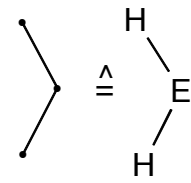
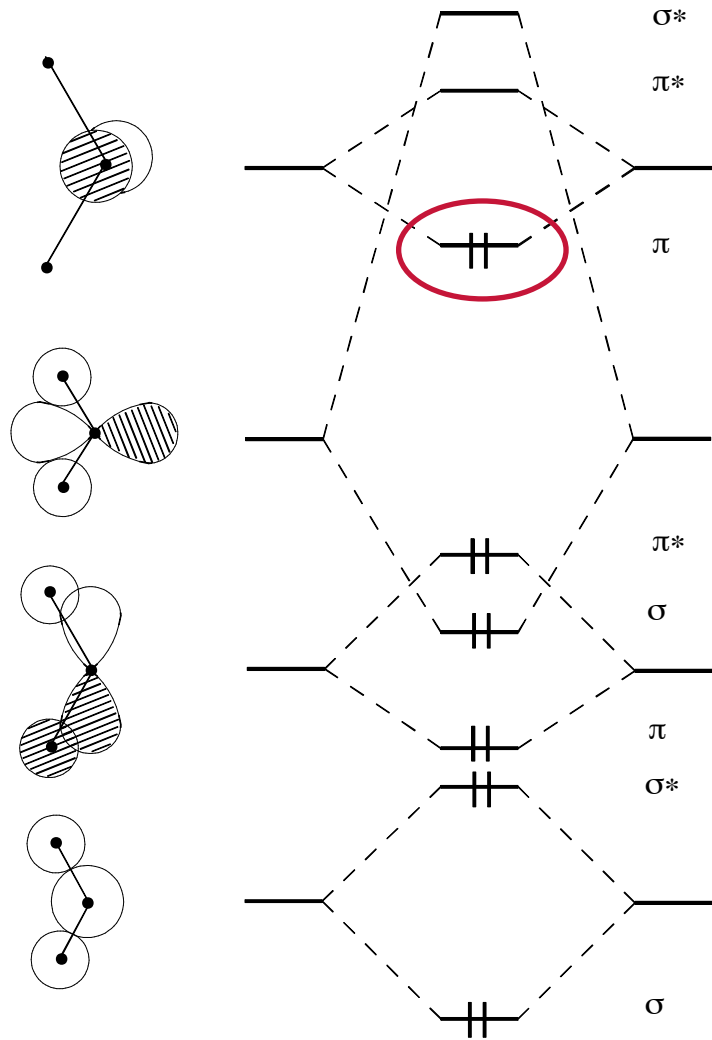


Elektronische Struktur von E_2H_4 D_{2h} :



in C_2H_4 12e

8 in b MO,
4 in ab MO

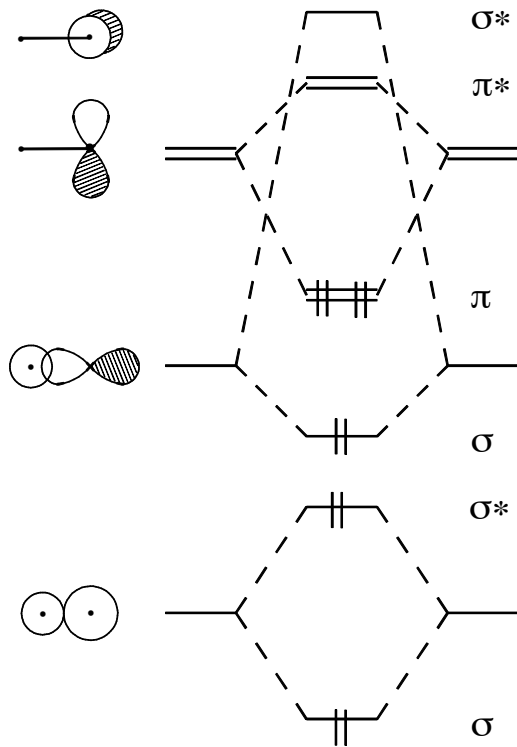
$\Rightarrow N = 2$

in B_2H_4 10e

$\Rightarrow N = 1$

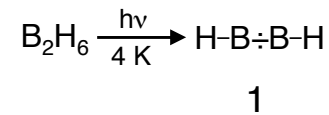
höhere Bindungsordnung
durch Reduktion

Elektronische Struktur von E_2H_2 $D_{\infty h}$



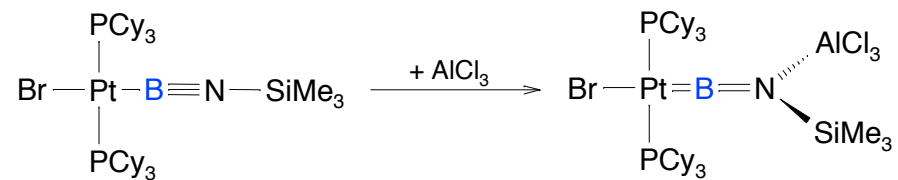
in C_2H_2 10e \implies N = 3

in B_2H_2 8e \implies N = 2 **und** Triplettgrundzustand
 \implies hochreaktiv, instabil



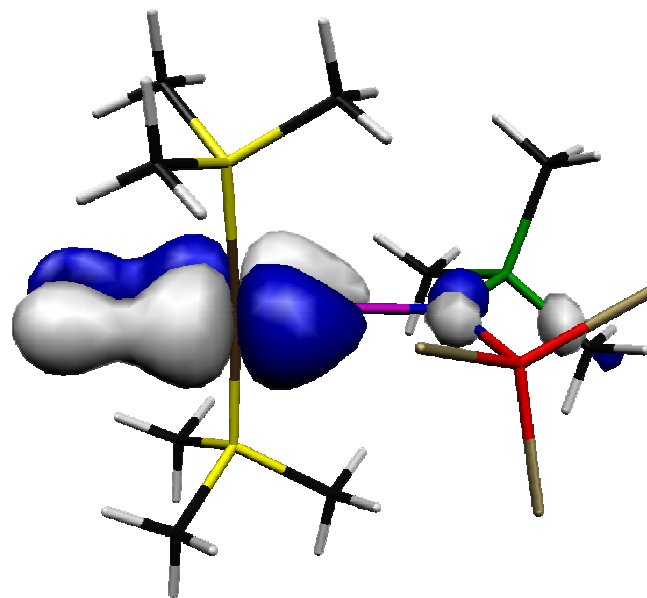
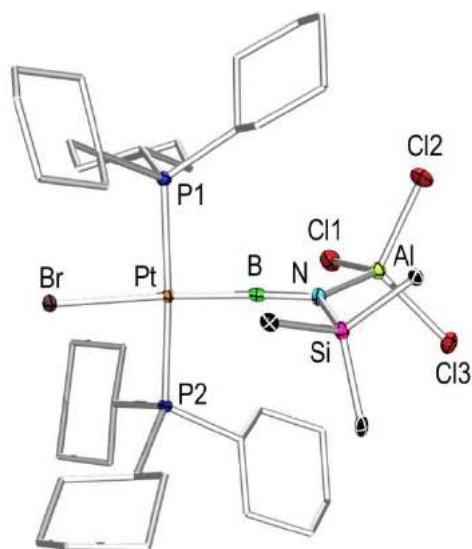
1 durch Photoionisation aus B_2H_6 in Edelgasmatrices bei 4K
 Charakterisierung über ESR \implies Triplett

Neutral Platinum Borylenecomplexes

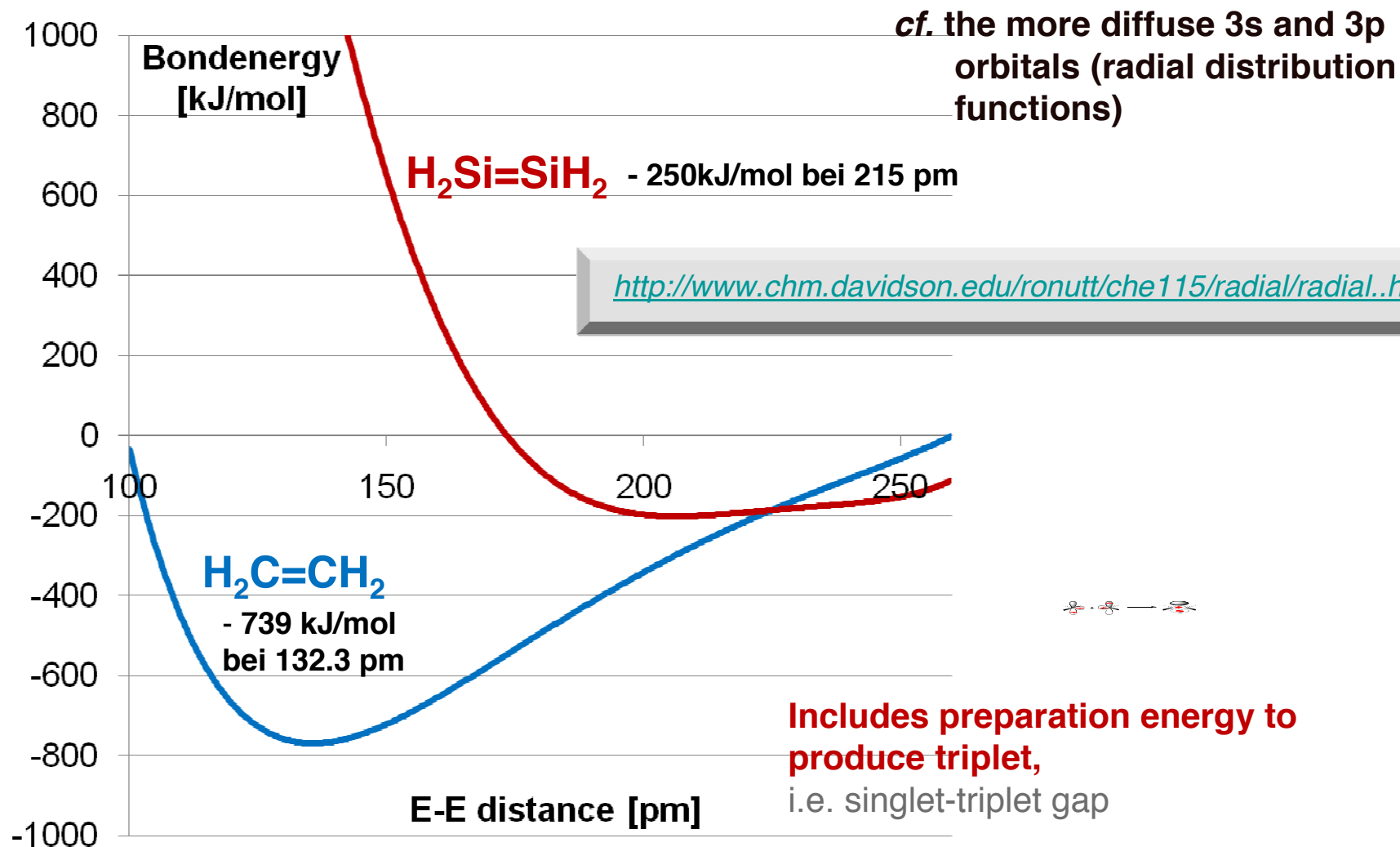


Pt-B = 196.0(3) pm
Pt-Br = 255.16(4) pm
B-N = 126.0(4) pm

Pt-B = 190.4(3) pm
Pt-Br = 252.80(2) pm
B-N = 133.0(3) pm



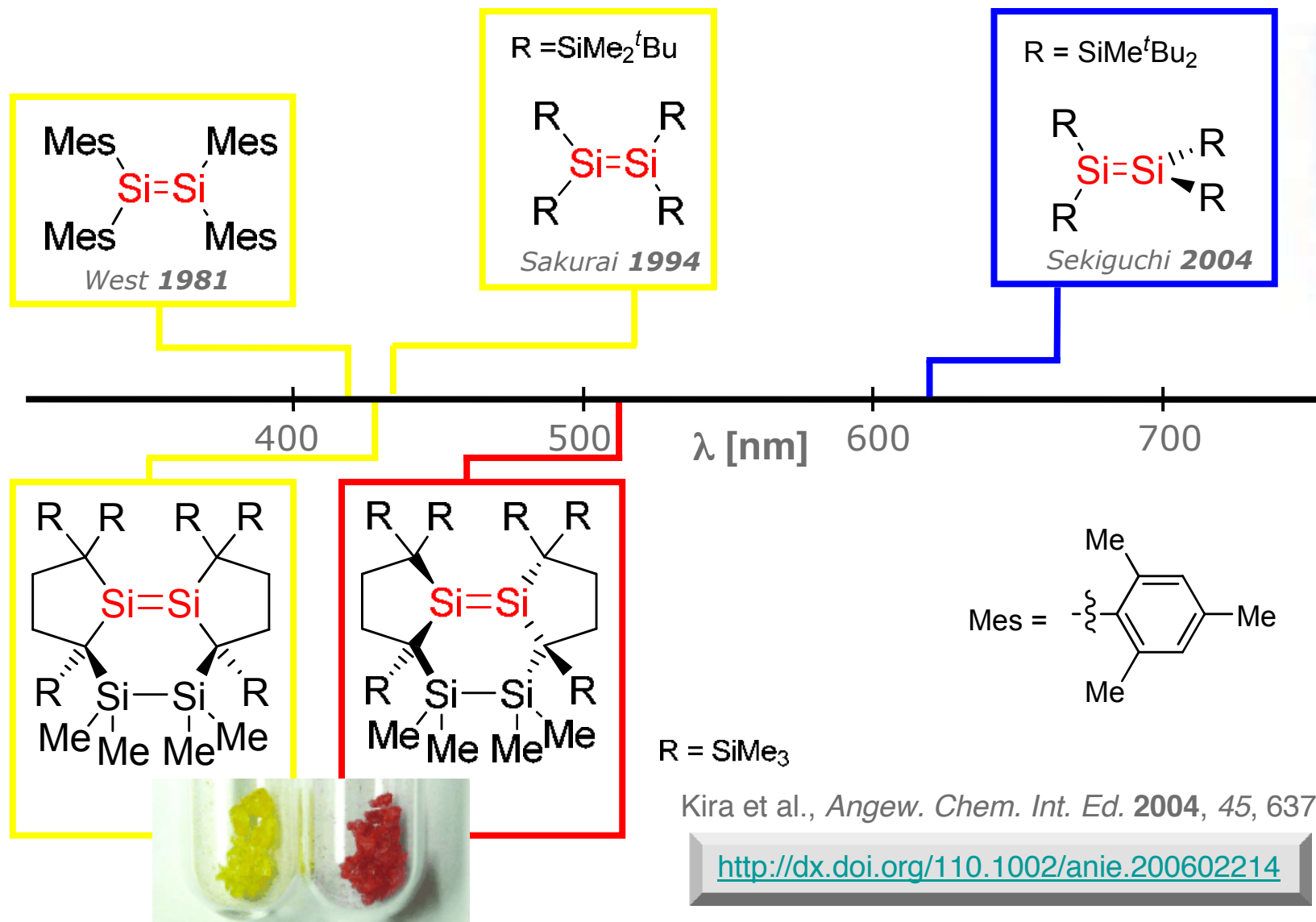
Potentialenergiefläche $\text{H}_2\text{C}=\text{CH}_2$ vs. $\text{H}_2\text{Si}=\text{SiH}_2$



Ziegler *et al.*, *J. Am. Chem. Soc.* 1994, 116, 3667.

