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

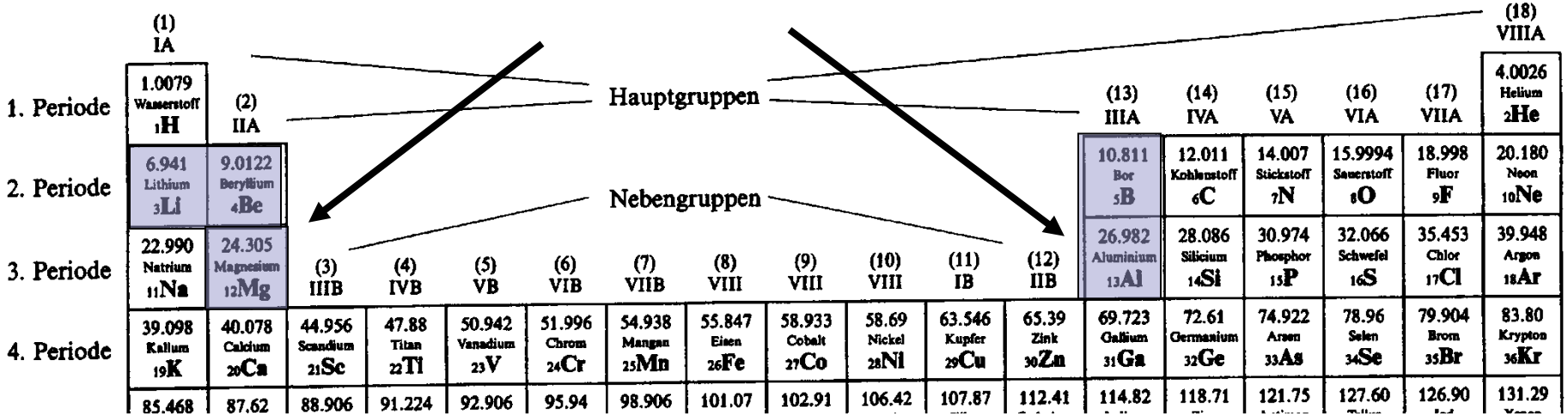
B	**C**
2.0	2.55
Al	
1.6	
Ga	
1.8	
In	
1.8	
Tl	
1.6	

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

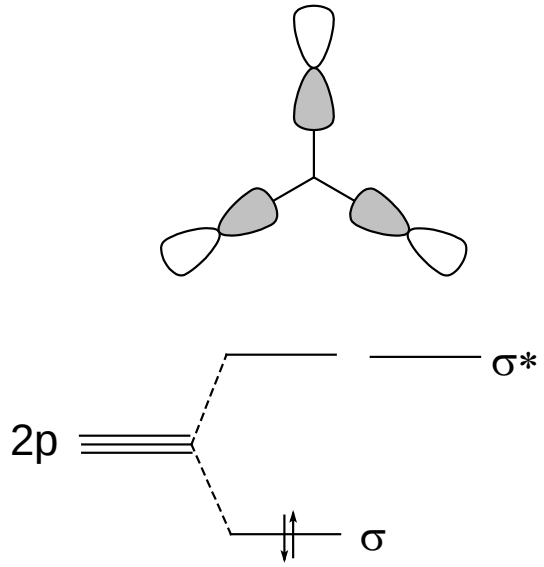
- Es besteht eine enge Verknüpfung zur Chemie der Borhydride

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

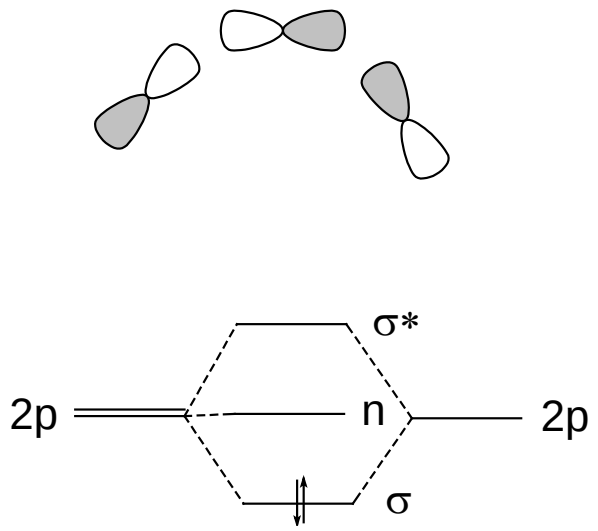
- Aluminiumorganyle dienen als Carbanionenüberträger (unschlagbar billig) und spielen eine Schlüsselrolle in großtechnischen Verfahren

Bindungsverhältnisse

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



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

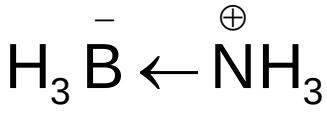


offene 3-Zentren-2-Elektronenbindung
C_{2v}-Symmetrie

Zum Vergleich: Bor-Stickstoff-Verbindungen

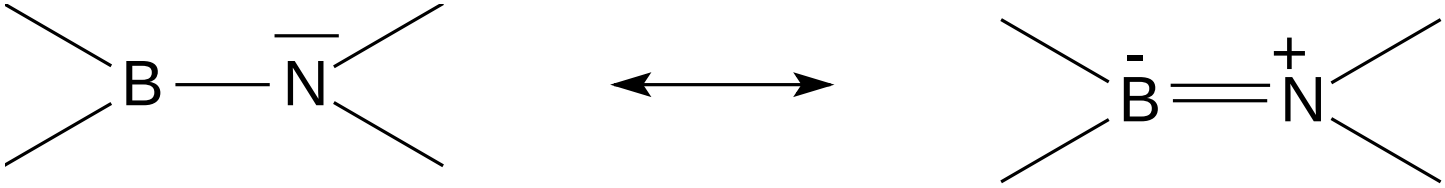
Bor-Amin-Addukte: Lewis-Säure verbunden mit Lewis-Base

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



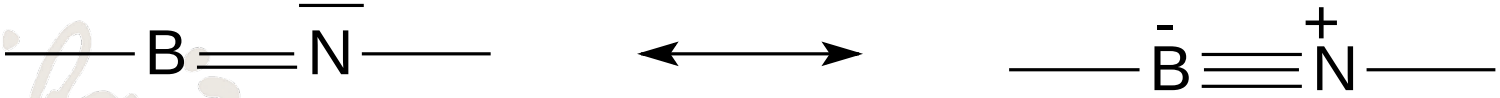
$H_3C\text{-}CH_3$
(d_{CC} = 154 pm, d_{BN} = 167 pm)

Aminoborane:



$H_2C{=}CH_2$

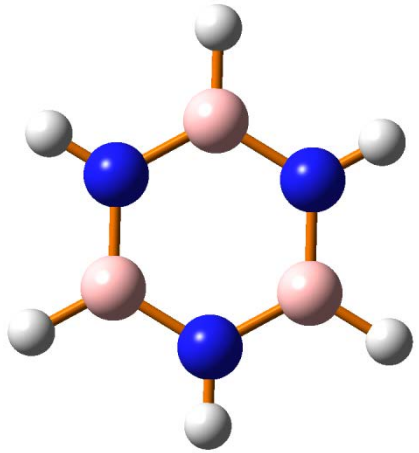
Iminoborane:



Borazol (Borazin)

