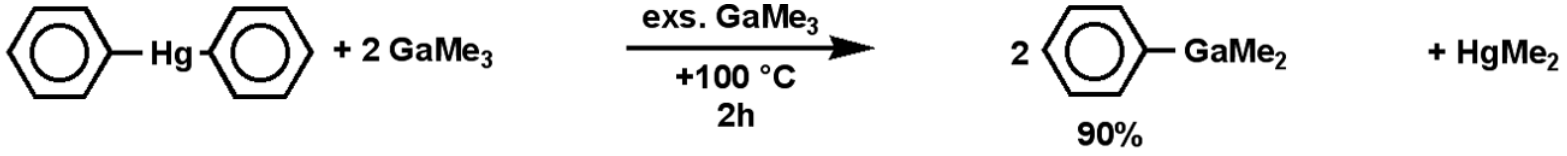
Ga(1)-C(1): 1.96

Ga(1)-C(2'): 3.09 - 3.51

Sum of angles [°]:

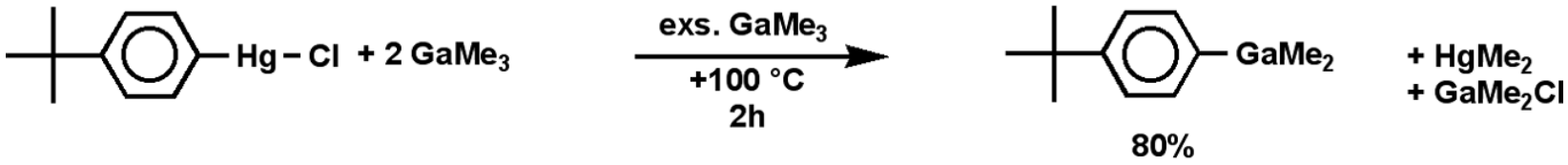
At Ga(1): 360

Synthesis of Methyl(phenyl)gallium Compounds



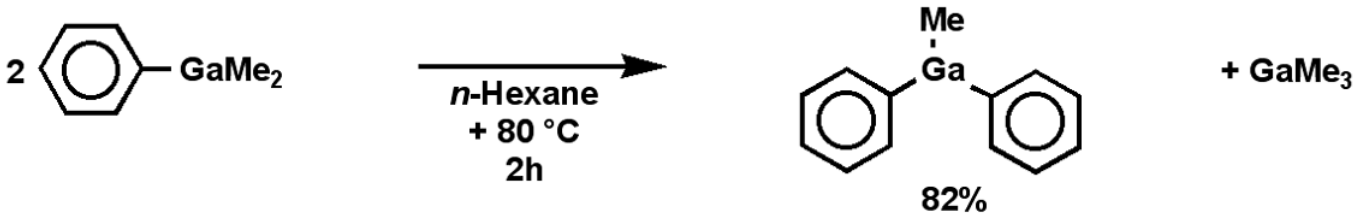
Suspension at RT → Solution → Colourless Crystals at RT

Trimethylgallium as solvent !



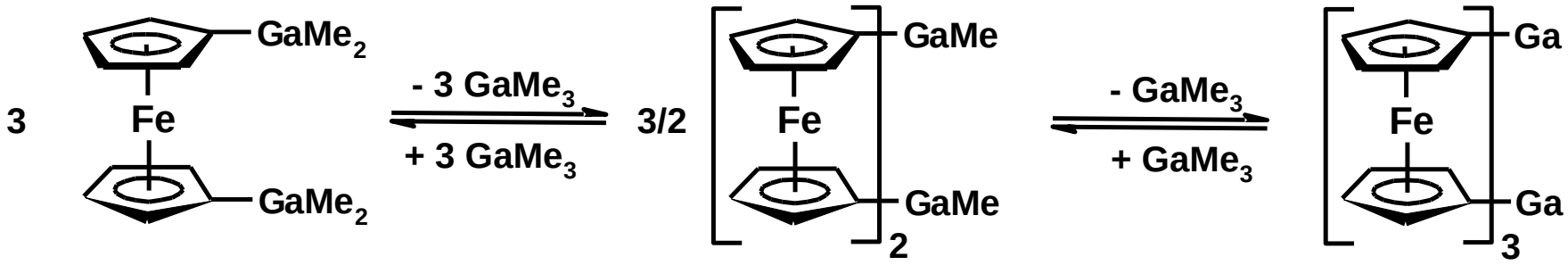
Suspension at RT → Solution → Colourless Crystals at + 40°C