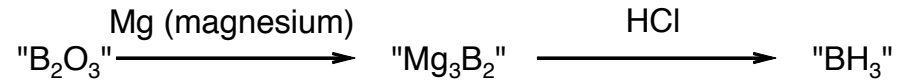
<http://pubs.acs.org/doi/pdf/10.1021/ja00088a001>

Farbigkeit von Disilenen



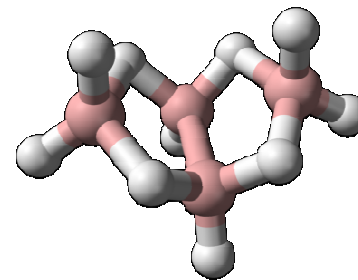
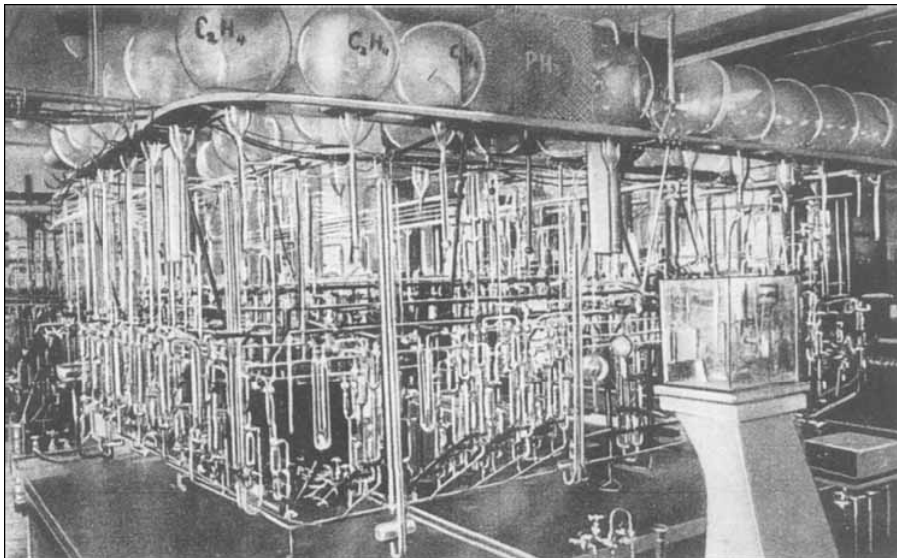
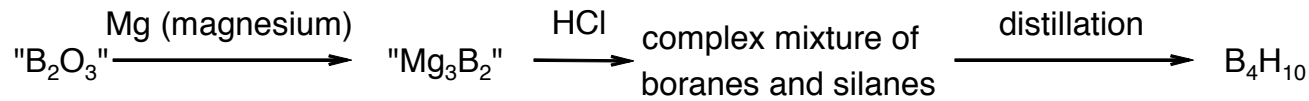
Boranes - Synthesis

➤ „On a Hydride of Boron“
F. Jones, *J. Chem. Soc.* **1879**, 35, 41.



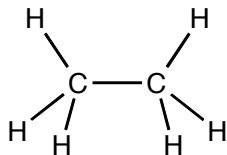
➤ At the turn of the 19th century, hydrides were known for all non-metals, **except boron**.

➤ Pioneering work by Alfred Stock (1876-1946) since 1909



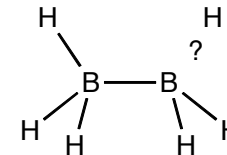
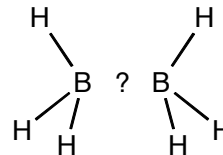
„Borwasserstoffe“
A. Stock, C. Massenez,
Ber. Dtsch. Chem. Ges. **1912**,
45, 3539.

Diborane(6) - Structure and Bonding



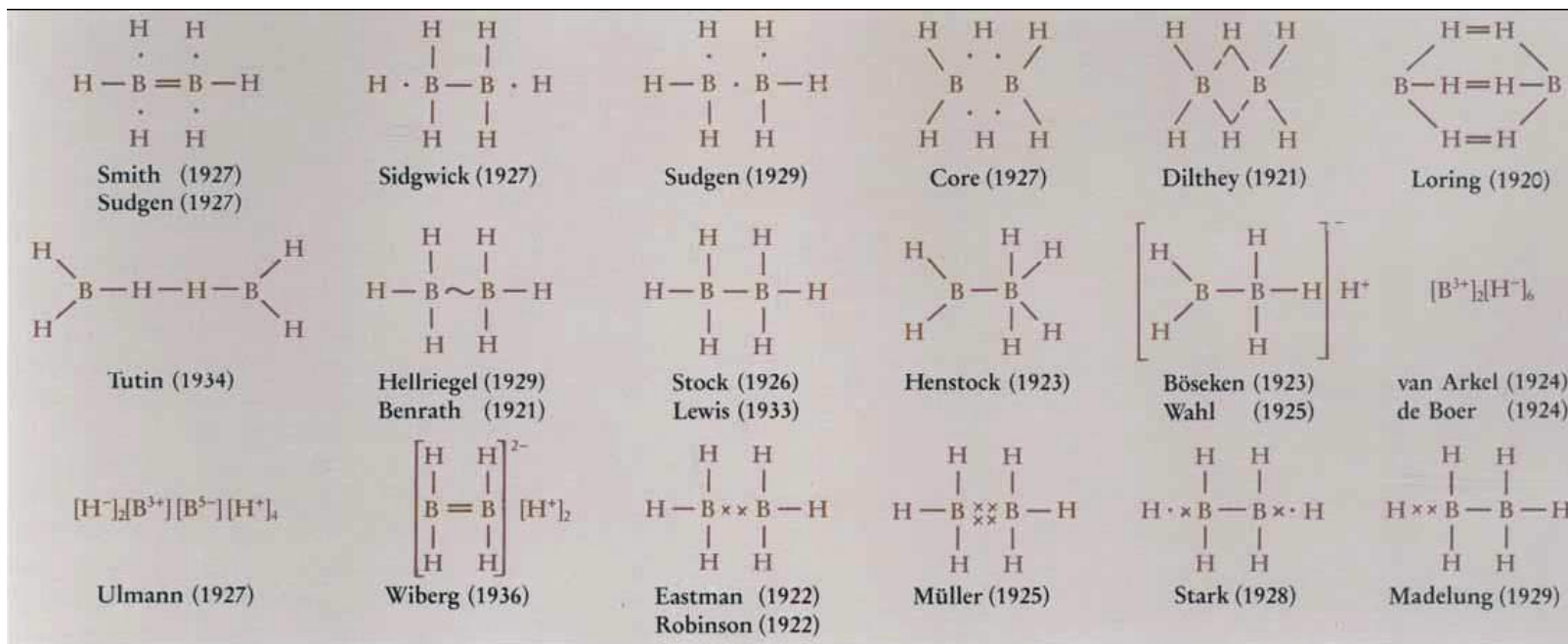
Ethane C_2H_6 :

- 14 electrons in 7 pairs (bonds)
- every carbon atom employs 8 electrons
- classical (electron precise) bonding situation



Diborane(6) B_2H_6 :

- 12 electrons
- non-classical (electron deficient) bonding situation

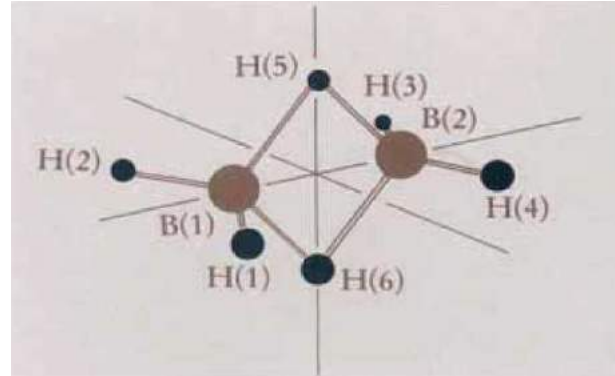


Selected examples attempting to describe the correct constitution and bonding of diborane(6)

Diborane(6) - Structure and Bonding



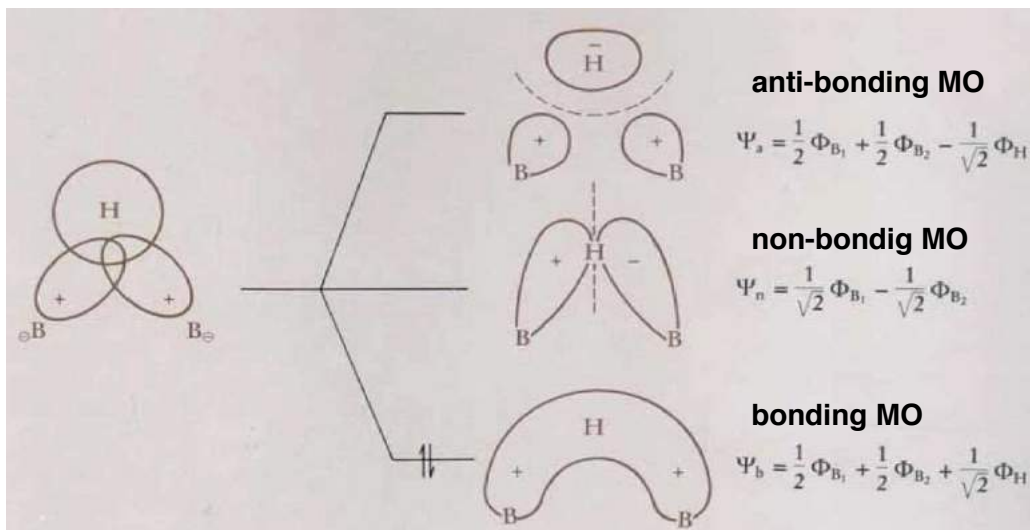
William Lipscomb
born 1919
Nobel Prize in Chemistry 1976



Diborane(6) B_2H_6 :

- structure confirmed by X-ray and electron diffraction
- 4 terminal and 2 bridging hydrogens
- not consistent with a classical bonding description

W. N. Lipscomb: "Boron Hydrides", W. A. Benjamin Inc., New York 1963.



Rationale:

- 2c-2e bonds for terminal hydrogens
- 3c-2e bonds for bridging hydrogens
- electronic structure can not be described by Lewis-formalism or Valence Bond theory
- breakthrough for Molecular Orbital theory

Higher Boranes - Structure and Bonding



Kenneth Wade, FRS
born 1932

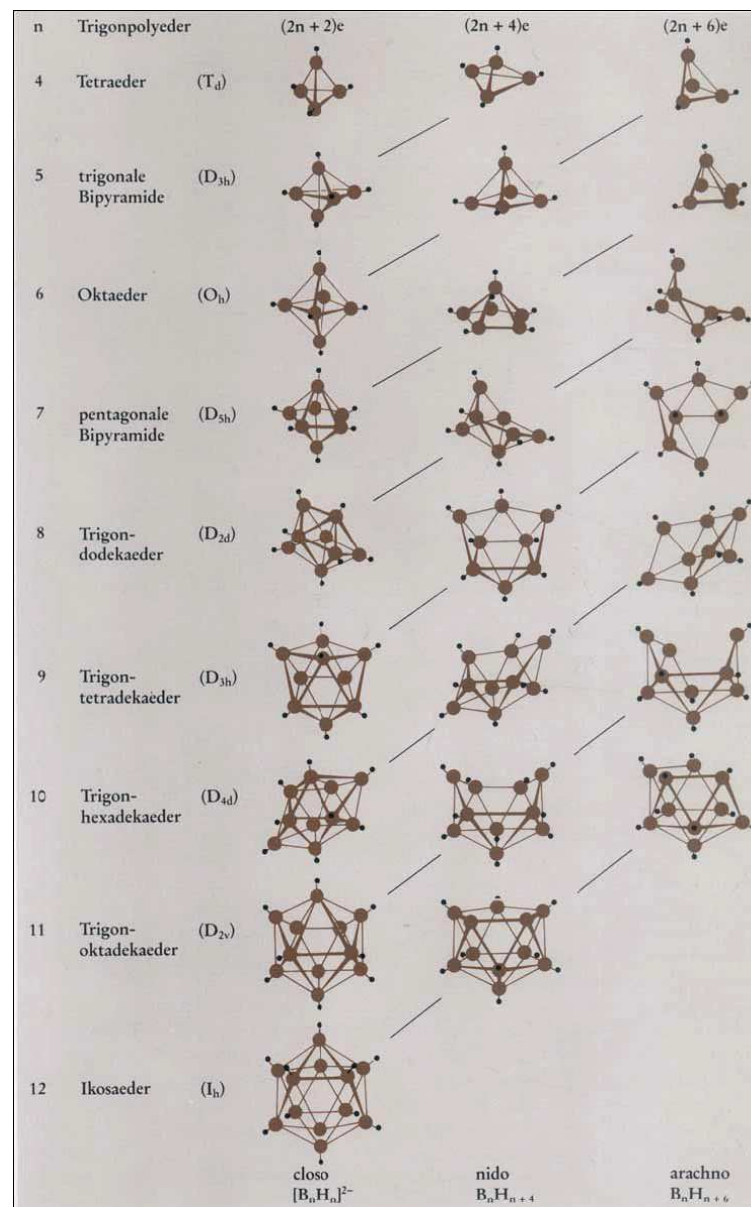
Classification of higher boranes:

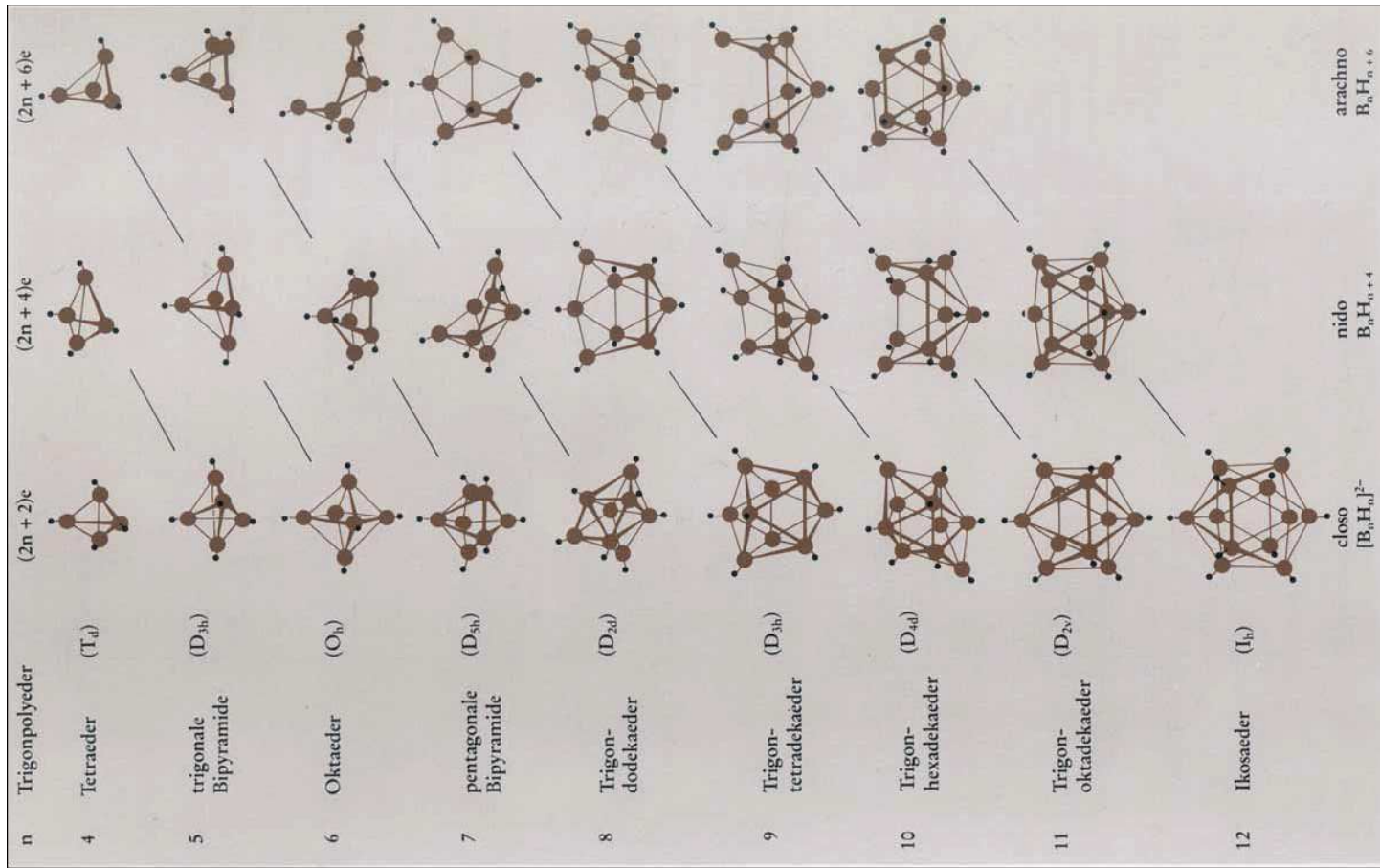
- counting scheme (based on MO theory) to predict the cluster geometry from the formula „**Wade's Rules**“
- rationale for the structural/electronic relationships between closo- nido- and arachno-boranes
- applicable to heteroboranes, metallaboranes, boron-free polynuclear species (e.g. Zintl-anions)
- extended to metal clusters „**Wade-Mingos-Rules**“

K. Wade, *J. Chem. Soc. Chem. Commun.* **1971**, 792.

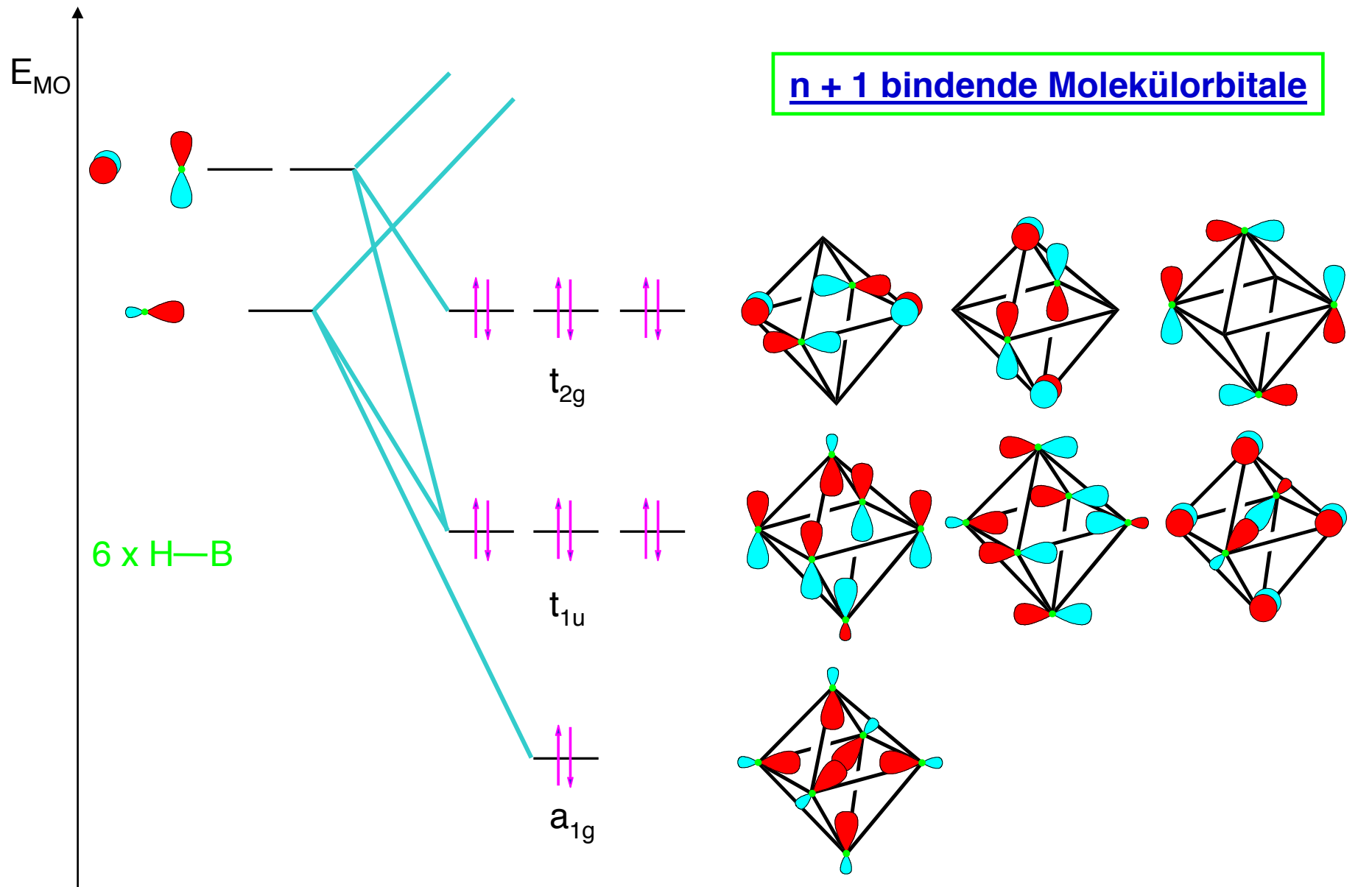
Examples:

- $B_{12}H_{12}^-$: 13 electron pairs, 12 vertices
(n+1) closo
- $B_{11}H_{15}$: 13 electron pairs, 11 vertices
(n+2) nido
- $B_{10}H_{16}$: 13 electron pairs, 10 vertices
(n+3) arachno

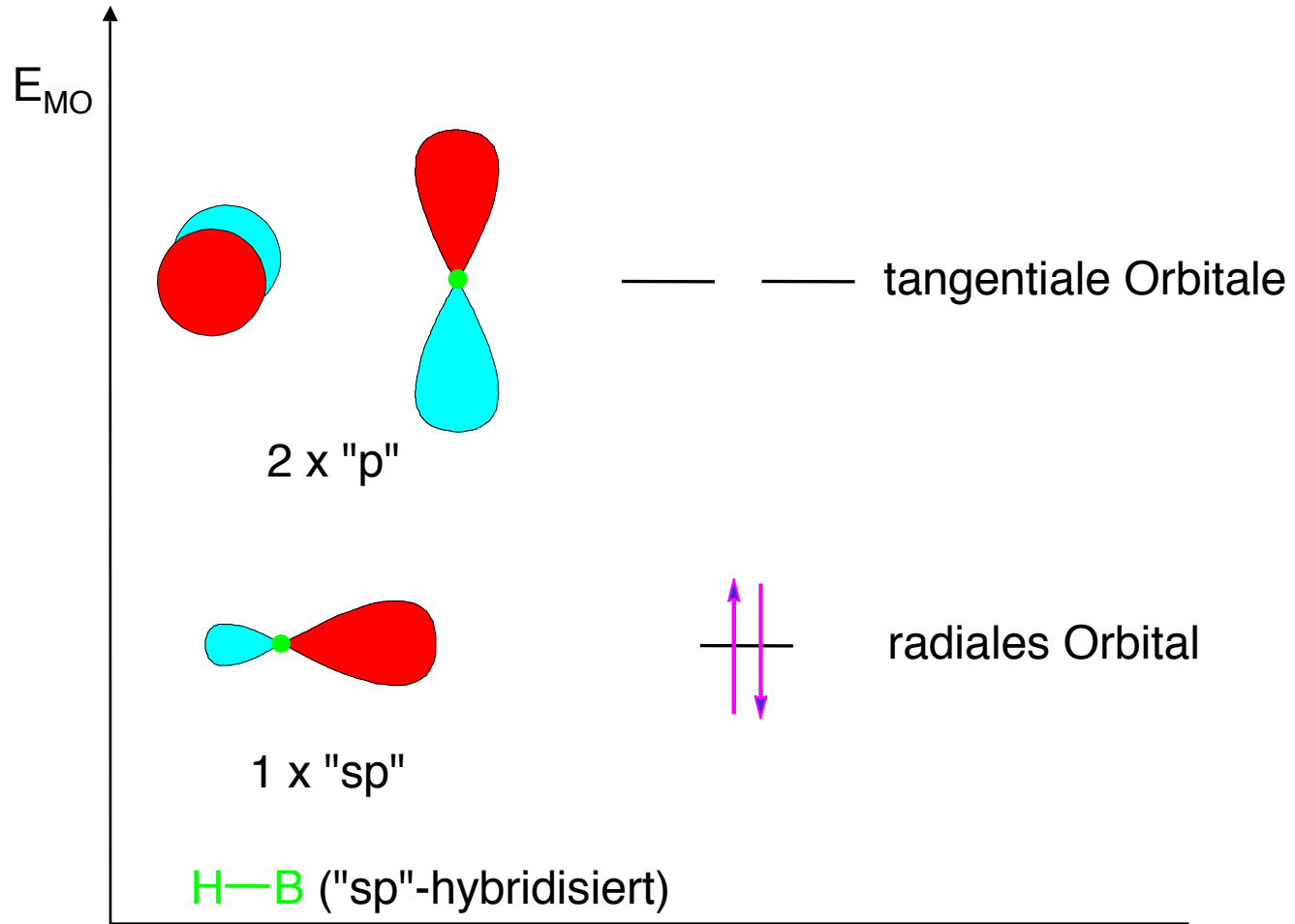




Cluster-bindende Orbitale von $[B_6H_6]^{2-}$

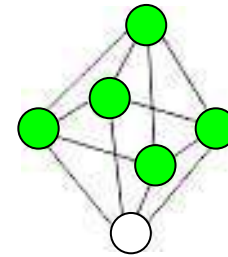
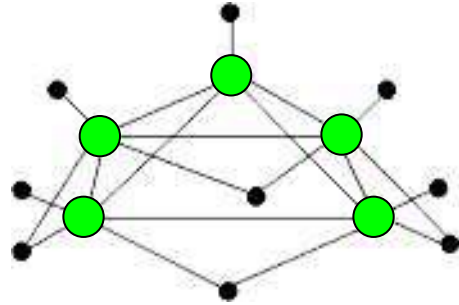


Für den Clusteraufbau zur Verfügung stehende MO's eines B-H Gerüstbausteines

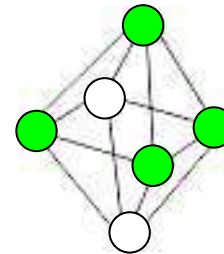
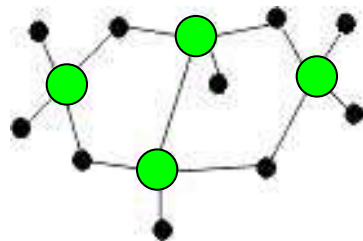


Beispiele:

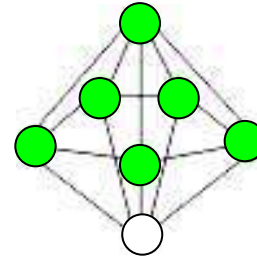
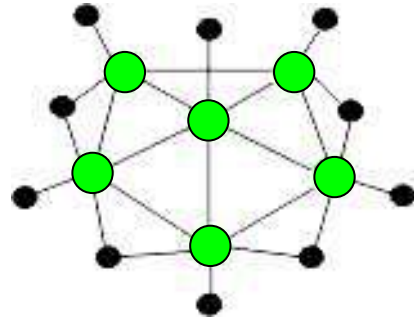
B_5H_9 nido-Pentaboran(9)



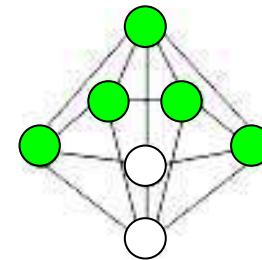
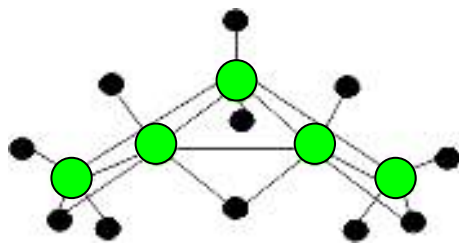
B_4H_{10} arachno-Tetraboran(10)