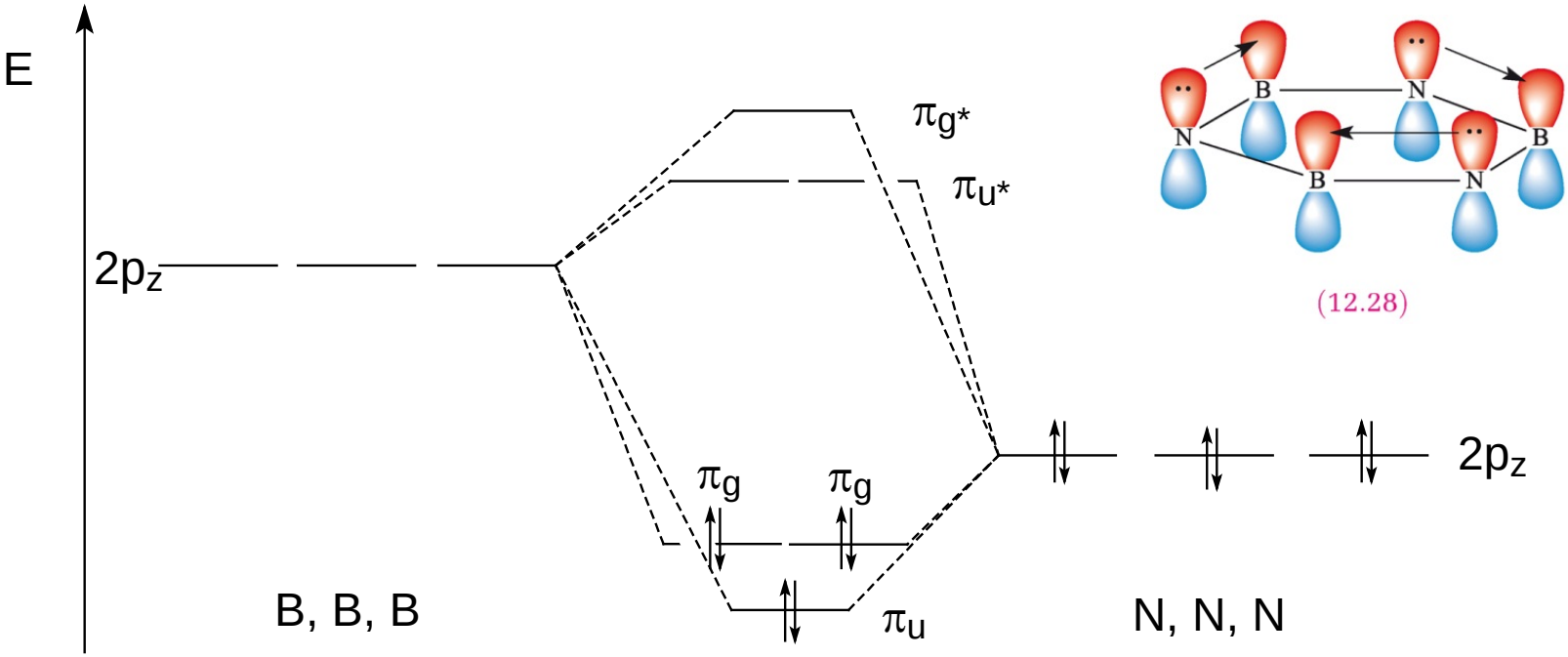
HB=NH ist unbeständig und oligomerisiert zum cyclischen $(HBNH)_3$

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



- 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 $B(OH)_3$

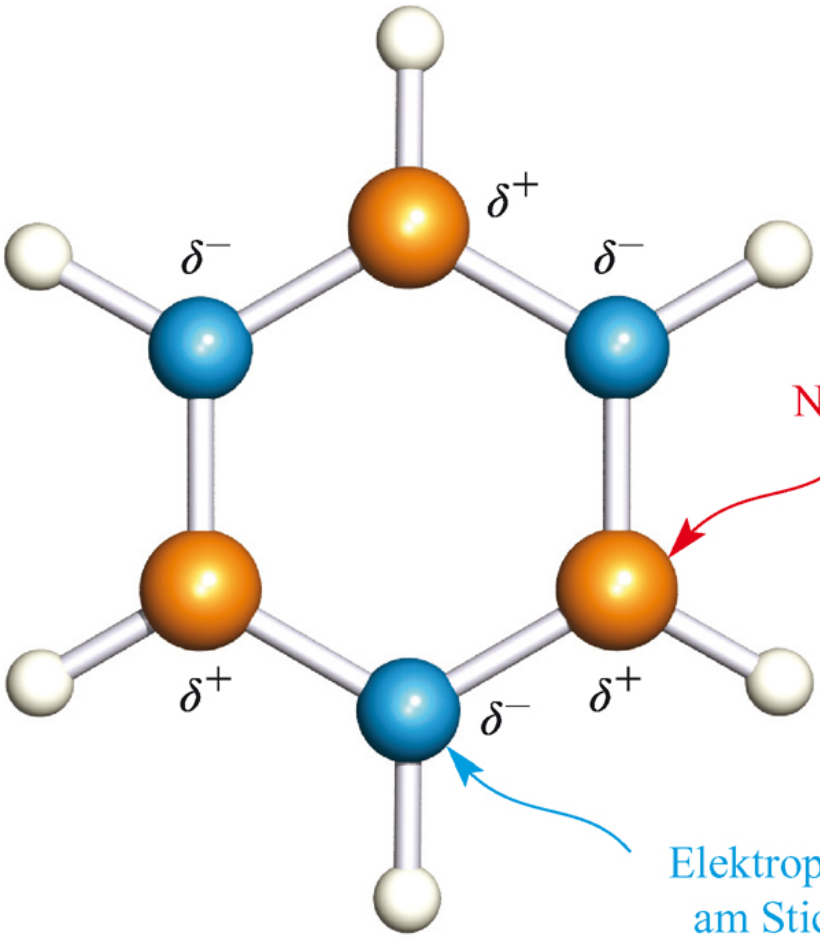
Energieniveaudiagramm für die MO's, die aus 3 $2p_z$ am Bor und entstehen.



Sandwich wie beim Benzol:

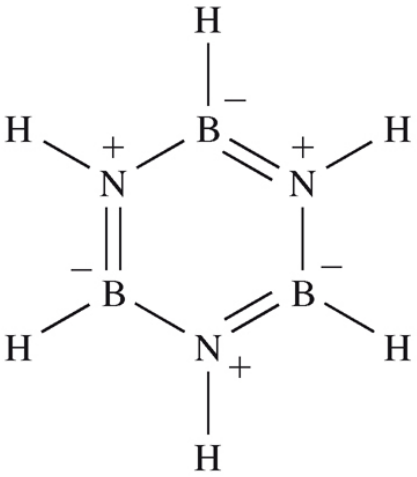
$$B_3N_3Me_6 + Cr(CO)_3(CH_3CN)_3 \longrightarrow [Cr(\eta^6 - B_3N_3Me_6(CO)_3] + 3CH_3CN$$

Hydrolyse: Formal- vs. Partialladung



Nucleophiler Angriff
am Boratom

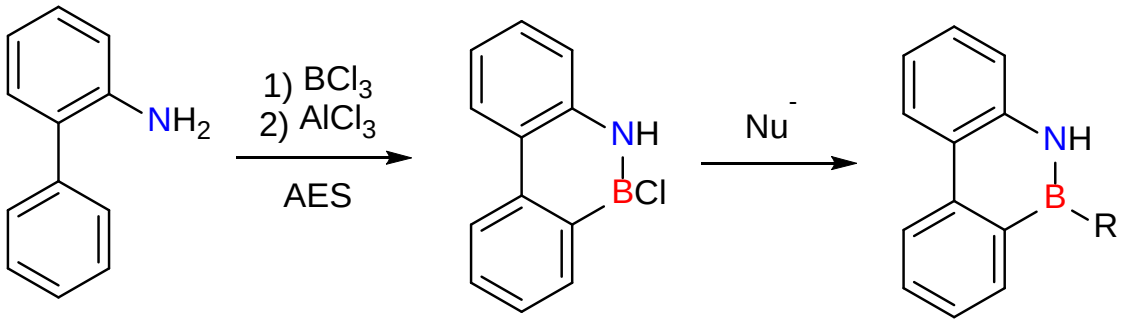
Elektrophiler Angriff
am Stickstoffatom



(12.27)

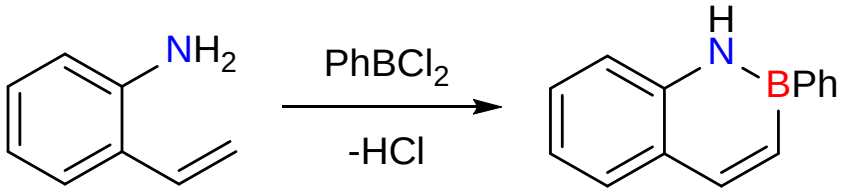
Hybride Organisch / Anorganische Benzol-Derivate