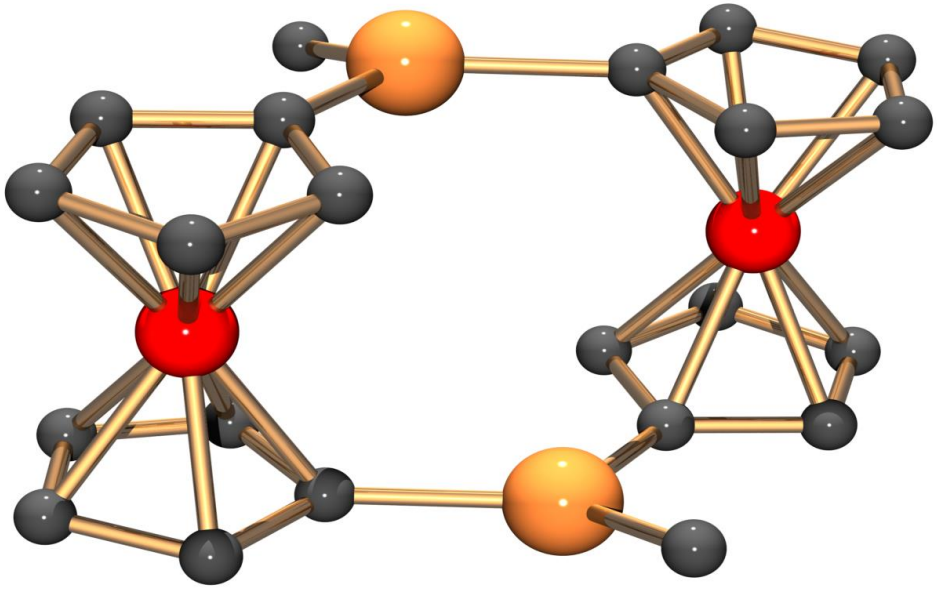
Trimethylgallium as solvent !



Suspension at RT → Solution → Colourless Crystals at -20°C

Catalysis LIKAT Leibniz-Institut für Katalyse e.V.





Selected distances [Å]:

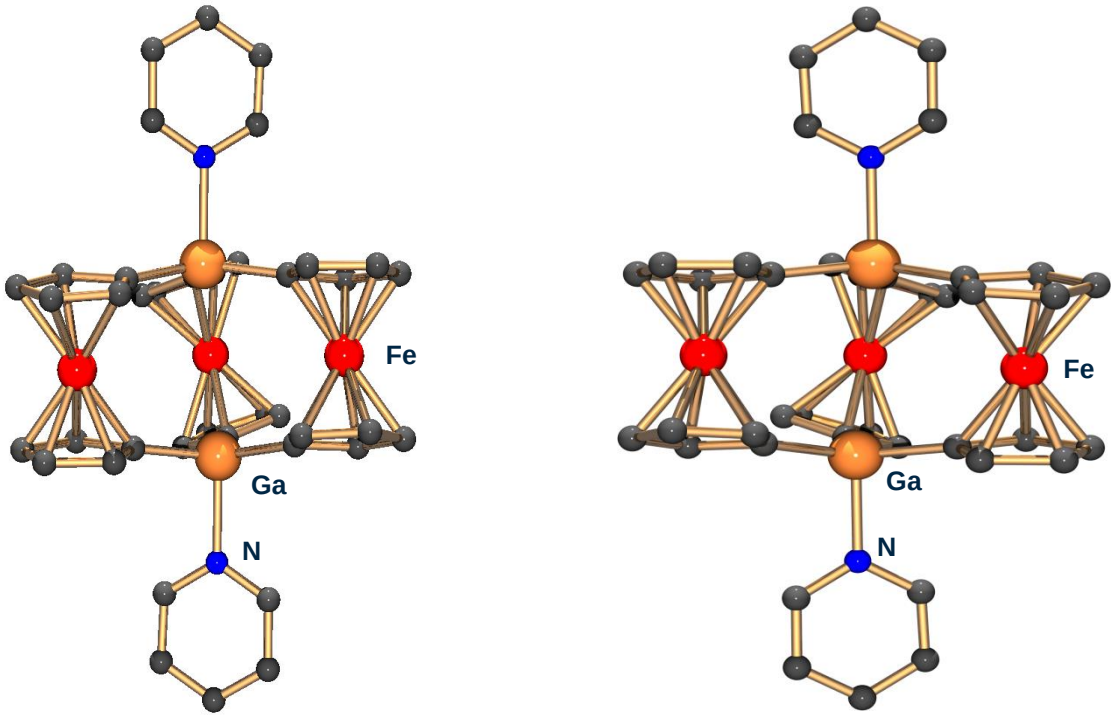
Ga-Ga:	4.41
Fe-Fe:	5.45
Ga-C(Cp):	1.96
Ga-C(Me):	1.94

Sum of angles [°]:

Σ Ga:	359

P. Jutzi, N. Lenze, B. Neumann, H.G. Stammler, *Angew. Chem. Int. Ed. Engl.* **2001**, *40*, 1424.
A. Althoff, P. Jutzi, N. Lenze *et al., Organometallics* **2003**, 22, 2766.

Ein molekulares Karussel



Distances [Å]:

Ga-Ga:	3.87
Fe-Fe:	5.46
Ga-C:	2.14
Ga-N:	2.14

Sum of angles [°]:

Σ Ga:	355

P. Jutzi, N. Lenze, B. Neumann, H.G. Stammler, *Angew. Chem. Int. Ed.* **2001**, *40*, 1424.