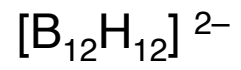


B_6H_{10} nido-Hexaboran(10)

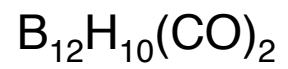
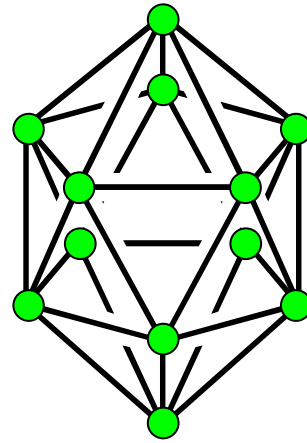


B_5H_{11} arachno-Pentaboran(11)

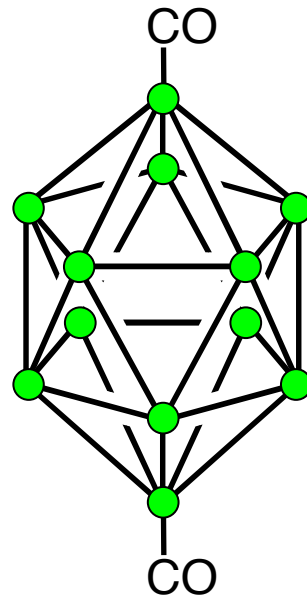




closo -Dodekahydrododekaborat(2-)

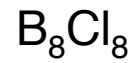


closo -1,12-Dicarbonyldodekaboran(10)

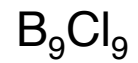
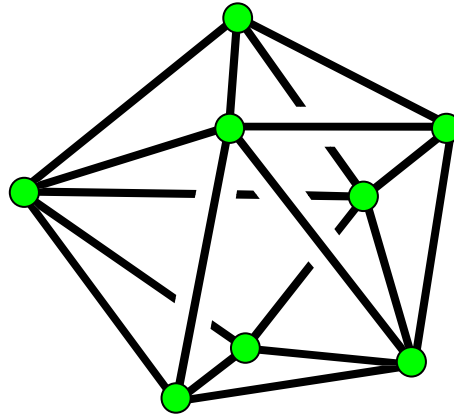


Borsubhalogenide B_nX_n (X = Hal, n = 6, 8 - 12)

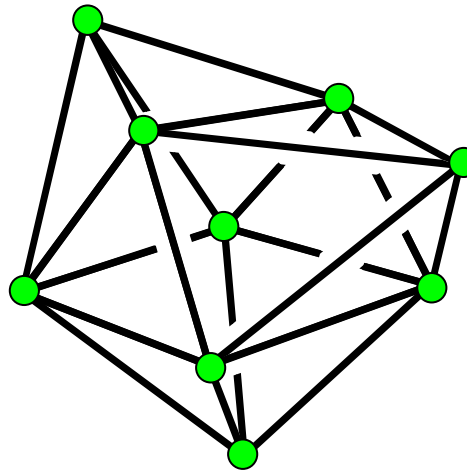
Beispiele:



hypercloso - Octachlorooctaboran(8)



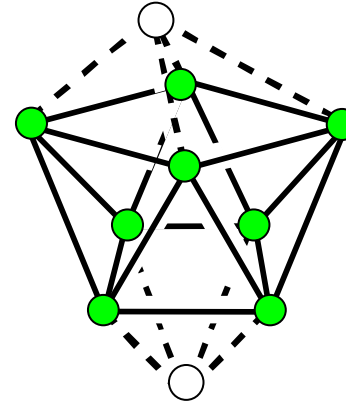
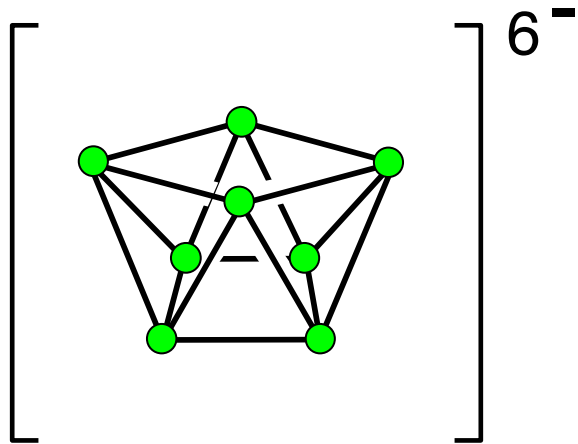
hypercloso - Nonachlorononaboran(9)



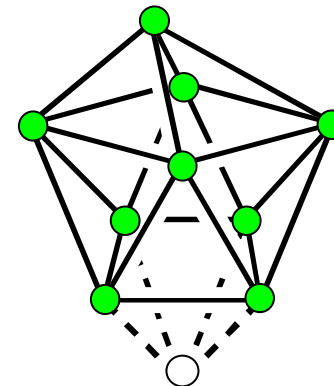
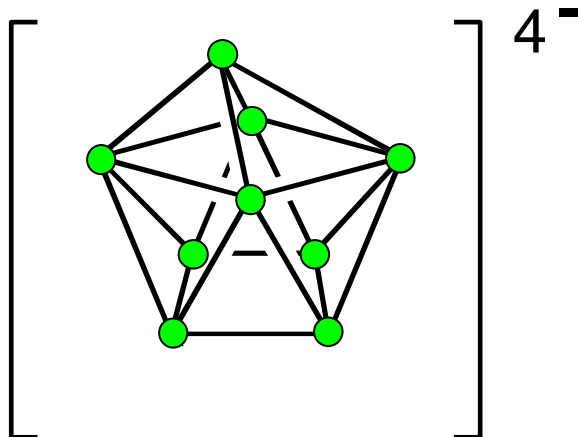
Derartige hypercloso-Cluster besitzen closo-Strukturen.

Zintl-Ionen:

$[\text{Sn}_8]^{6-}$ Clustertyp? **arachno**

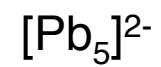
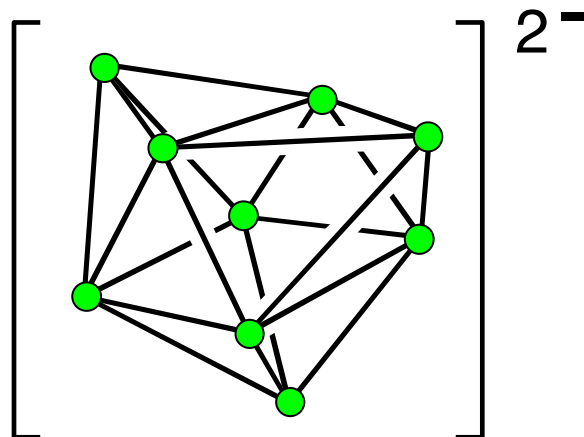


$[\text{Sn}_9]^{4-}$ Clustertyp? **nido**

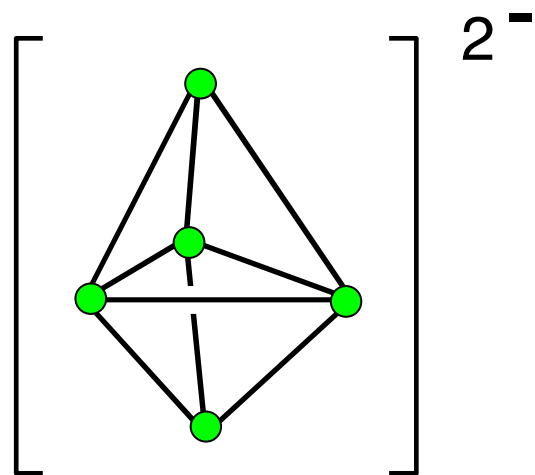




Clustertyp? **closo**

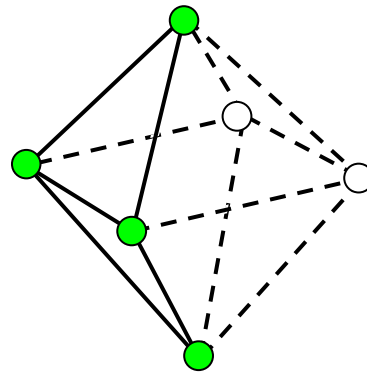
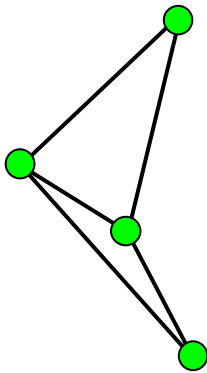


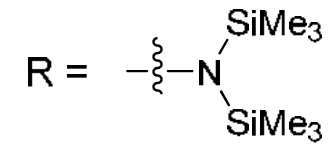
Clustertyp? **closo**



$[\text{Si}_4]^{6-}$ (in Ba_3Si_4)

Clustertyp? **arachno**





$\text{Al}_{69}\text{R}_{18}^{3-}$ und $\text{Al}_{77}\text{R}_{20}^{2-}$ aus AlX und $\text{LiN}(\text{SiMe}_3)_2$ (60°C)

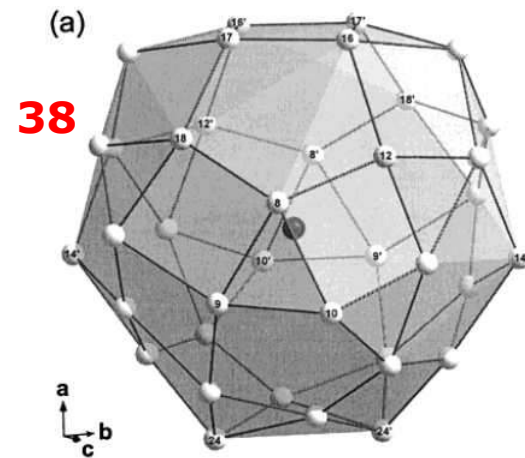
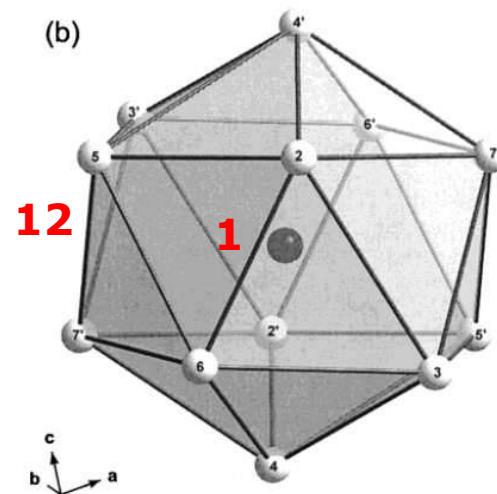
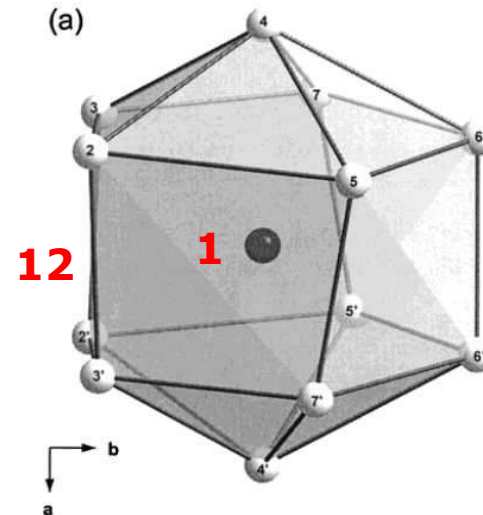
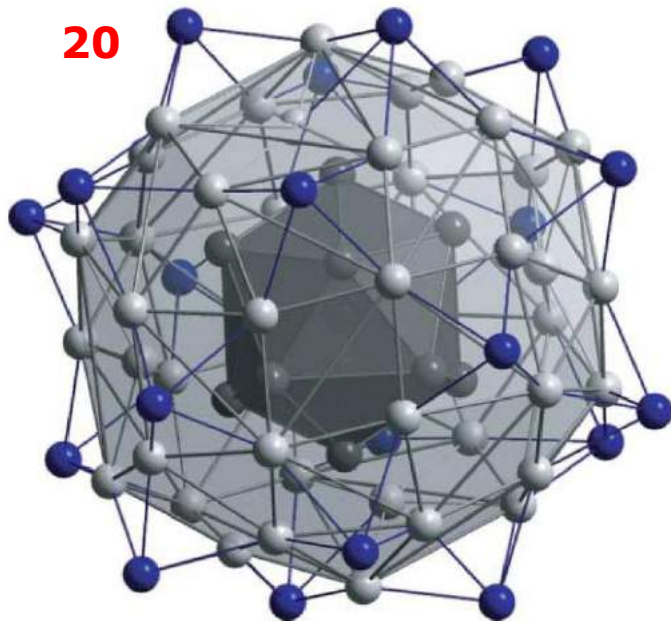
aus Aluminium(I)chlorid

outer shell
18

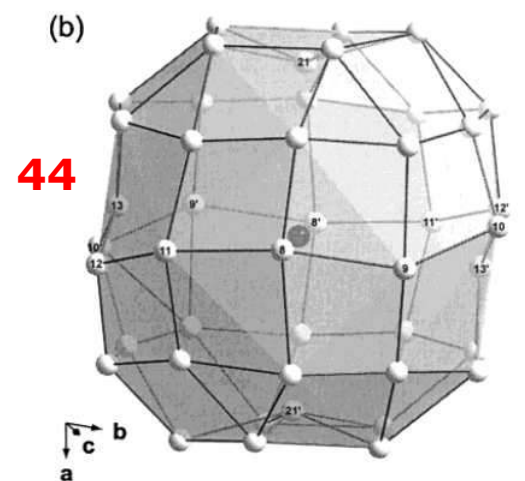


aus Aluminium(I)iodid

20



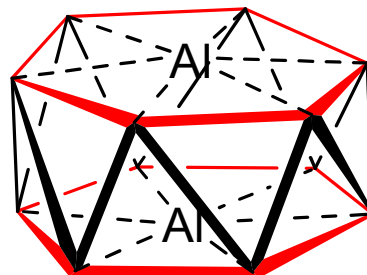
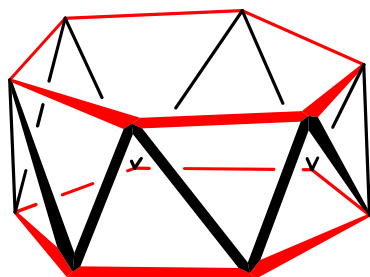
$$\text{Ox} = (18-3)/69 = 0.217$$