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



R = OH, Me, Ph, H

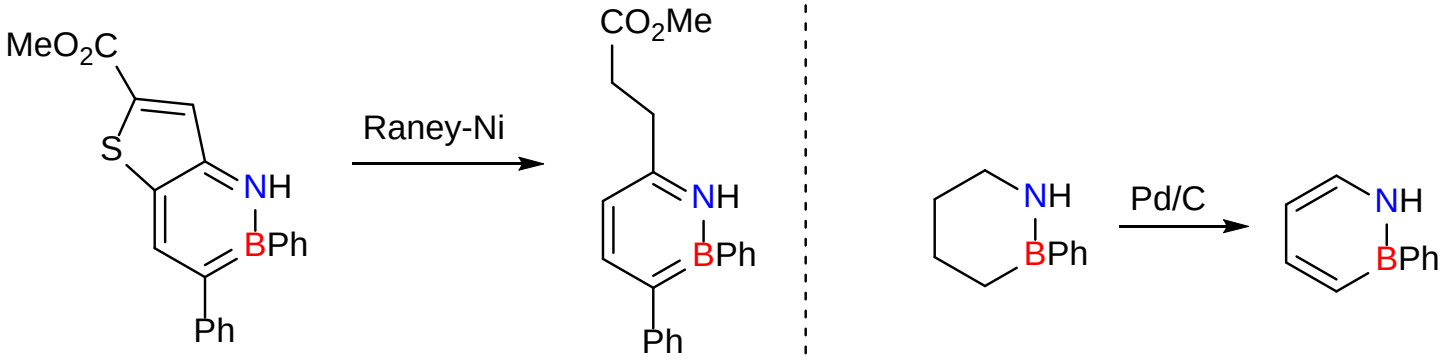
- 1959 dann das erste BN-Naphtalen:



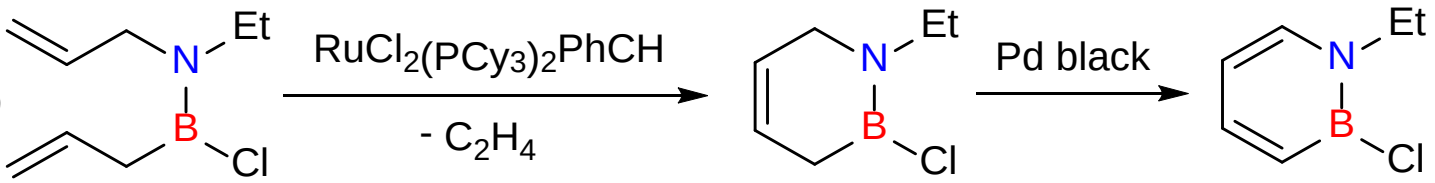
a) M. J. S. Dewar, V. P. Kubba, R. Pettit, *J. Chem. Soc.* **1958**, 3073; b) M. J. S. Dewar, *Tetrahedron* **1959**, *7*, 213

Hybride Organisch / Anorganische Benzol-Derivate

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



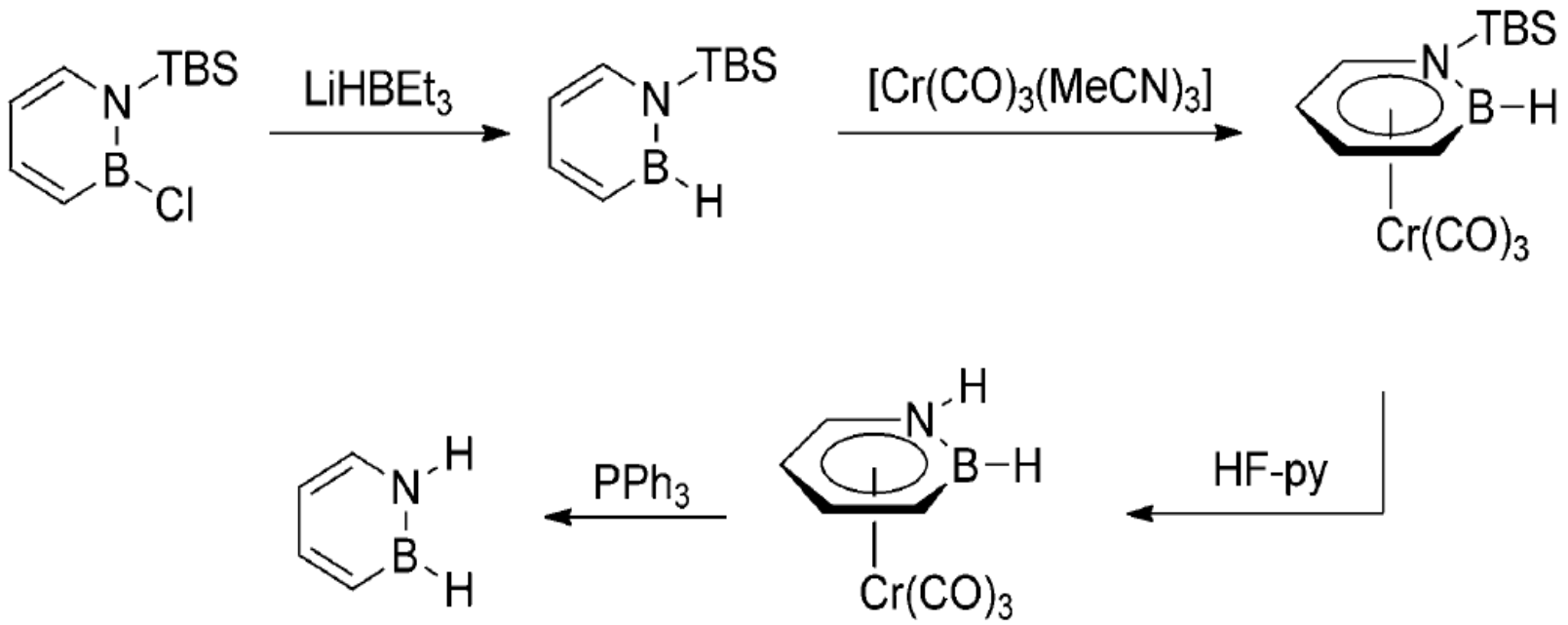
- Liu et al. nutzen ROMP zur Darstellung von funktionalisierten 1,2-Azaborinen



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

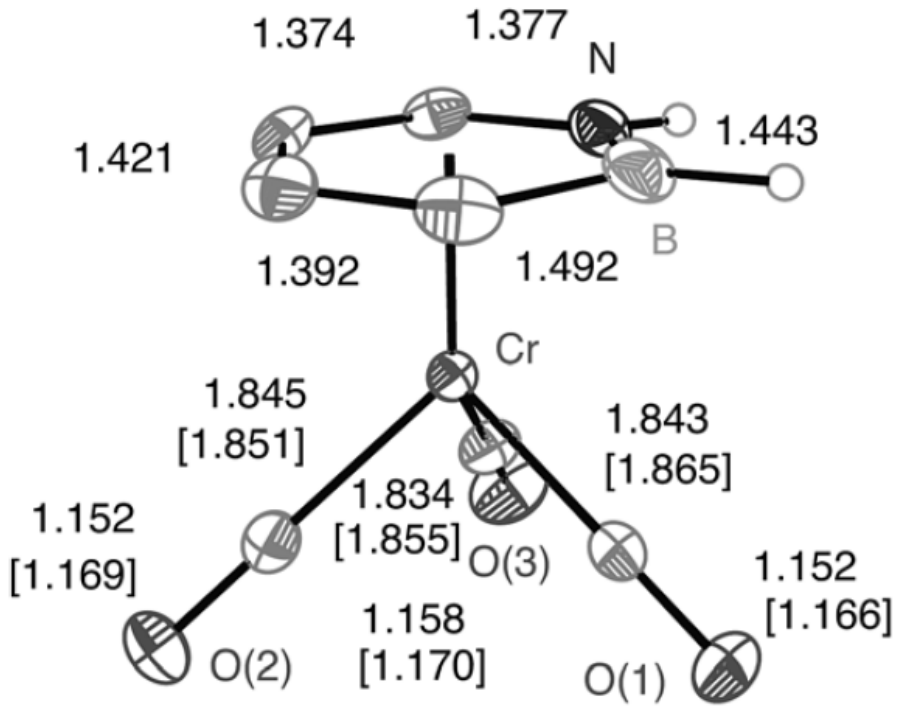
- 2009 Synthese des „Stamm“ 1,2-Dihydro-1,2-Azaborins