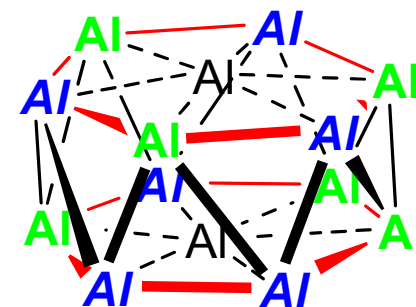
$$\text{Ox} = (20-2)/77 = 0.234$$



Paddle wheel structure



$$\text{Ox} = (12-2)/14 = 0.714$$

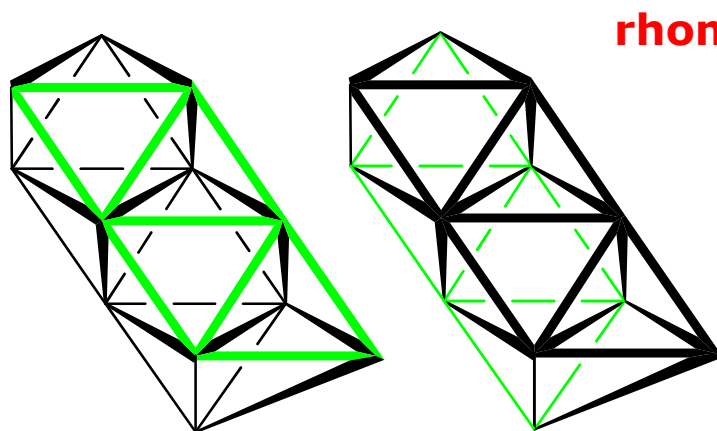
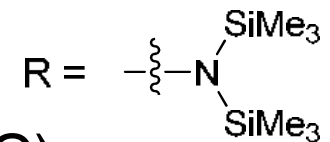


Al = bare aluminium
 Al = iodide-bearing
 Al = amide-bearing

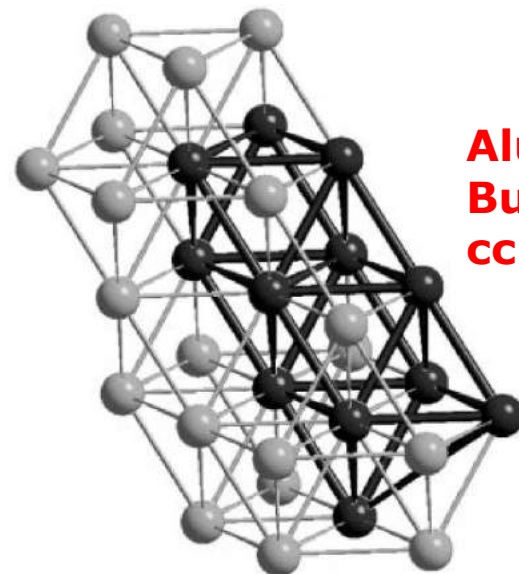
Schnöckel *et al.*, *Angew. Chem. Int. Ed.* 2000, 39, 799.

<http://www3.interscience.wiley.com/cgi-bin/fulltext/70001477/PDFSTART>

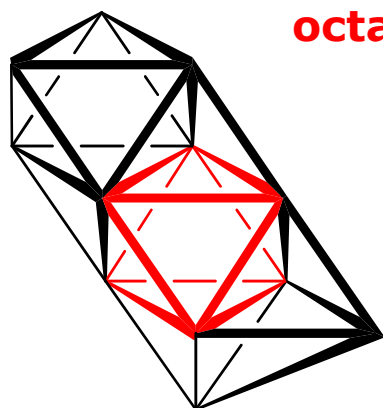
$\text{Al}_{12}\text{R}_8^-$ aus AlCl_3 und $\text{LiN}(\text{Me}_3\text{Si})_2$ (25°C)



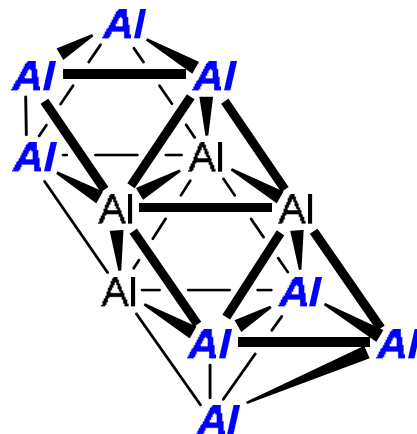
rhomboids



**Aluminium
Bulk
ccp**



octahedra



$$\text{Ox} = (8-1)/12 = 0.583$$

Al = bare aluminium
Al = amide-bearing

Voraussetzung für hohen Umsatz ist die exakte Stöchiometrie (1:1) der Reaktanden, d.h. Edukte müssen möglichst rein vorliegen.

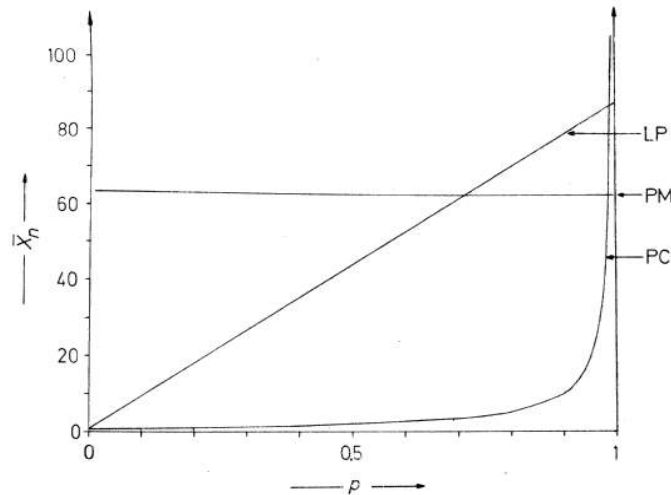


Abb. 15-1: Änderung des Zahlenmittels des Polymerisationsgrades mit dem Umsatz bei lebenden Polymerisationen (LP), Polymerisationen mit monofunktionellem Abbruch (PM) und Polykondensationen (PC). Die Lagen der Geraden bei LP und PM hängen noch vom Monomer/Initiator-Verhältnis ab.

STEP-GROWTH SYNTHESIS

TABLE 2.2 Average Degree of Polymerization as a Function of Extent of Reaction and Reactant Ratios in Step-Growth Reactions^a.

Extent of Reaction	Reactant Ratios			
	Exactly 1.00:1.00	1.01:1.00	1.02:1.00	1.05:1.00
99.9 %	1000	168	92	39
99.	100			
98.	50	40	34	23
97.	33			
96.	25			
95.	20			14
90.	10	<10	9	8

^aThese values are based on the formula $DP = (N_M + N_R) / (N_M + N_R - 2r)$ where N_M and N_R are the moles of the two components M and R, r is the extent of reaction, and DP is the average degree of polymerization.

Polykondensationen beruhen auf der Reaktion bifunktioneller Moleküle; funktionalisierte anorganische/metallorganische Spezies sind i.A. wesentlich reaktiver als organische und kaum in ausreichender Reinheit für hohe Umsätze bei Polykondensationen darstellbar.

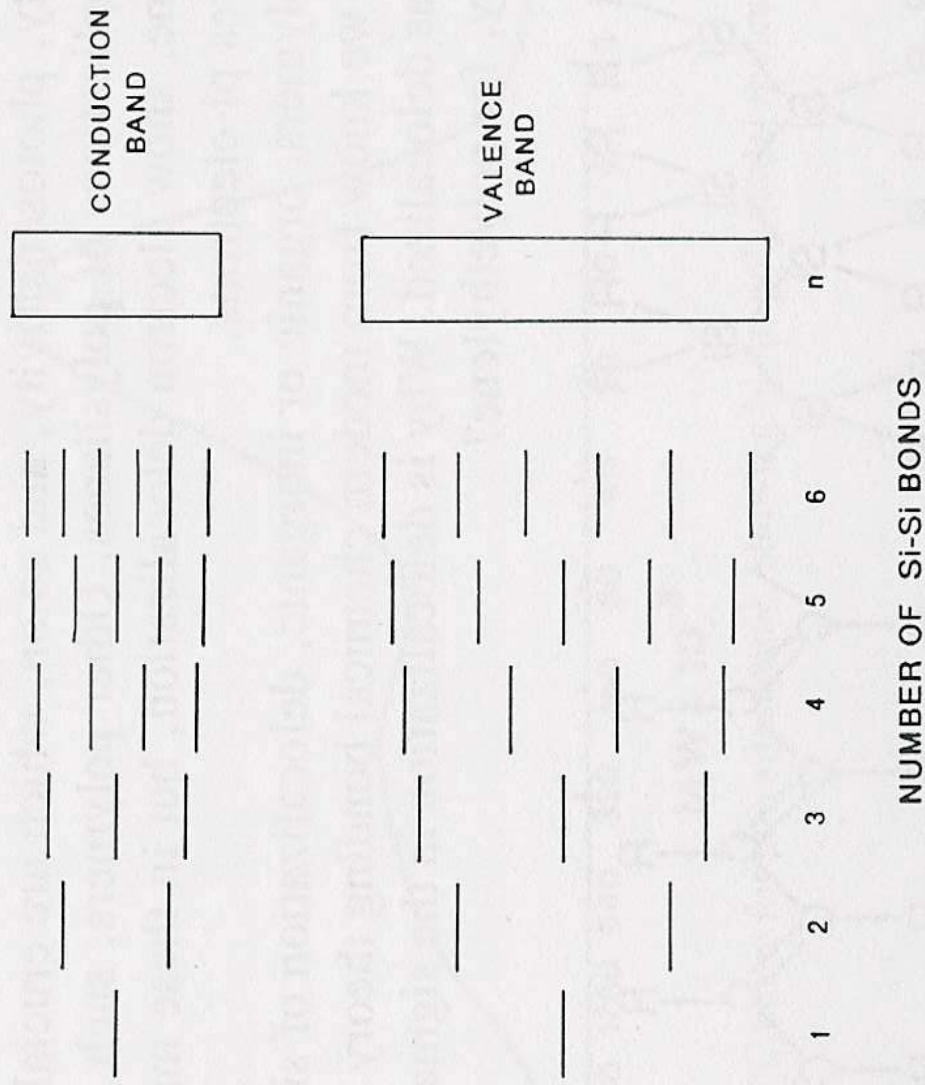
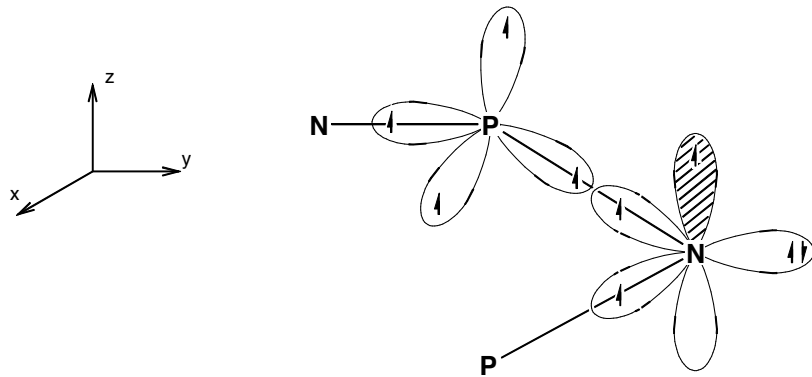


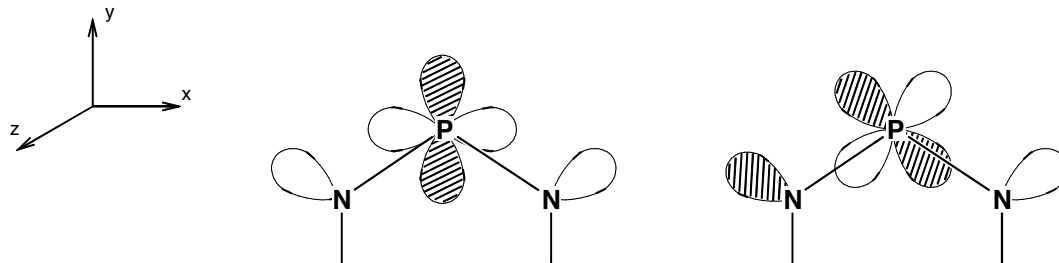
Figure 5.8 Schematic diagram showing splitting of filled and unfilled energy levels for a polysilane as the length of the chain increases, leading to formation of a valence band and a conduction band.



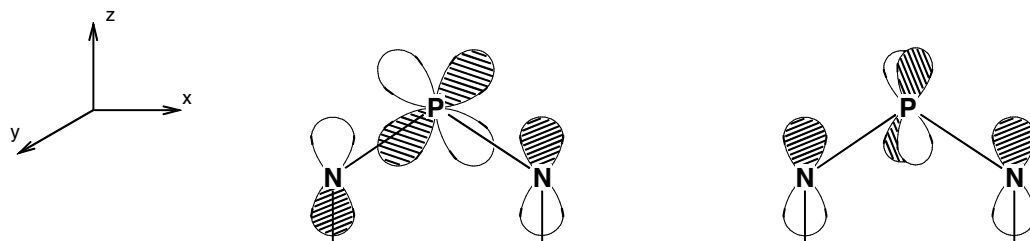
hybridisation at N (sp^2) and P (sp^3) showing a lp on N

Erklärung der Bindungsverhältnisse unter Beteiligung von d-Orbitalen am Phosphor (sog. π' -Bindung wg. Knotenebene am P und Unterbrechung der Delokalisation)

trifft nicht zu.