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

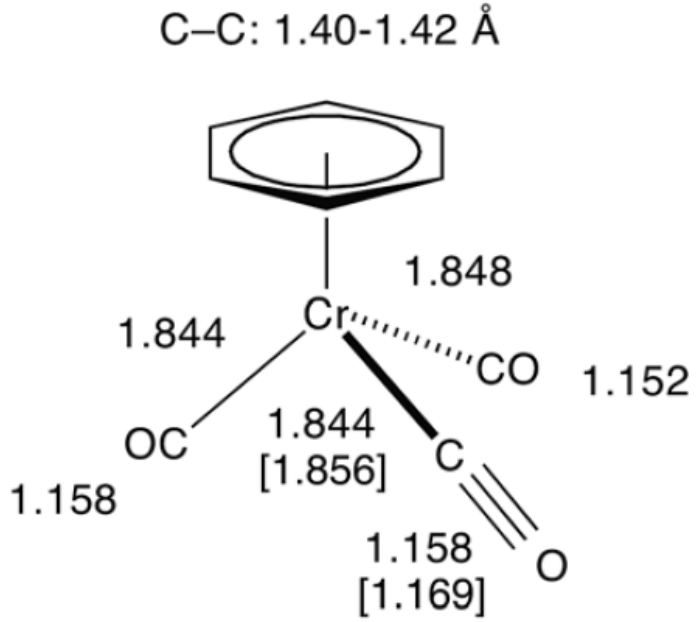
Das 1,2-Dihydro-1,2-Azaborin

ν(CO) = 1898,1975 cm^{-1}



81

ν(CO) = 1892,1972 cm^{-1}

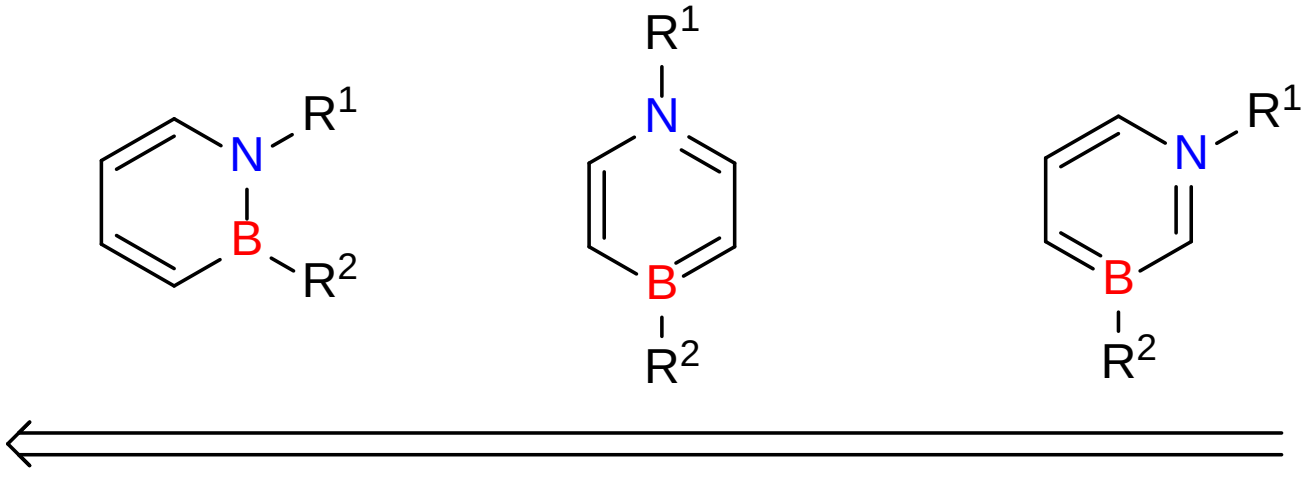


$[Cr(CO)_3(C_6H_6)]$

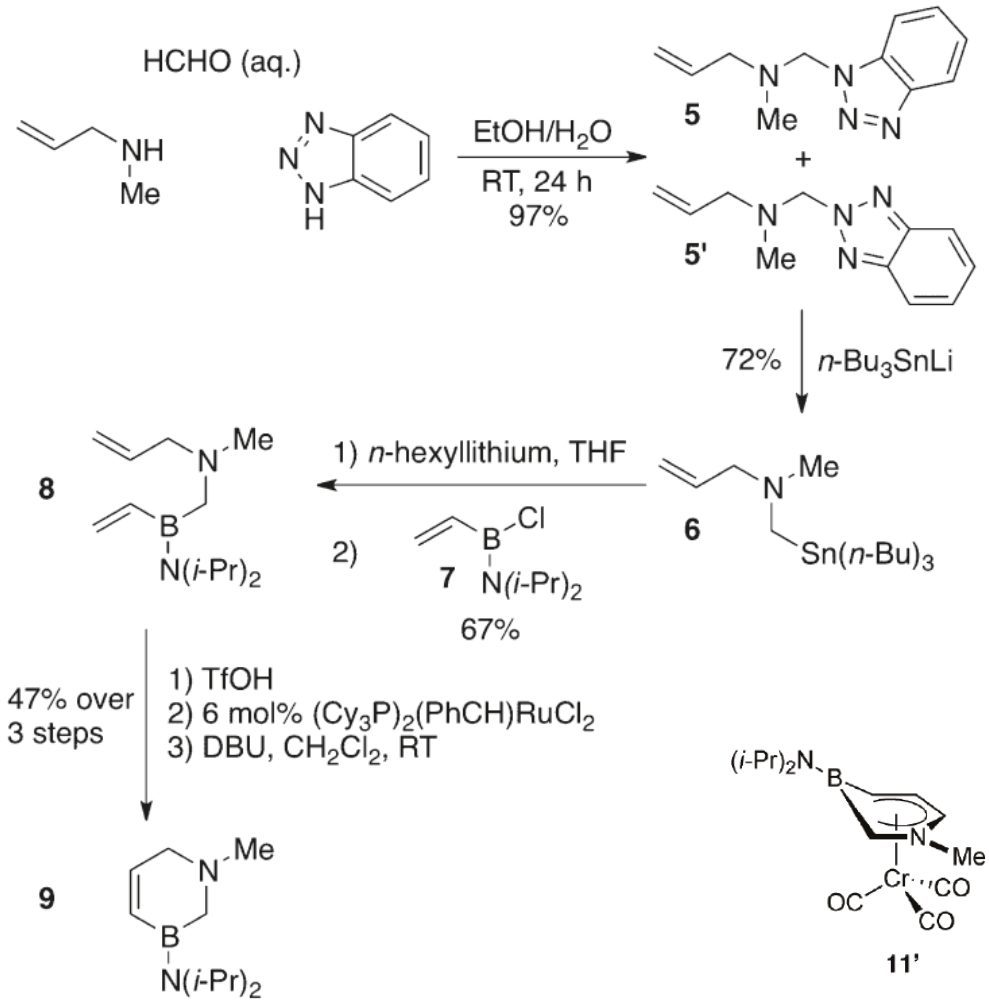
A. J. V. Marwitz, M. H. Matus, L. N. Zakharov, D. A. Dixon, S.-Y. Liu, *Angew. Chem. Int. Ed.* **2009**, *48*, 973.