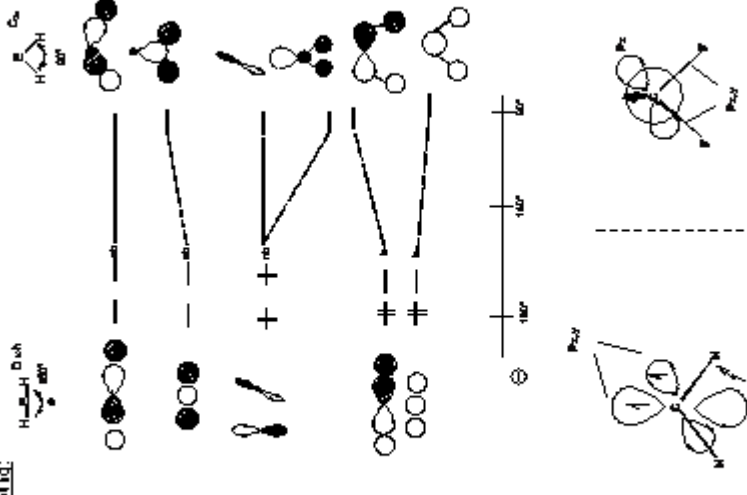


π' interactions in the ring plane between lp on N and d-AO's on adjacent P



π interactions between p_z AO on N and d-AO's on adjacent P

MO-Beschriftung:

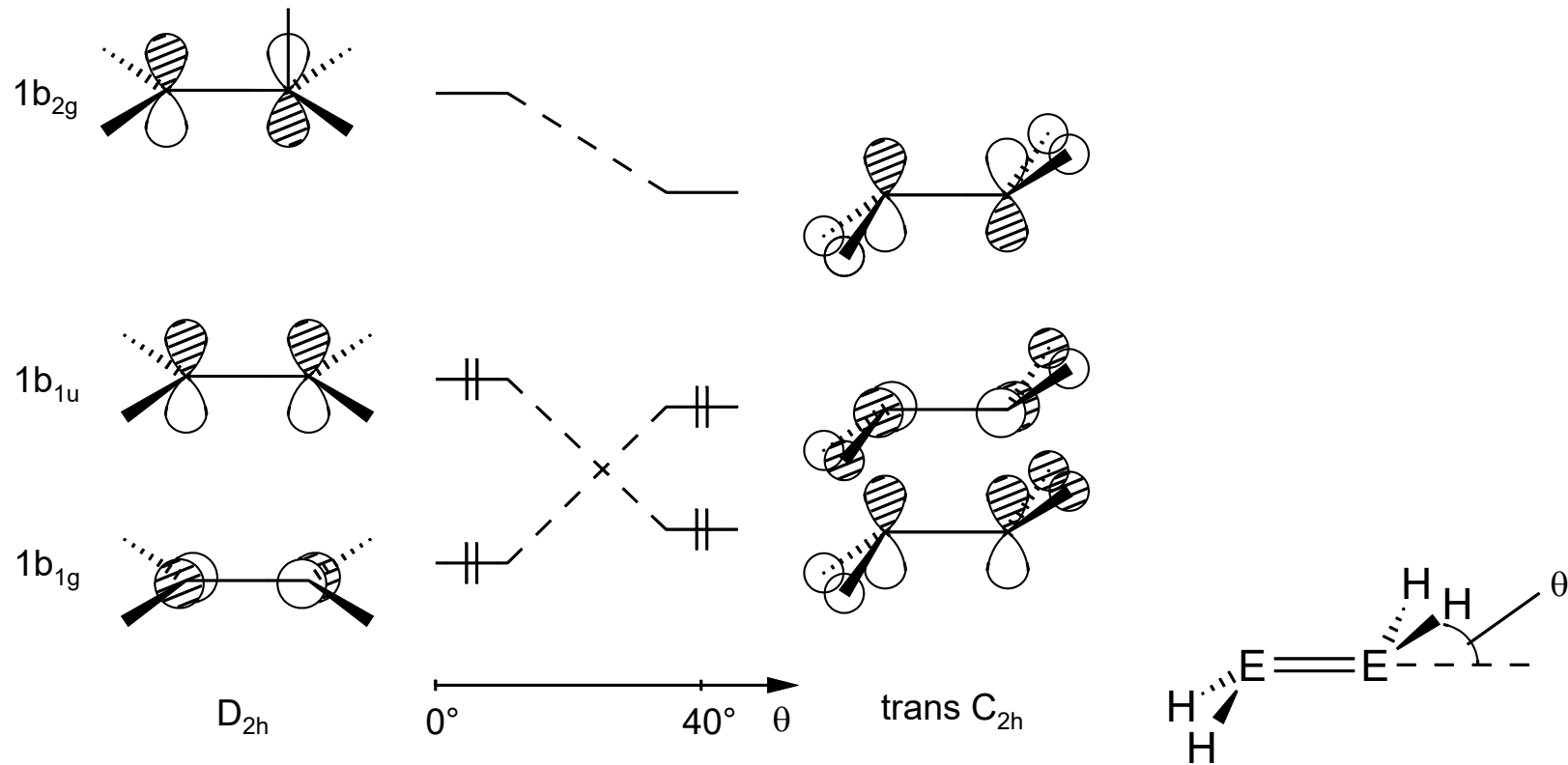


sp-Hybrid (aus beiden sp²)

sp²-Hybridisierung

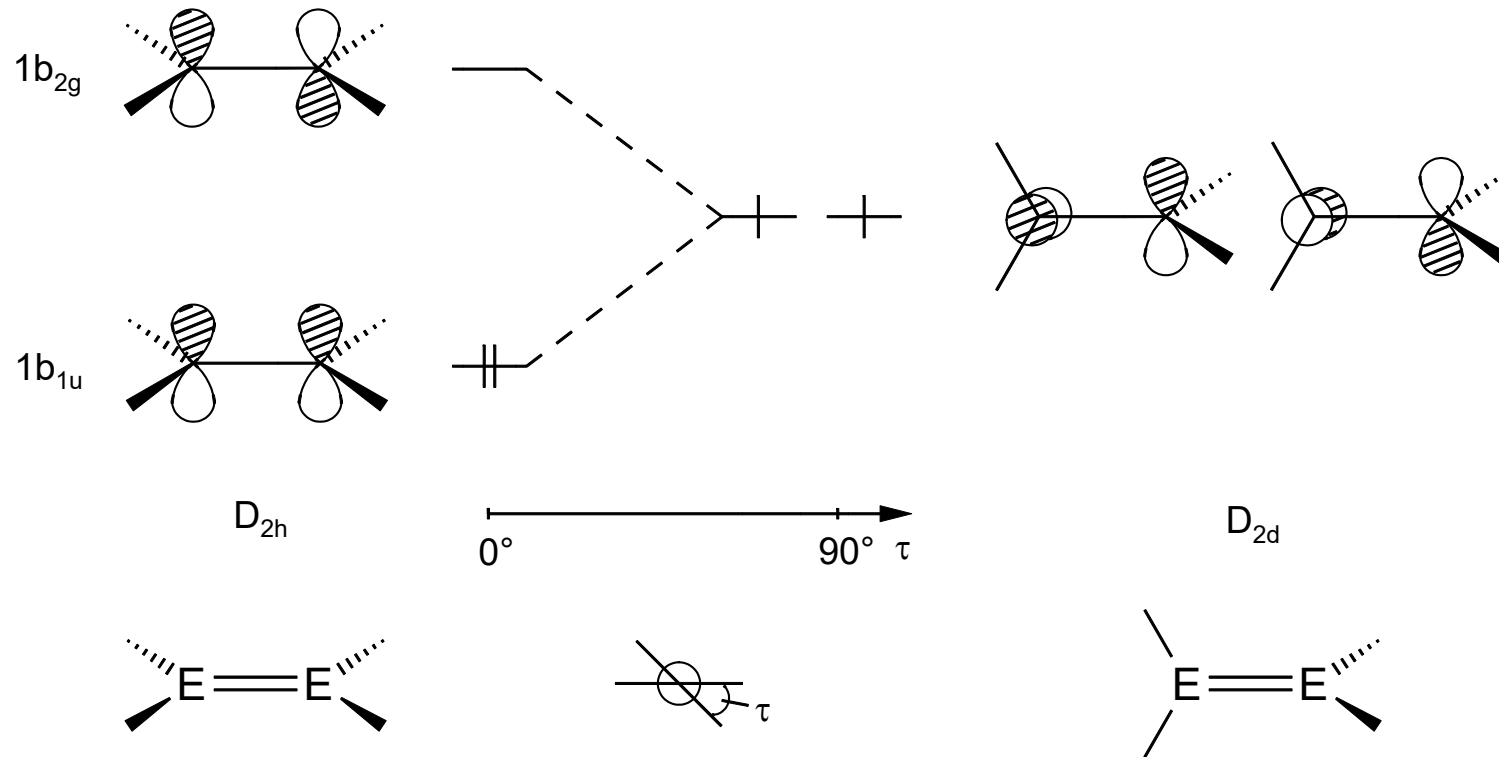
Benzische Regel:
 erregte Substanzien (f) bezeugen p-orbitale
 C-F Bindung überlagert p-orb., LP ins-NO

Korrelationsdiagramm für $D_{2h} \rightarrow C_{2h}$ (trans-bent) (Orbitale um 90° gedreht)



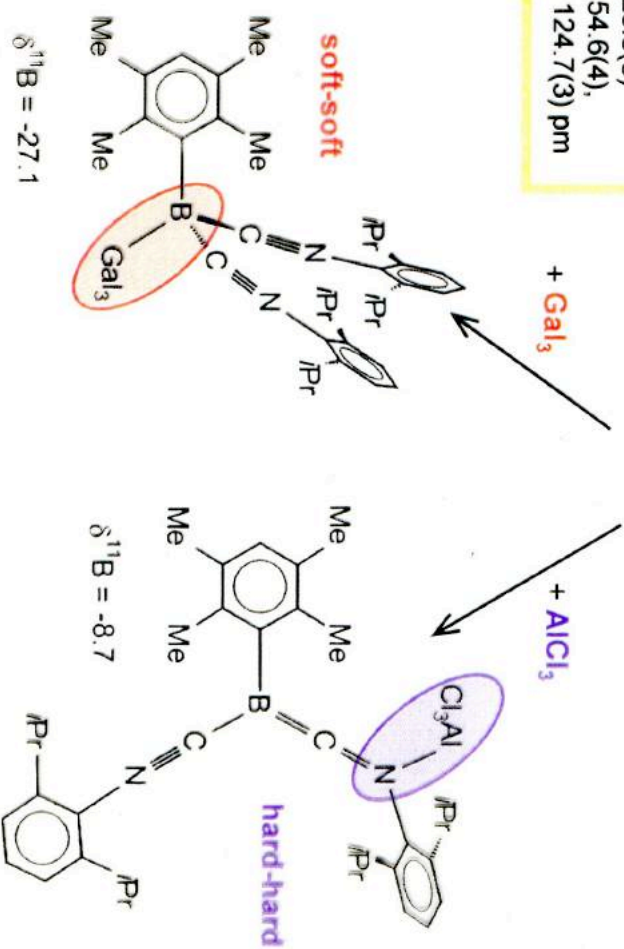
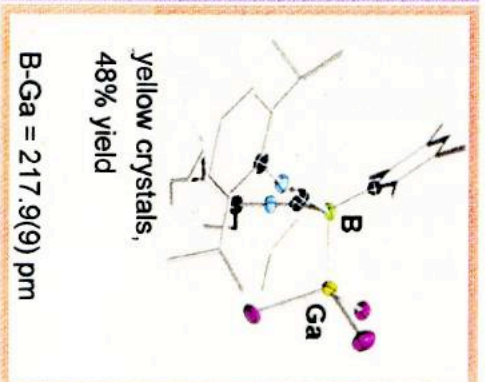
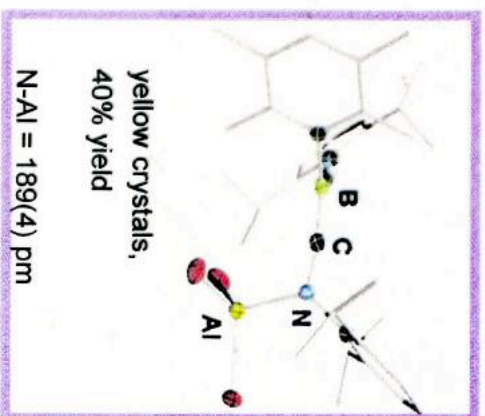
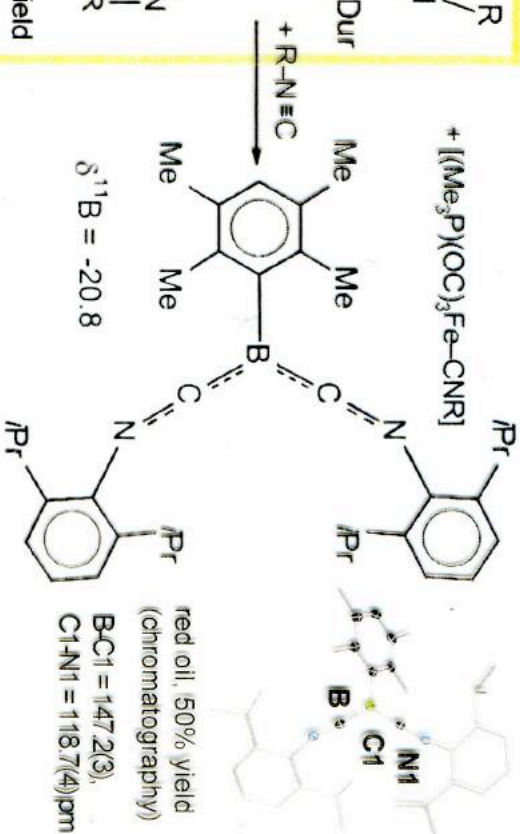
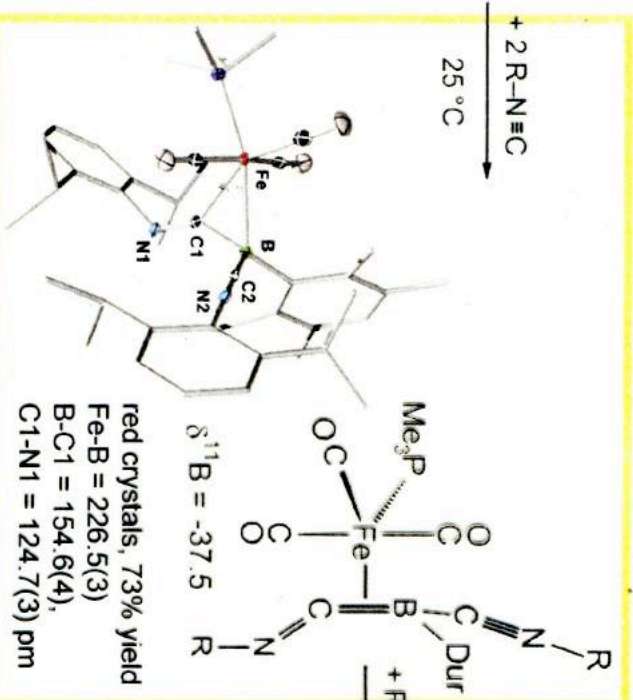
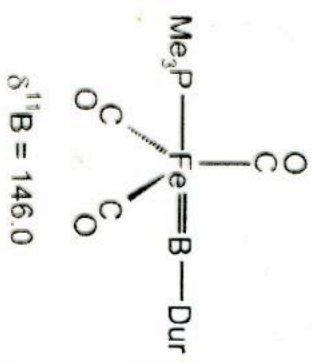
HOMO-LUMO Gap wird kleiner und hängt vom Winkel θ ab

Korrelationsdiagramm für $D_{2h} \rightarrow D_{2d}$ (twisted) (Orbitale um 90° gedreht)



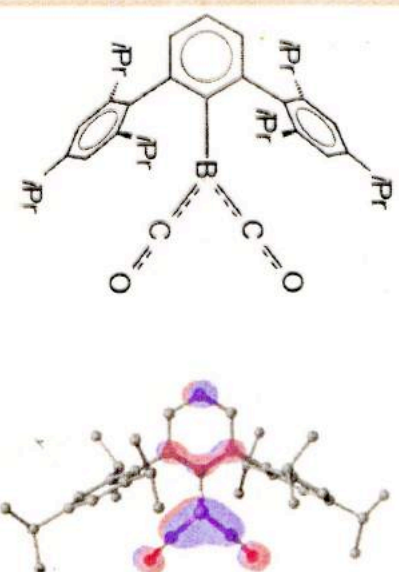
HOMO-LUMO Gap wird kleiner und hängt vom Winkel τ ab; für $\tau = 90^\circ$ entartete Orbitale m. Triplett-Zustand.

Borylene Bisisonitrile Adducts: Formation and Reactivity



Borylene CO and R-NEC Adducts: Metal-like Properties

synergistic, metal-like B-CO σ - π -bond



B1-C1 = 147.5(3),
C1-O1 = 115.2(2) pm
 $\nu_{CO} = 1942, 2060 \text{ cm}^{-1}$

HOMO @ B3LYP/6-311G*
Nature **2015**, 522, 327.

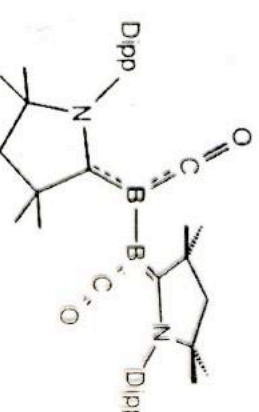
borane-CO σ -complex



B1-C1 = 166.0(3),
C1-O1 = 110.5(5) pm
 $\nu_{CO} = 2249 \text{ cm}^{-1}$

Willner, 2010

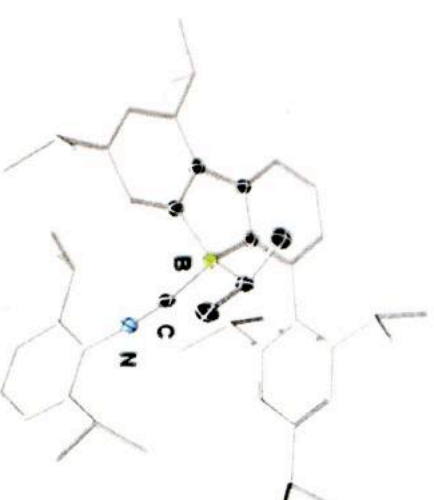
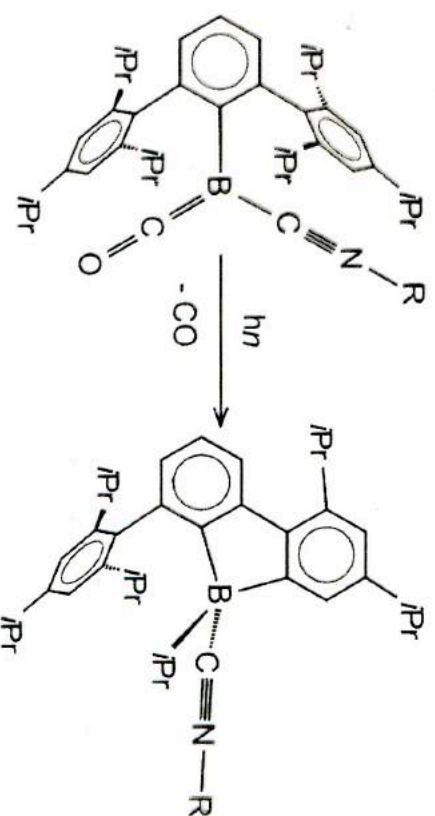
bis-boraketene



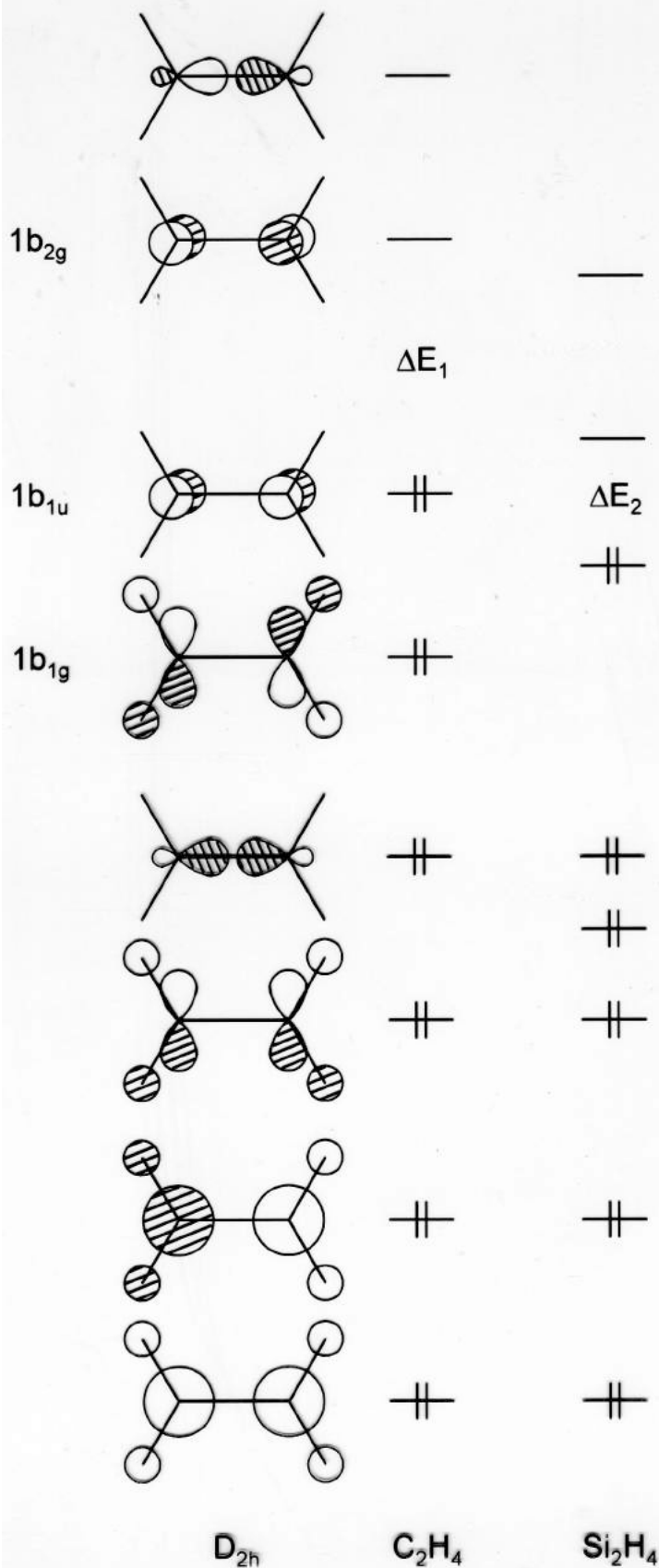
B1-C1 = 147.7(2), C1-O1 = 117.3(2) pm
 $\nu_{CO} = 1928 \text{ cm}^{-1}$

Angew. Chem. Int. Ed **2015**, 54,
DOI: 10.1002/anie.201506368.

photoytic CO-release and C-C-bond activation

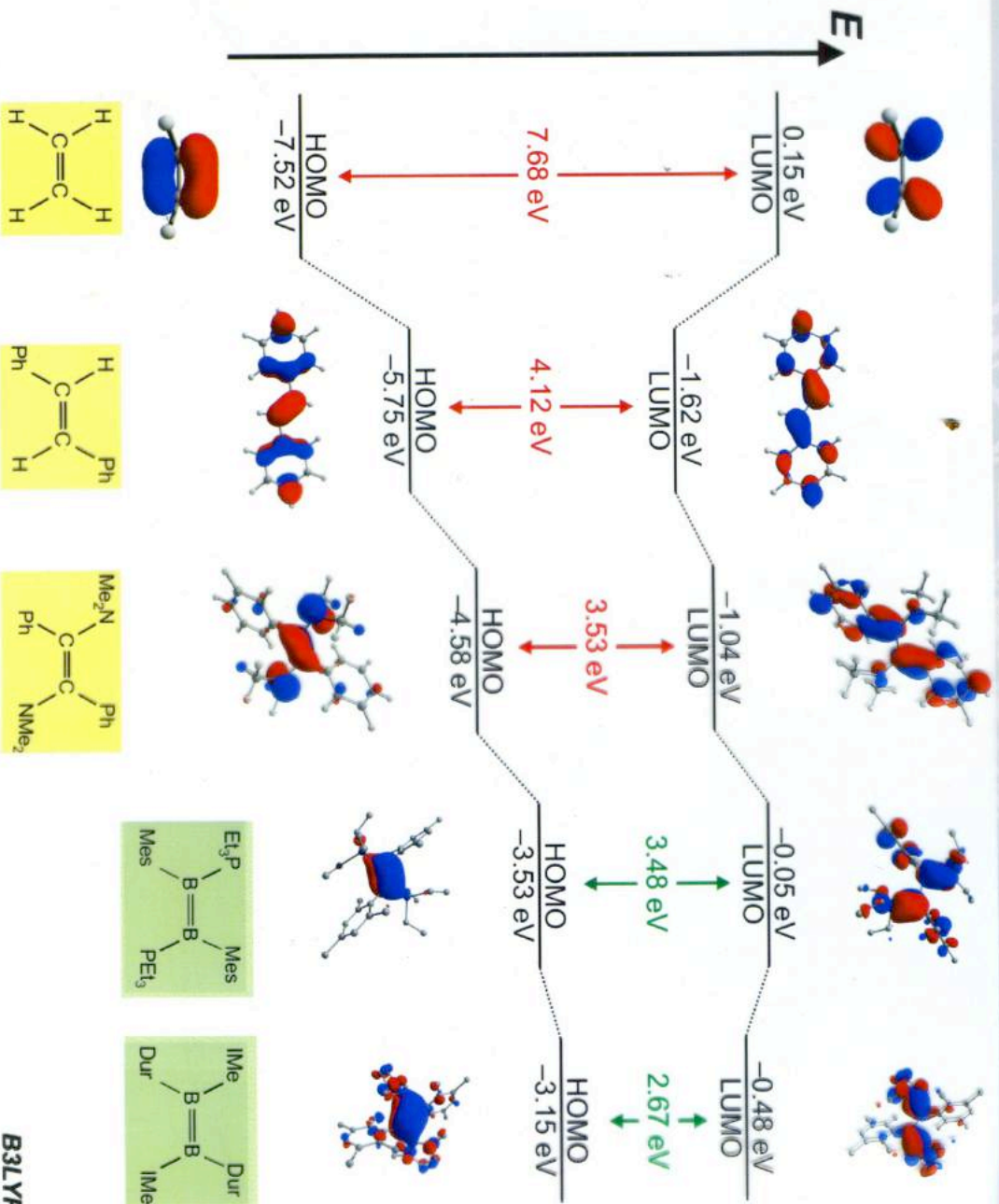


Beschreibung über MO; JACS, 1994, 116, 3667.



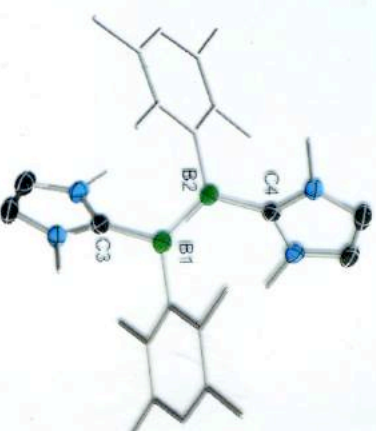
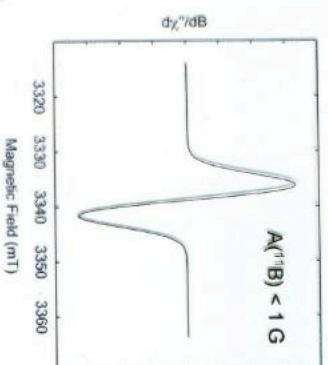
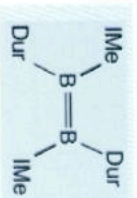
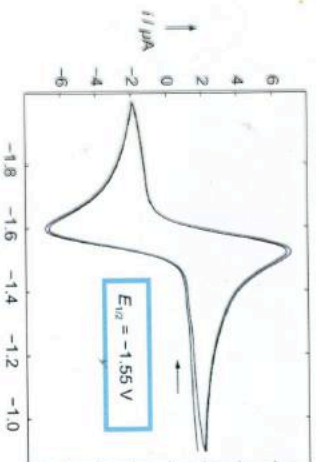
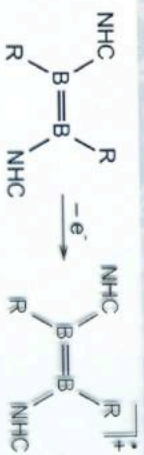
- gleiche Abfolge wie bei C₂H₅
aber kleineres HOMO-LUMO
gap ($\Delta E_2 < \Delta E_1$)

Diborenes: Electronic Properties

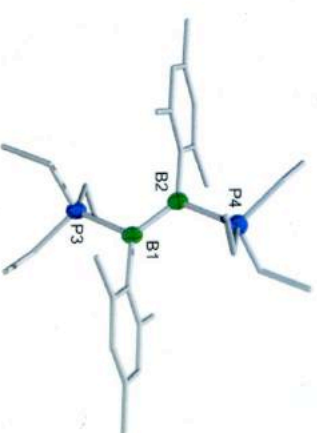
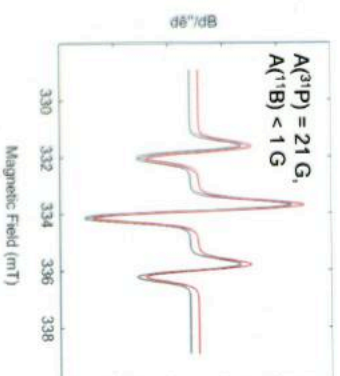
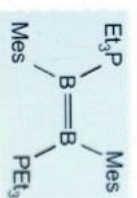
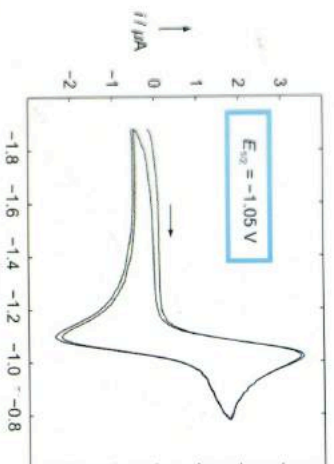