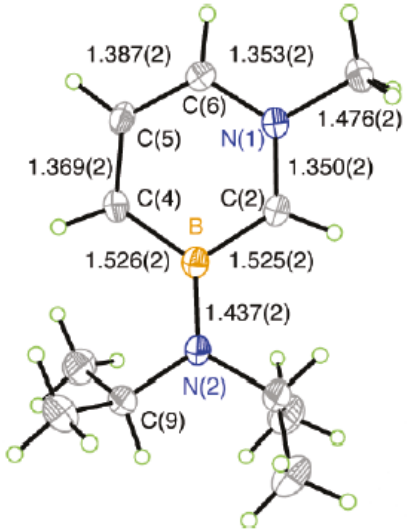
Konstitutionsisomere des Azaborins

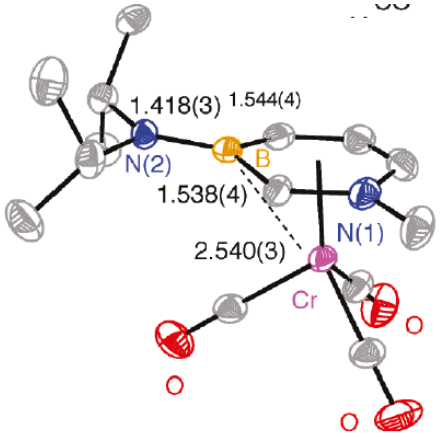
- 1,2-Isomer thermodynamisch am stabilsten
- 1,2 > 1,4 > 1,3



Das 1,3-Azaborin



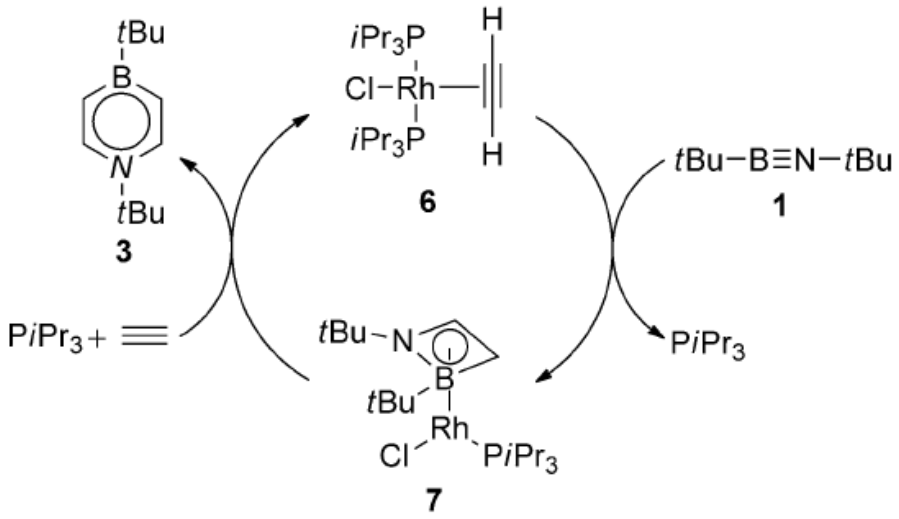


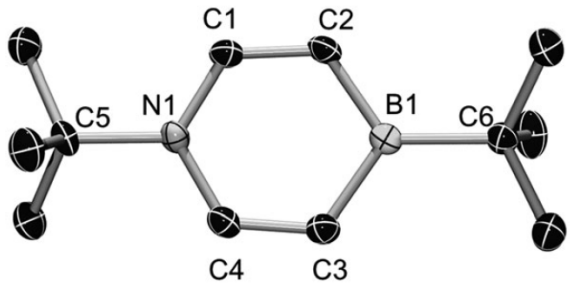


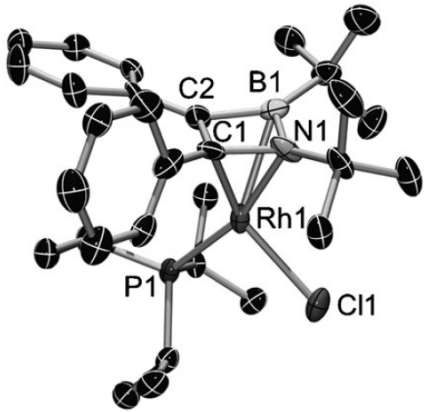
S. Xu, L. N. Zakharov, S.-Y. Liu, *J. Am. Chem. Soc.* **2011**, *133*, 20152

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





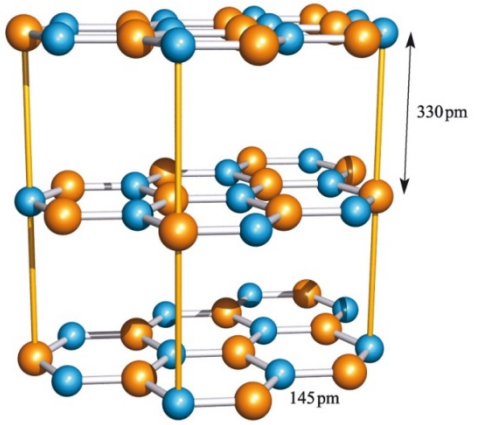


H. Braunschweig, A. Damme, J. O. C. Jimenez-Halla, B. Pfaffinger, K. Radacki, J. Wolf, *Angew. Chem.* **2012**, *124*, 10177.

Weitere Analogien - Bornitrid

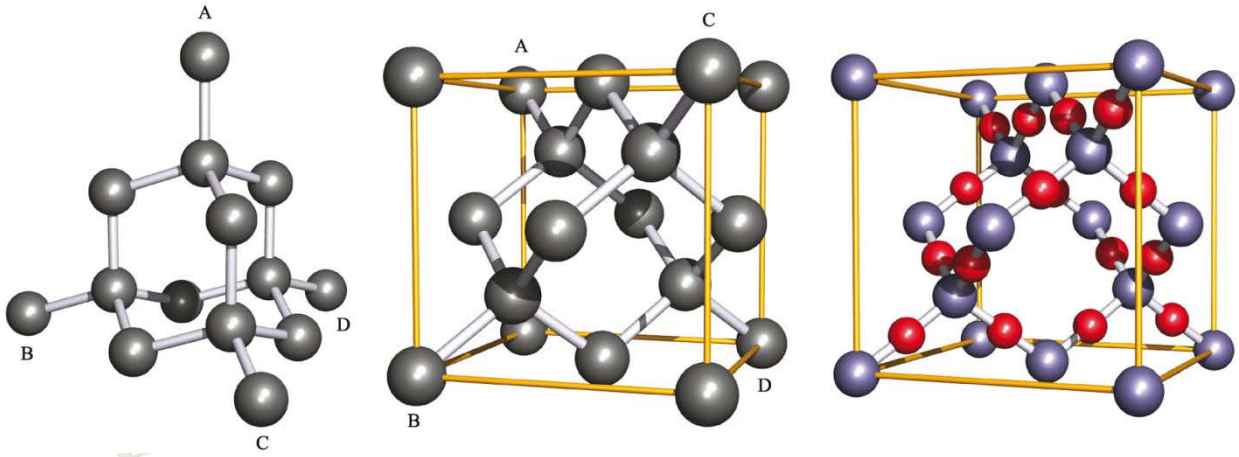
Bornitrid (**Graphit** analog):

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



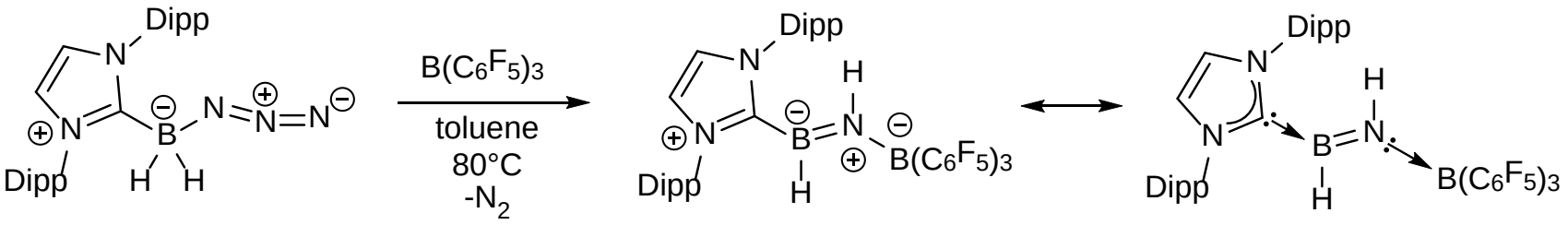
Graphit / Diamant Analogie:

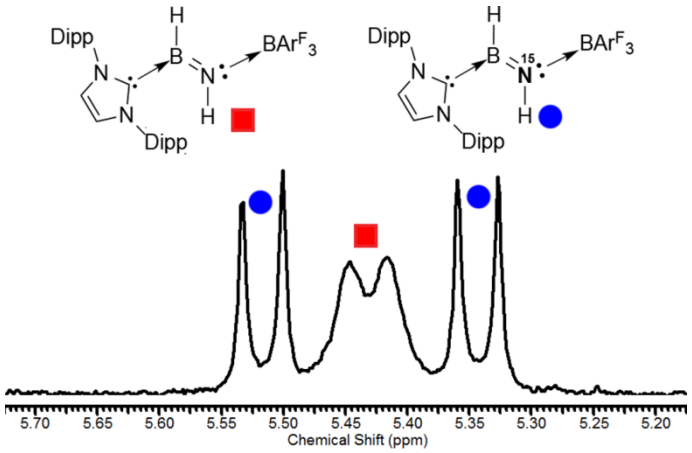
$(BN)_x$ hexagonal $\xrightarrow{60-90x10^8\,Ps,\,1500-2000°C}$ *anorganischer Diamant*



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:

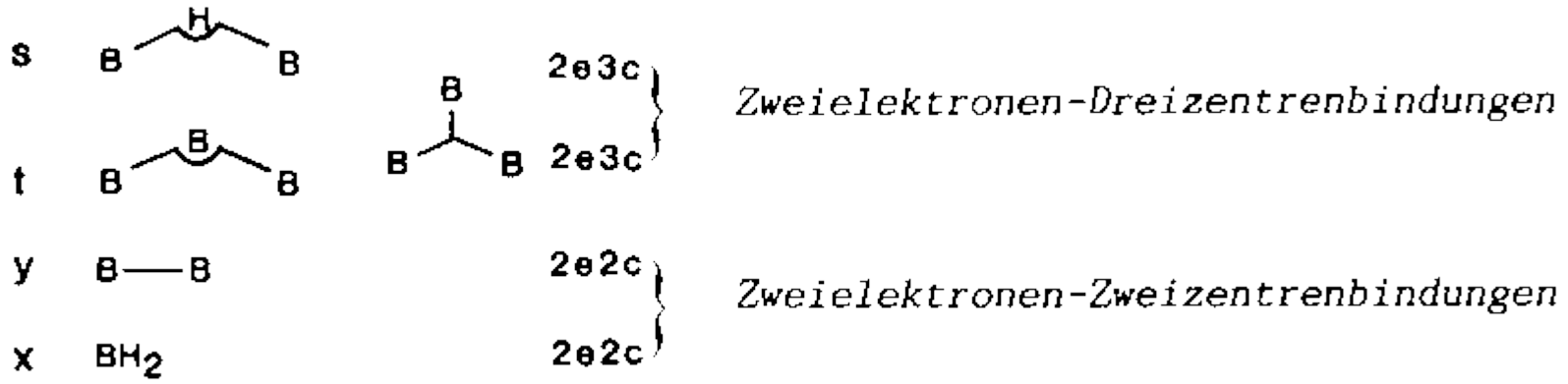
B_nH_{n+2}	B_nH_{n+4}	B_nH_{n+6}	B_nH_{n+8}
closo	**nido**	**arachno**	**hypho**
Käfig	-1 Ecke	-2 Ecken	-3 Ecken

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: $B_2H_6 + 3\ O_2 \rightarrow B_2O_3 + 3\ H_2O$ $D_fH°(298) = -2138$ KJ/mol
- Nomenklatur: BH_3: Boran (3); B_2H_6: Diboran (6); B_4H_{10}: Tetraboran (10)

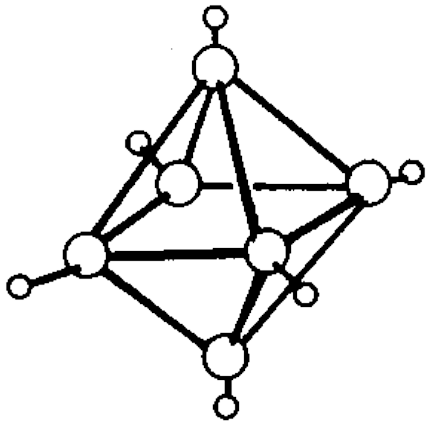
Mehrzentrenbindungen in Boranen

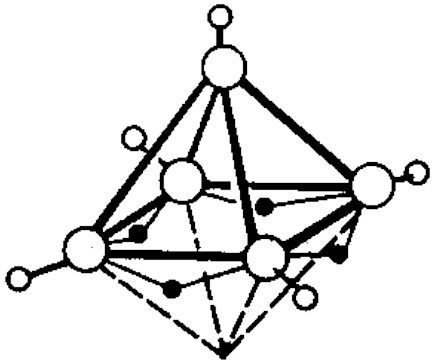
- In Boranen (auch C-substitutierten) liegen immer mehr Gerüstverbindungslinien als Elektronenpaare vor (LIPSCOMB)
- Styx - Code

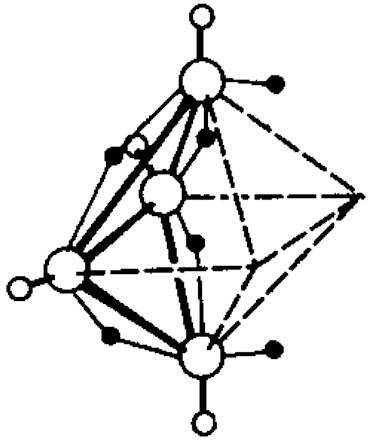


z.B. B_2H_6 styx code = 2002

Borhydride – Eine Wiederholung







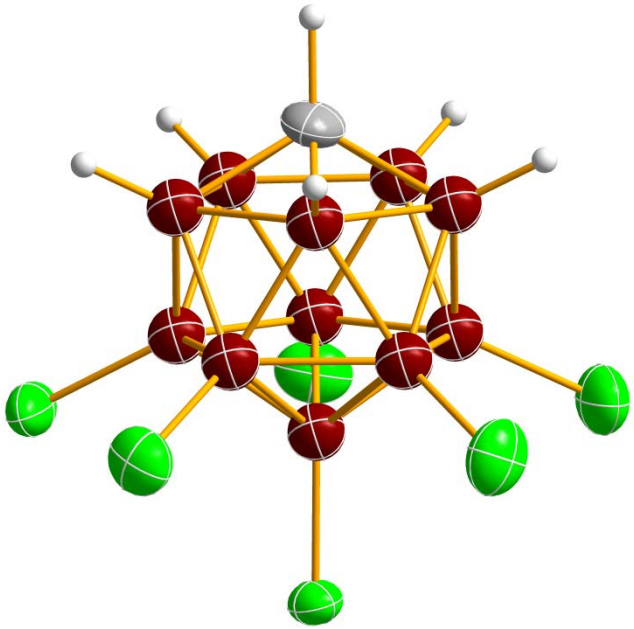
$2n+2$ | $2n+4$ | $2n+6$ Gerüstelektronen

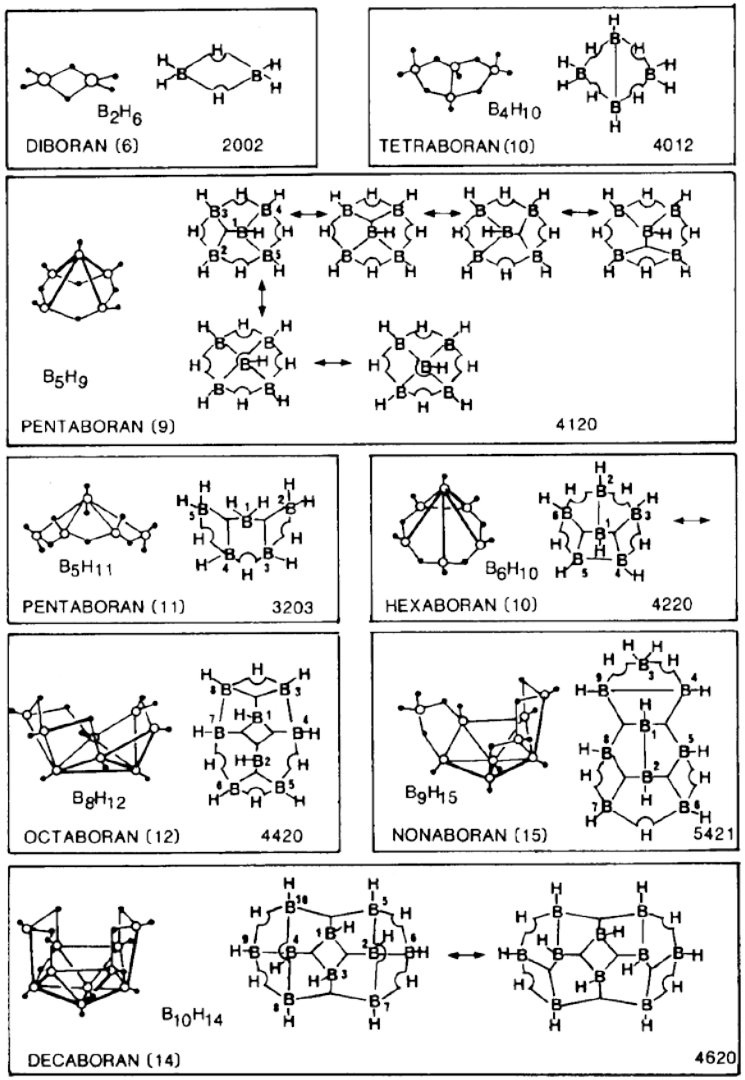
closo ($B_6H_6^{2-}$) | ***nido*** (B_5H_9) | ***arachno*** (B_4H_{10})

- 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

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

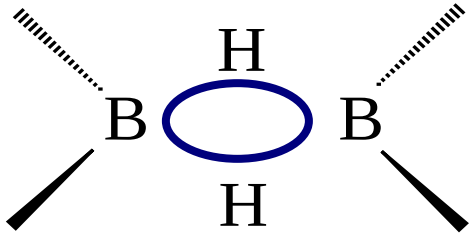
$$4BF_3 + 3NaBH_4 \xrightarrow[25°C]{\text{Ether}} 2B_2H_6 \uparrow + 3NaBF_4$$

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

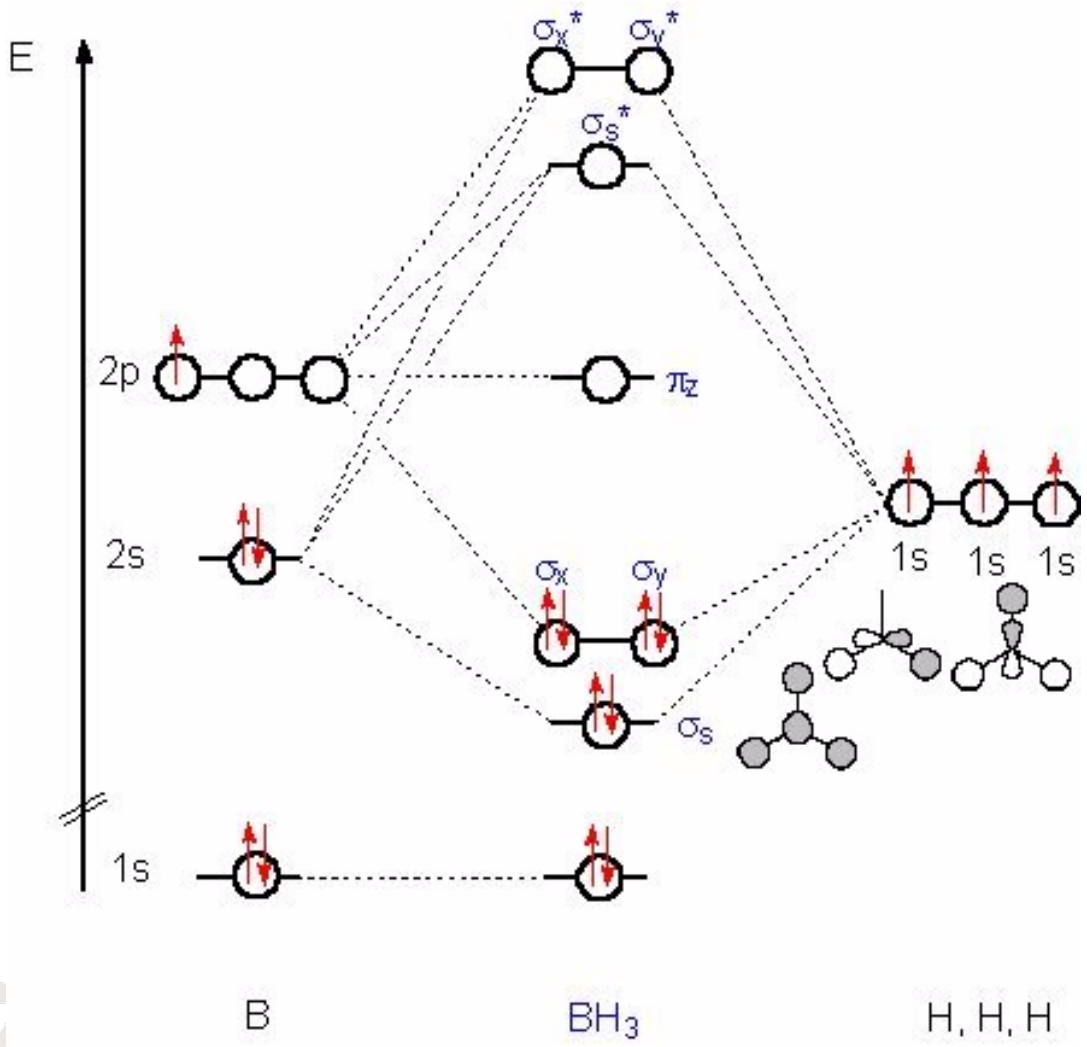
Gleichgewicht:

$$B_2H_6 \rightleftharpoons 2\,BH_3$$

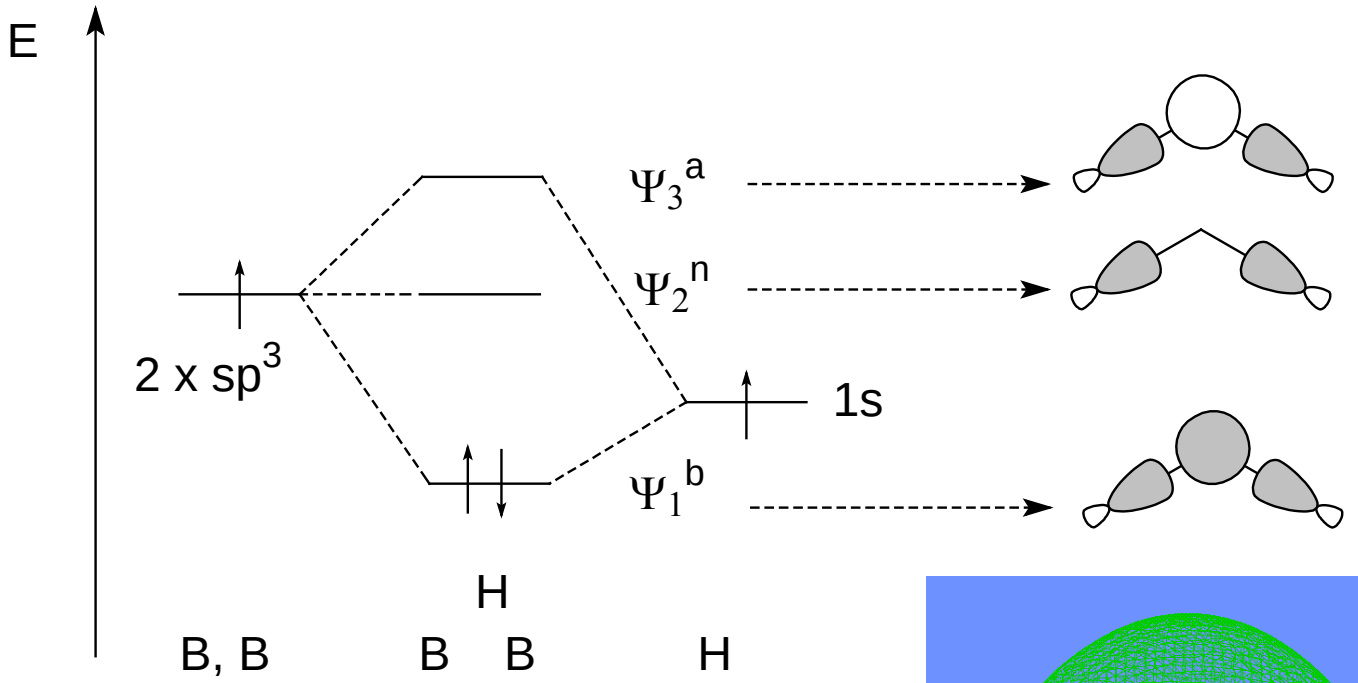
$\Delta H_{Diss.}(298) = 150$ kJ/mol

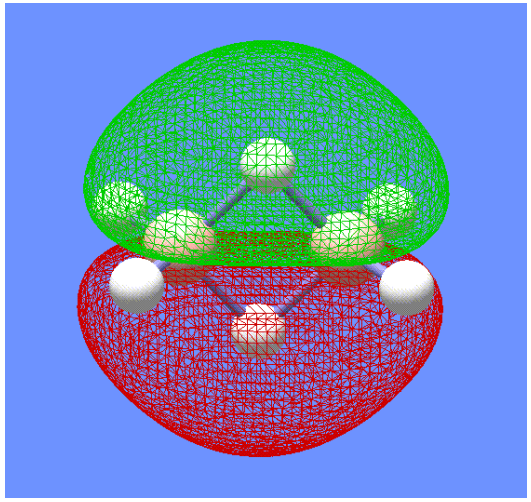


MO-Diagramm unter Verwendung delokalisierter MO's



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, $-C_6F_5$

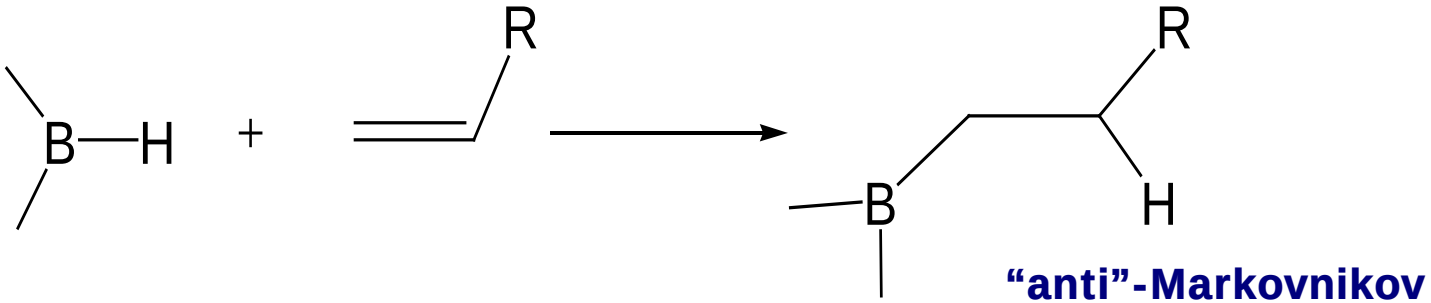
Auf genaue Stöchiometrie achten, da sonst “at”-Bildung

im Gegensatz:

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

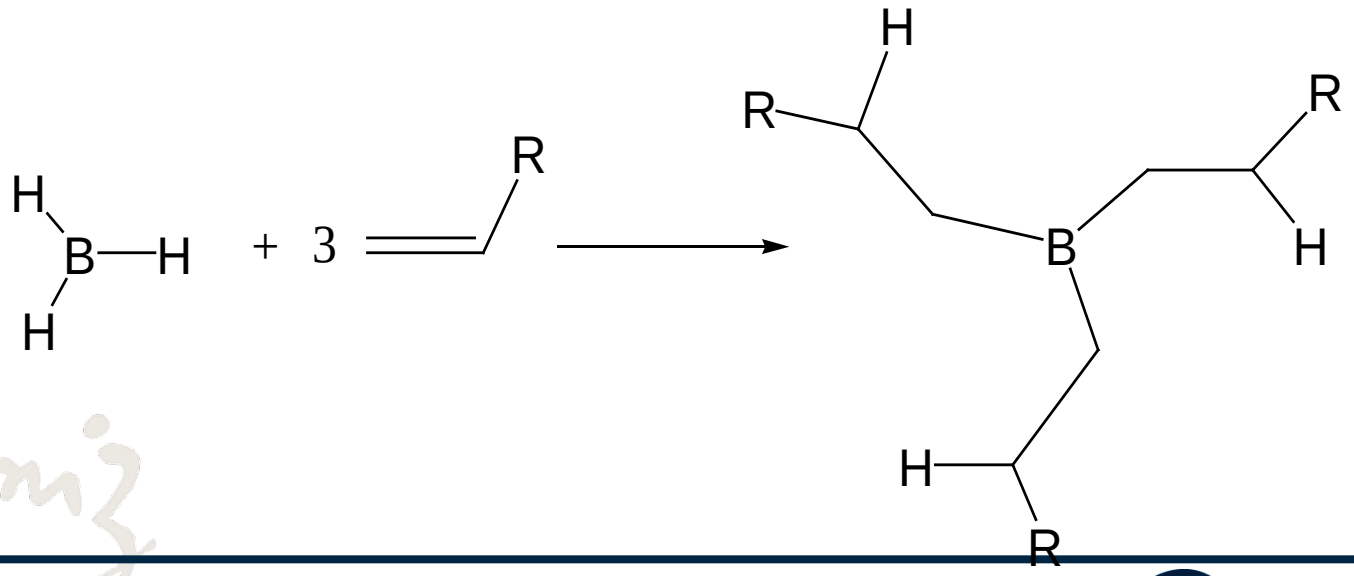
Darstellung

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

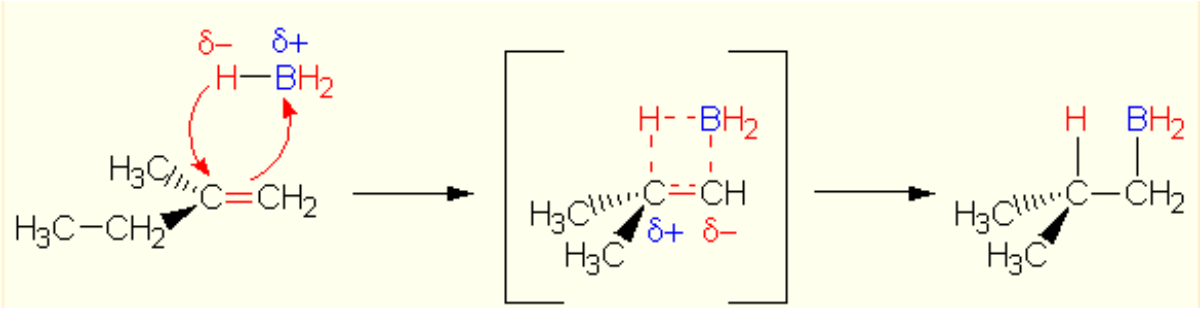


“anti”-Markovnikov

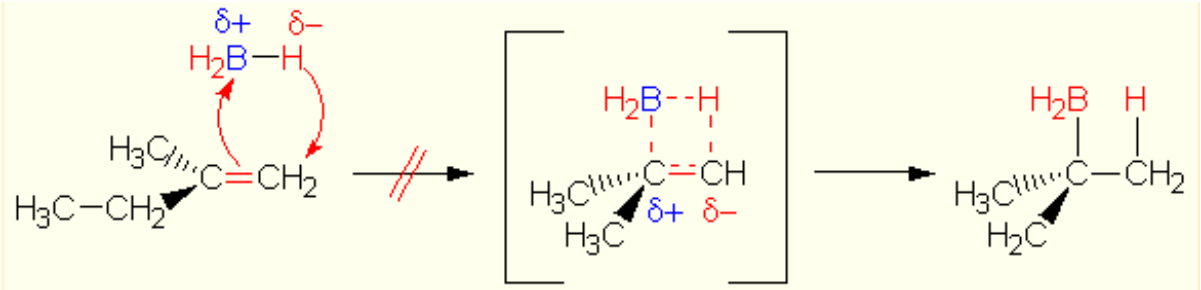
oder 3-fach



anti-Markovnikov



Beobachtetes Produkt



Nicht beobachtetes Produkt

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