B3LYP/6-311G*

Diborenes: Redox Properties

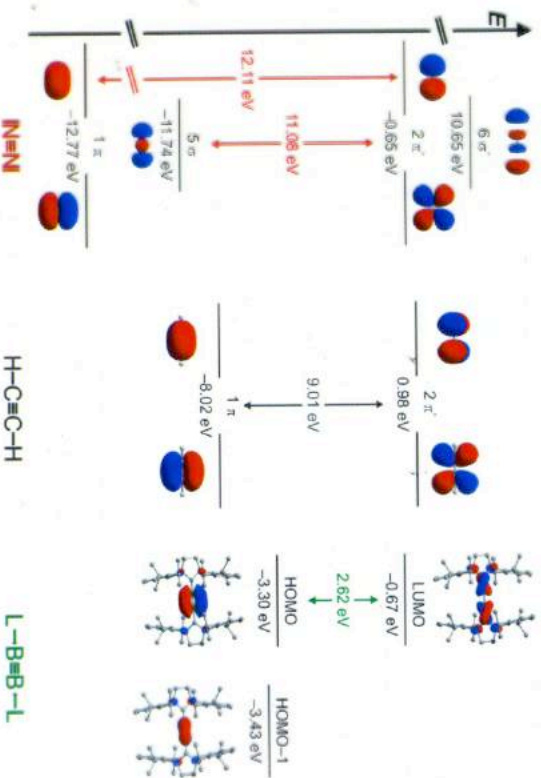


B-B = 163.6(4) pm (c.f. 159.0(56))

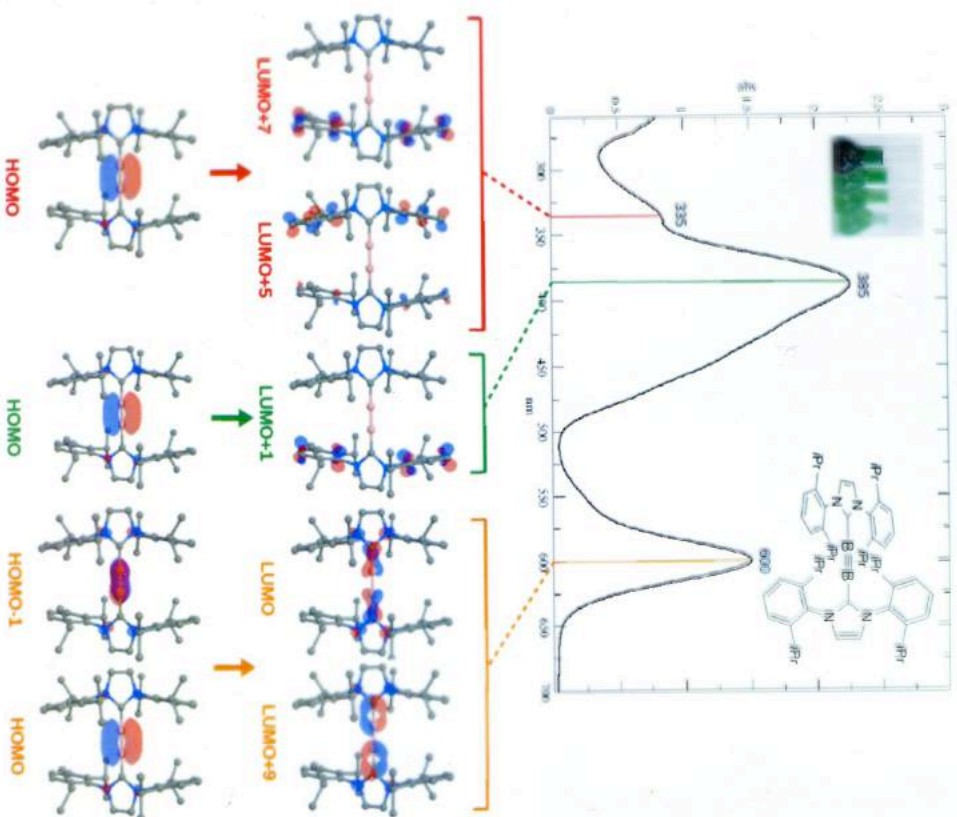


B-B = 163.1(6) pm (c.f. 157.9(3))

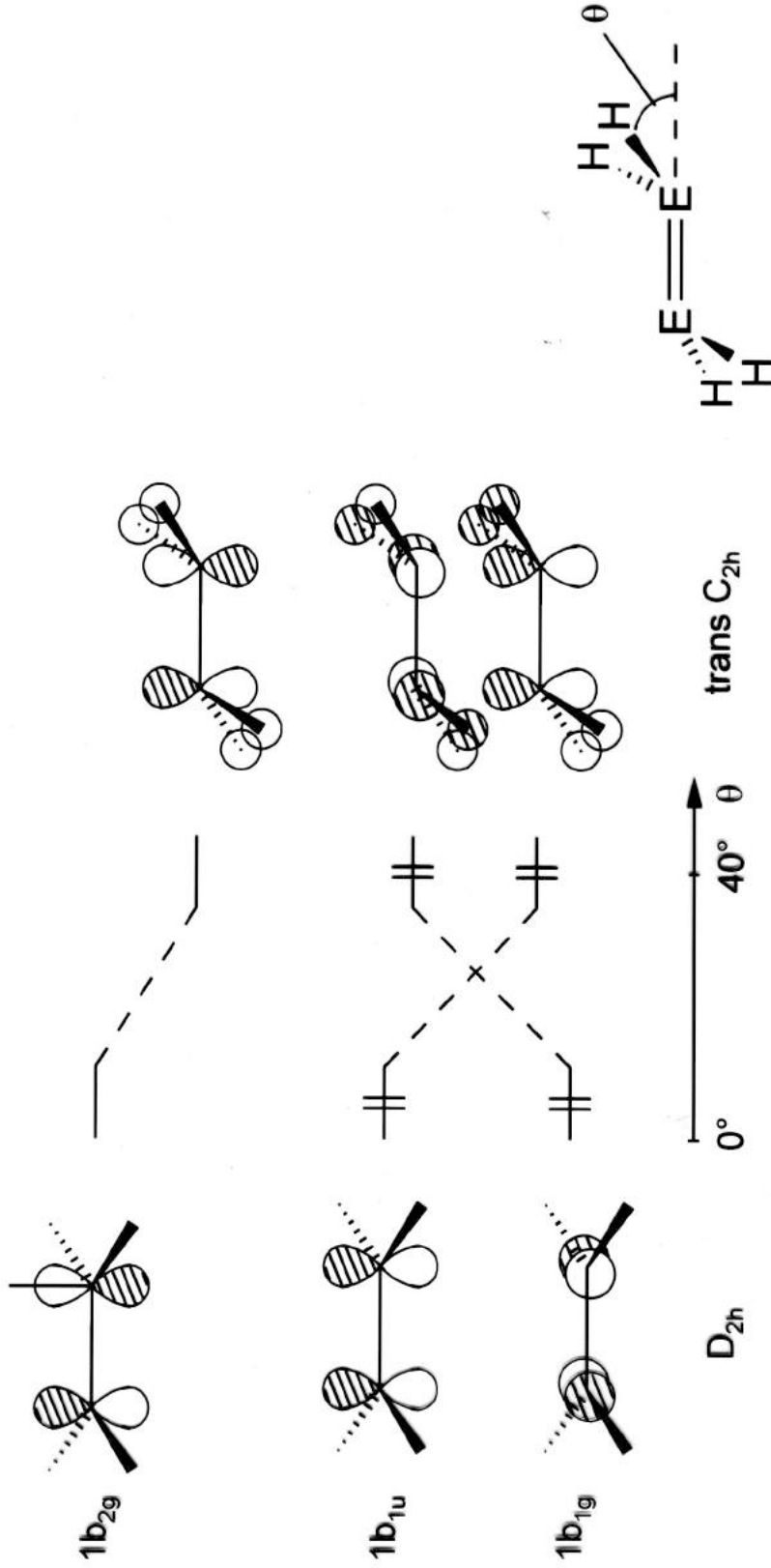
- Diborynes $\text{NHC}-\text{B}\equiv\text{B}-\text{NHC}$:
- highly reactive
 - strong chromophores
 - strong reductants!!



small HOMO-LUMO gap \rightarrow high HOMO \rightarrow
 -colour
 -reactivity
 -very electron rich
 -strong reductants

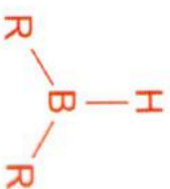


Korrelationsdiagramm für $D_{2h} \rightarrow C_{2h}$ (trans-bent) (Orbitale um 90° gedreht)

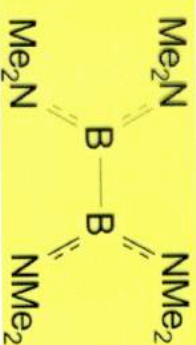
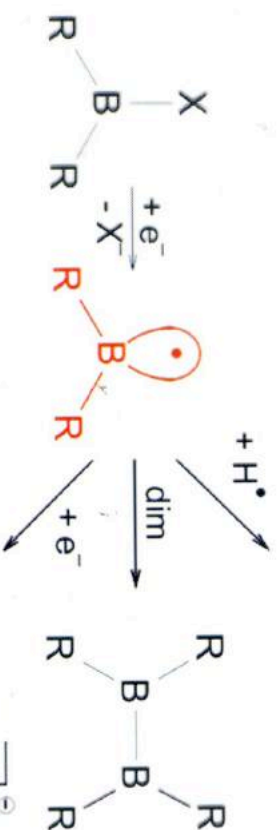


HOMO-LUMO Gap wird kleiner und hängt vom Winkel θ ab

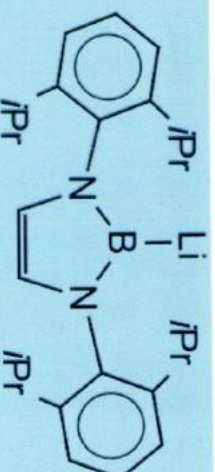
Reduction of Haloboranes: Diboranes(4) and Borylanions



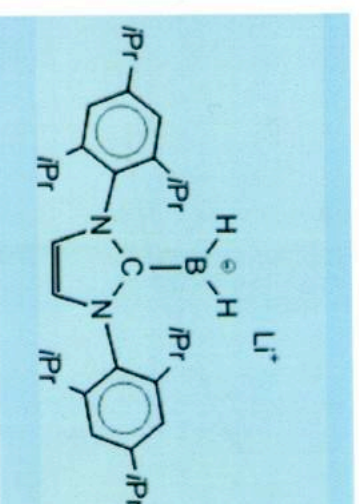
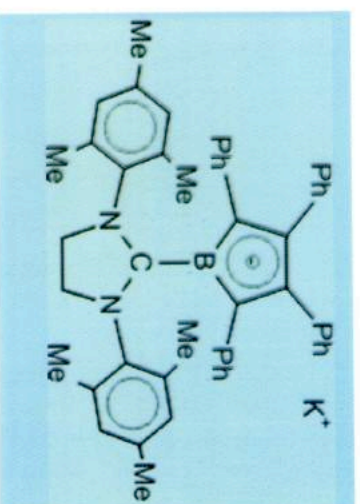
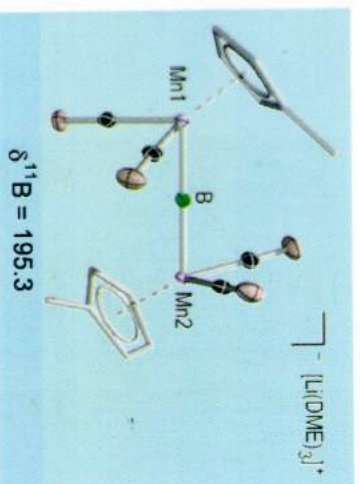
**radical (H) abstraction
occurs in > 99% of all cases**



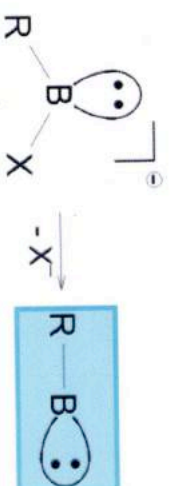
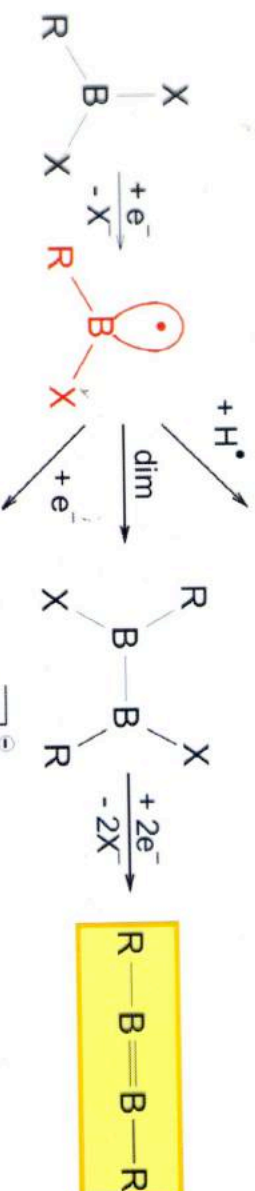
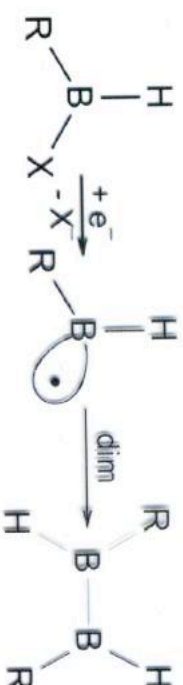
diborane(4) formation by radical
homocoupling **ONLY** for R = NMe₂.
Brotherton,
J. Am. Chem. Soc. **1960**, 82, 6242.



borylanion formation by
2nd 1e⁻-reduction in 4 cases:
Yamashita, Nozaki
Science, **2006**, 314, 113.



Reduction of Dihaloboranes: Diborenes and Borylenes



- 20 years of efforts met with little success:
- no selective synthesis developed
 - no diborene/borylene isolated



use of carbenes (NHC's) to stabilize intermediates and products

carbene (NHC) stabilized:

