

# Strukturaufklärung in der molekularen anorganischen Chemie

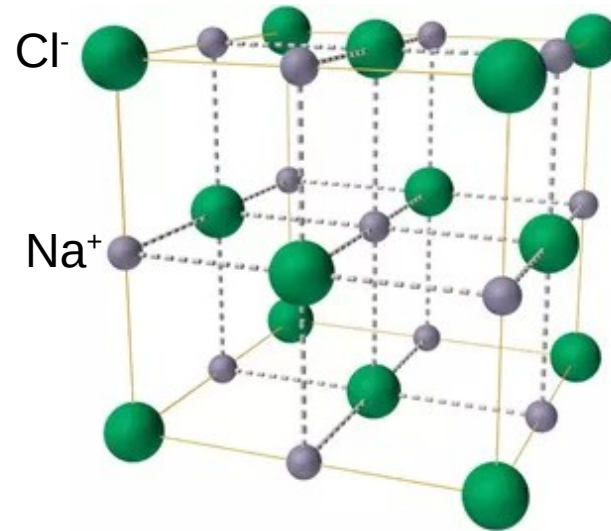
## 11. Strukturverfeinerung,

## Phasenabhängige Strukturen

# Strukturverfeinerung

# Als Anekdote...

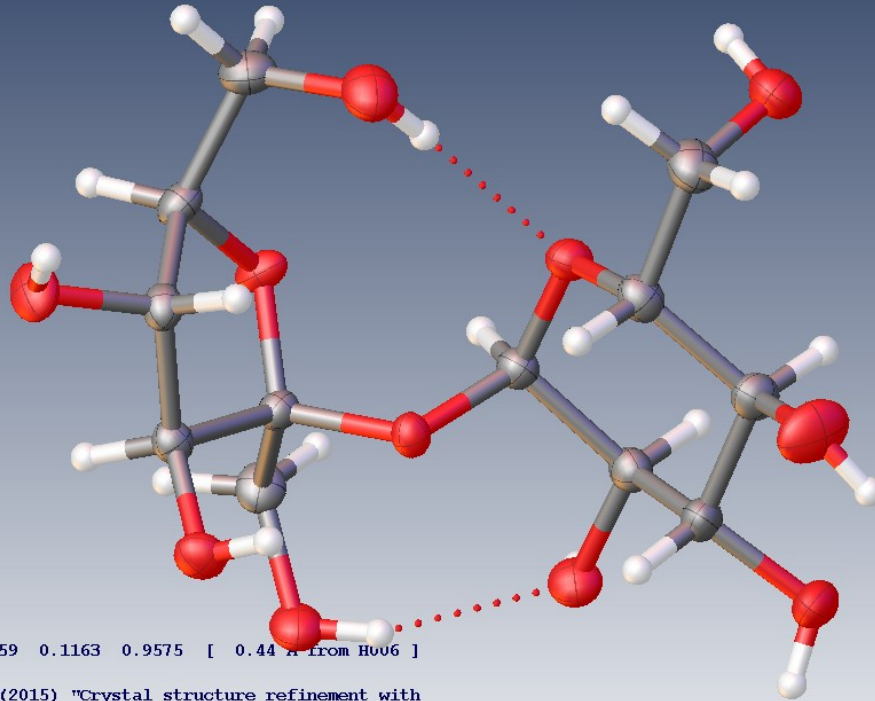
Natriumchlorid



Kubisch  $Fm3m$

Dichte  $\rho = 2.1615 \text{ g}\cdot\text{cm}^{-3} \rightarrow r(\text{Na}-\text{Cl})$  aus  $\rho$  [Versuche selber zu rechnen]

# Olex2 für XRD



Deepest hole -0.18 at 0.3159 0.1163 0.9575 [ 0.44 Å from H006 ]

Please cite: G.M. Sheldrick (2015) "Crystal structure refinement with SHELXL", Acta Cryst., C71, 3-8 (Open Access) if SHELXL proves useful.

```
+++++  
+ sucrose finished at 20:45:34 Total elapsed time: 0.50 secs +  
+++++  
Hoofst y: -0.0(4), Parson's q: -0.3(5), Flack x: 0.6(9)
```

**Sucrose** P2<sub>1</sub>  
/home/yjura/Apps/Olex2/sucrose/sucrose.res

**C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>**

a = 7.7727(9)	α = 90°	Z = 3	R <sub>1</sub> <b>3.11</b> % wR <sub>2</sub> <b>7.46</b> %
b = 8.7216(11)	β = 102.983(11)°	Z' = 1.5	
c = 10.8637(11)	γ = 90°	V = 717.63(15)	

d min (Mo) 0.73 | I/σ(I) 32.7 | Rint 3.39% | Full 50.5° 99.7%  
2θ=58.4° | Shift -0.003 | Max Peak 0.2 | Min Peak -0.2 | GooF 1.059 | Hoofst -0.0(4)

Cell contents from UNIT instruction and atom list do not agree

Home | **Work** | View | Tools | Info

Solve | Refine | **Draw** | Report

Program ShelXL | L.S. | Cycles 5 | Peaks 4

hkl file sucrose.hkl | hkl: Tue Jan 11 20:44:18 2022

Weight  .035 | .033 | .079 | .096 | EXTI  0.020(4) | ACTA

Use Solvent Mask This is the Olex2 implementation of BYPASS (a.k.a. SQUEEZE)

Refinement Settings Extra

**Toolbox Work**

Labels Labels OFF/ON

C H O ...  Add H

QC to QH | Hx | Z' = 1.5

Select atom(s) and then mFit mSplit Split SAME SHIFT+Move

MAP Show Map Map Settings

Peak & Uiso Sliders

Growing

Finishing

History

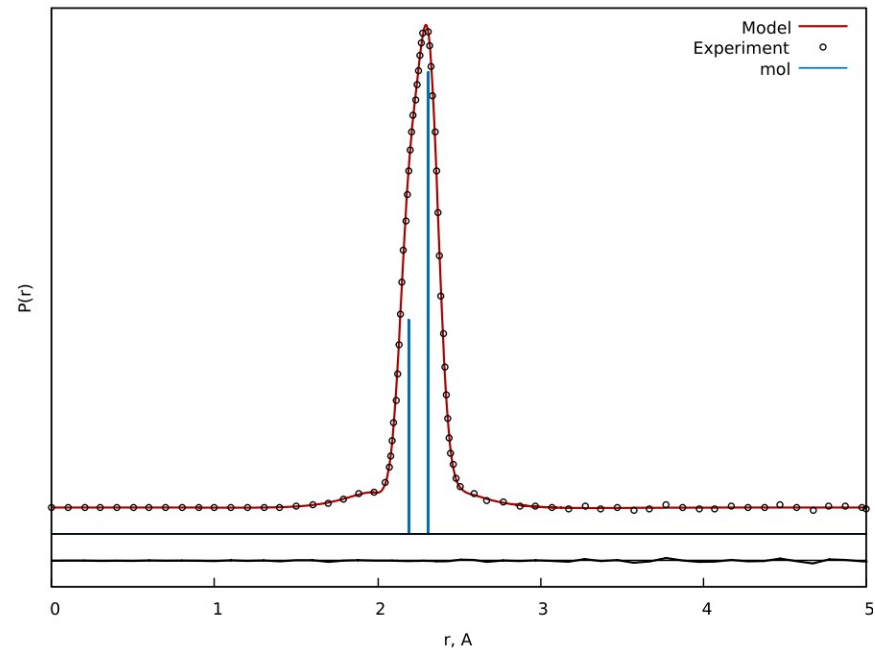
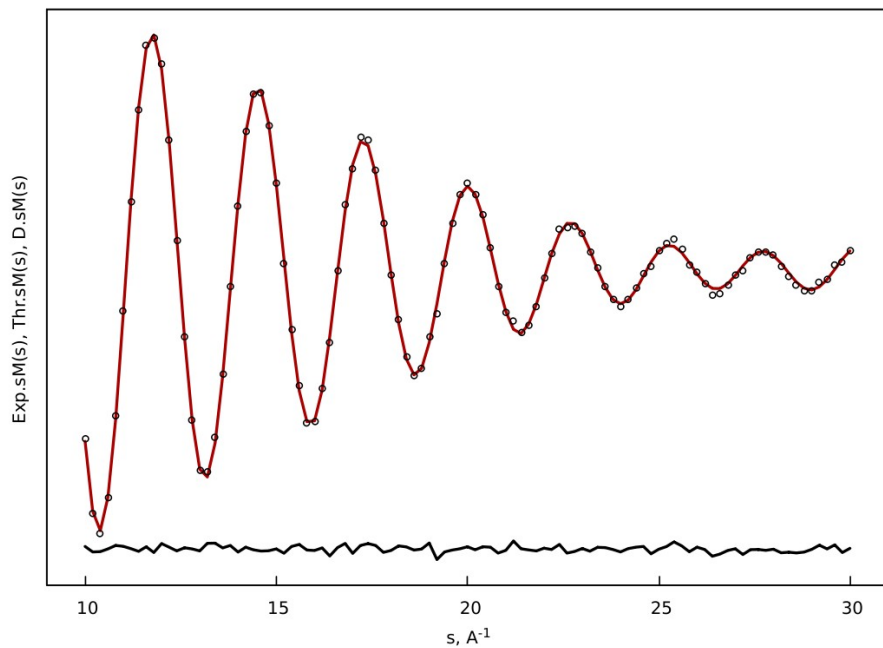
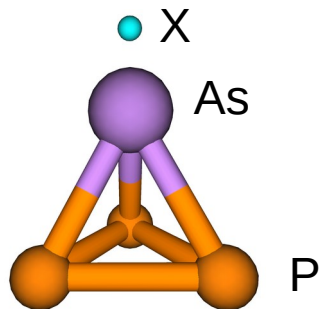
Select

Naming

Sorting

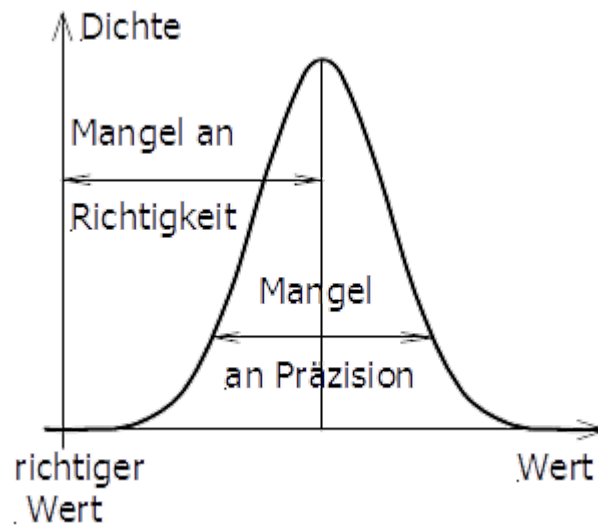
# UNEX für GED u./o. Rot. Konstanten

s. Beispiel für  $\text{AsP}_3$



# Statistik

$$r = 1.234(5)$$



Präzision  $\neq$  Richtigkeit  
Präzision + Richtigkeit = Genauigkeit

# Phasenabhängige Strukturen



Feststoff

≠



Flüssigkeit

≠



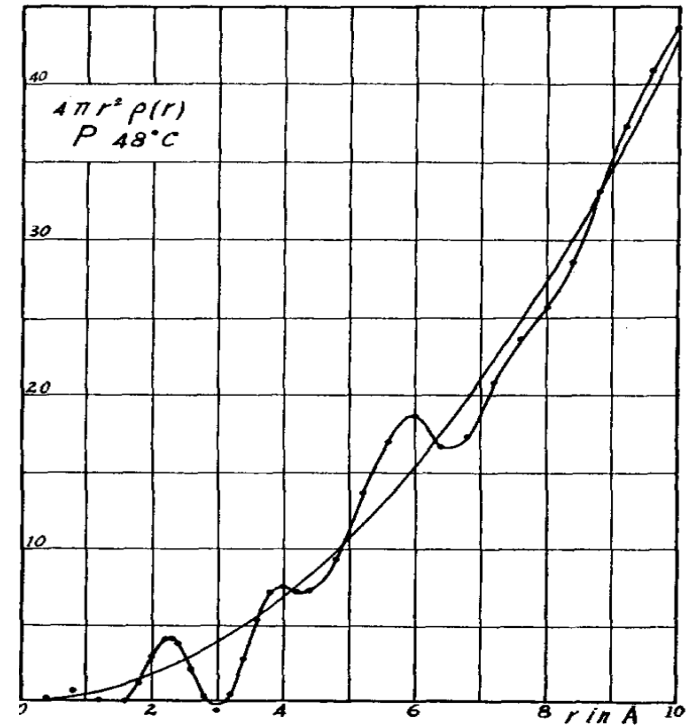
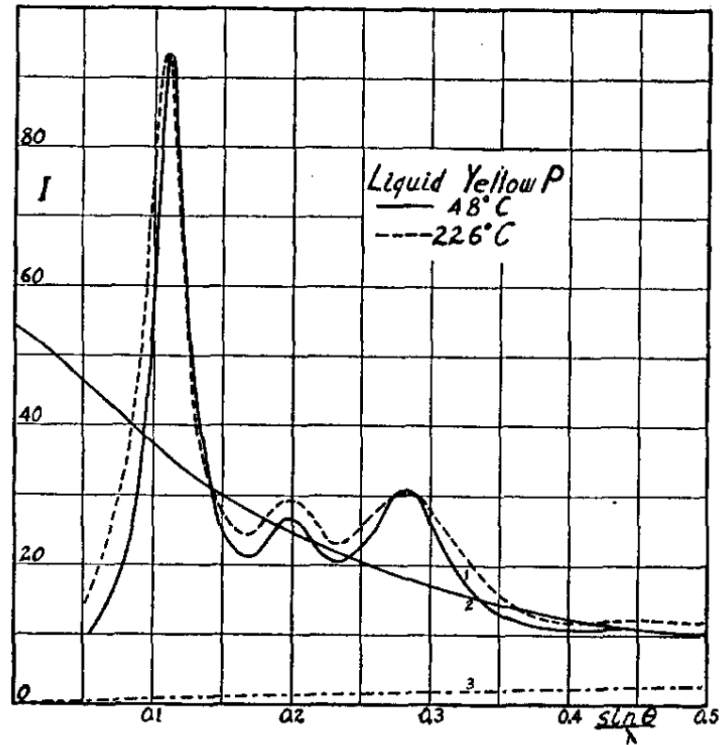
Gas

# Themen

- Bindungslängenvariationen
- Schwache Bindungen / Sterische Effekte
- Packungseffekte generell
- Mesomerie / Polarität
- Dative Bindungen / Polarität
- Polymorphie
- Dispersive Wechselwirkungen



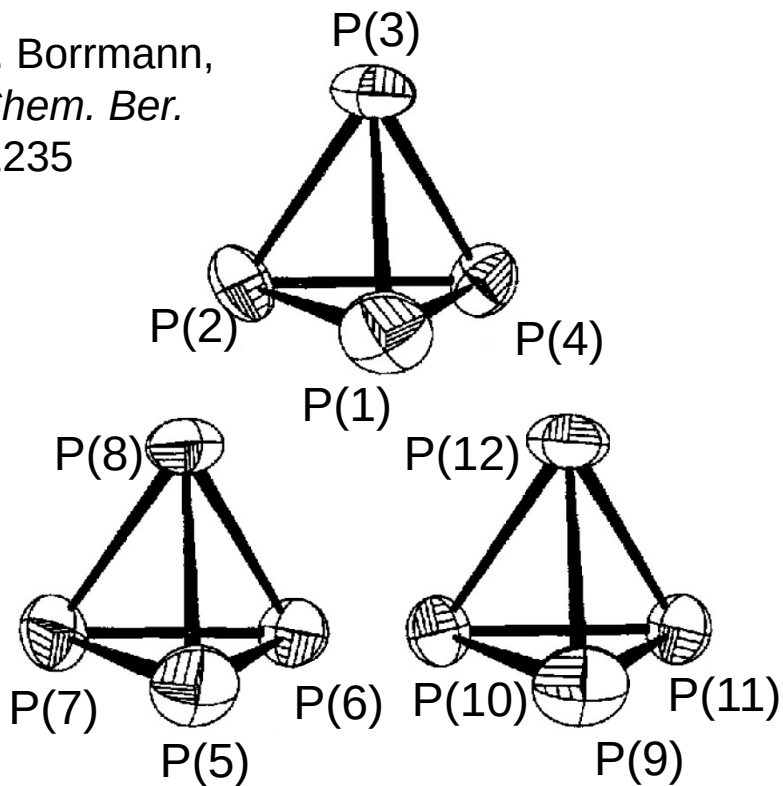
# XRD an flüssigem P<sub>4</sub>



$r = 2.25 \text{ \AA}$  bei 48°C

# P<sub>4</sub> Kristall

A. Simon, H. Borrmann,  
J. Horakh, *Chem. Ber.*  
**1997**, 130, 1235



P(1)-P(2)	2.1819(5)	
P(1)-P(3)	2.1910(5)	
P(1)-P(4)	2.1801(5)	
P(2)-P(3)	2.1828(5)	
P(2)-P(4)	2.1849(5)	
P(3)-P(4)	2.1768(5)	
P(5)-P(6)	2.1771(5)	
P(5)-P(7)	2.1756(5)	← min
P(5)-P(8)	2.1866(5)	
P(6)-P(7)	2.1920(5)	← max
P(6)-P(8)	2.1777(5)	
P(7)-P(8)	2.1808(5)	
P(9)-P(10)	2.1851(5)	
P(9)-P(10)	2.1834(5)	
P(9)-P(12)	2.1834(5)	
P(10)-P(11)	2.1818(5)	
P(11)-P(12)	2.1841(5)	
P(10)-P(12)	2.1874(5)	

Vgl.:

**GED:**  $r_g(\text{P-P}) = 2.1994(3) \text{ \AA} @ 373 \text{ K}$

**XRD** am flüssigk.: 2.25 @ 321 K

**Rechnung:**  $r_e = 2.1860$  [CCSD(T)-F12/apwCV5Z]

**XRD Durchschnitt: 2.183(5) \AA**

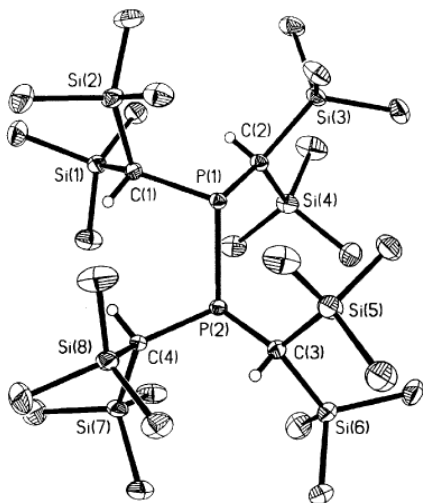
# Schwache Bindungen + Sterische Effekte

“Persistente Phosphinyl-Radikale vs. Diphosphin: ein molekularer Kistentenauflöser“

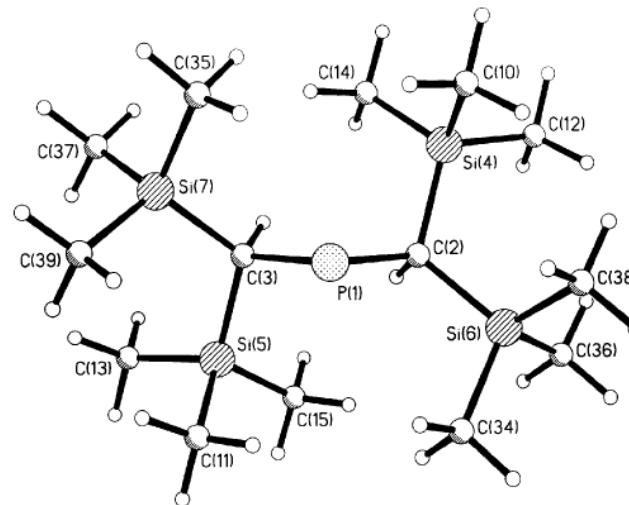
S. L. Hinchley et al., *J. Am. Chem. Soc.*, **2001**, 123, 9045.



P–P  
2.310(1) Å



Festkörper (dimer)  
P–C 1.892(2) - 1.896(2) Å  
C–P–C 103.0(1) - 103.6(1) °



Gasphase (monomer)  
1.856(11) Å  
104.0(10) °

P–C  
C–P–C

# Polarität + Mesomere Effekte

XRD

GED  $r_a$

1.453(2)

1.410(5)

112.7(2)  
115.9(24)

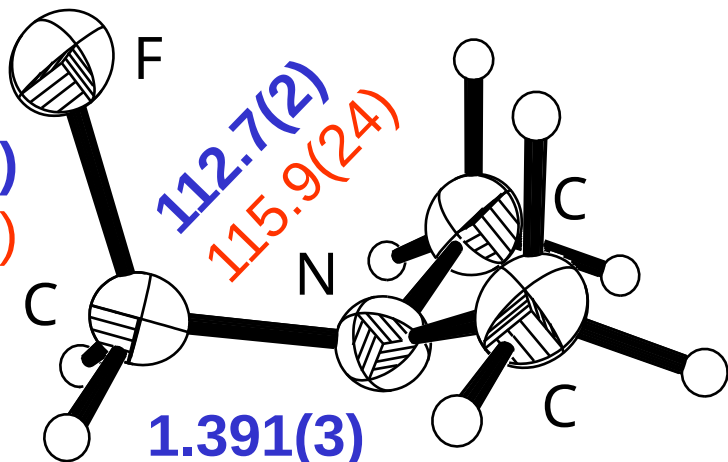
1.391(3)

1.408(13)

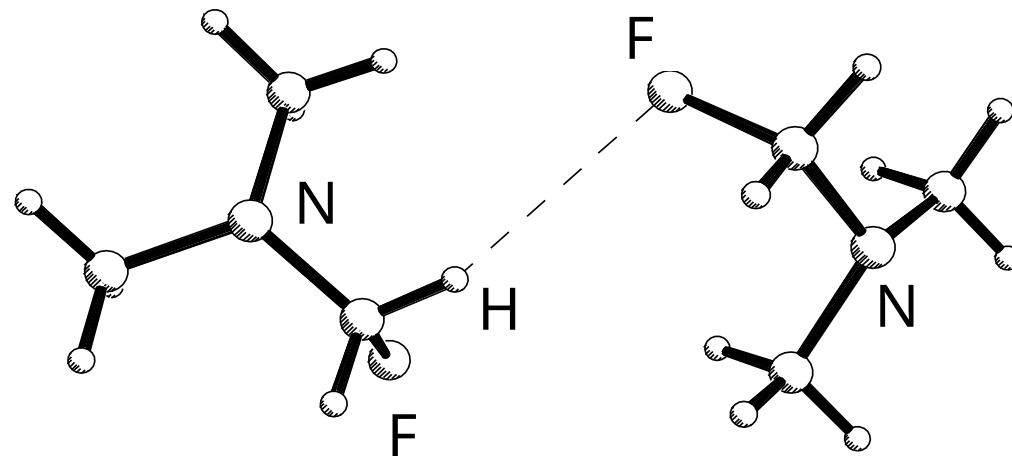
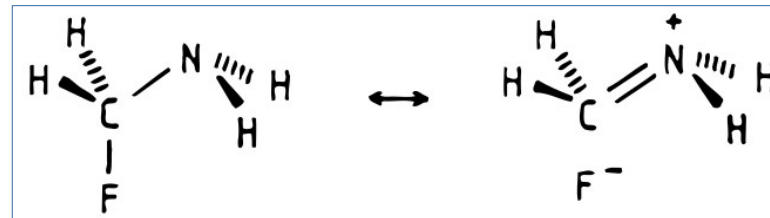
$\Sigma\alpha(N)$ :

343.4

334.8



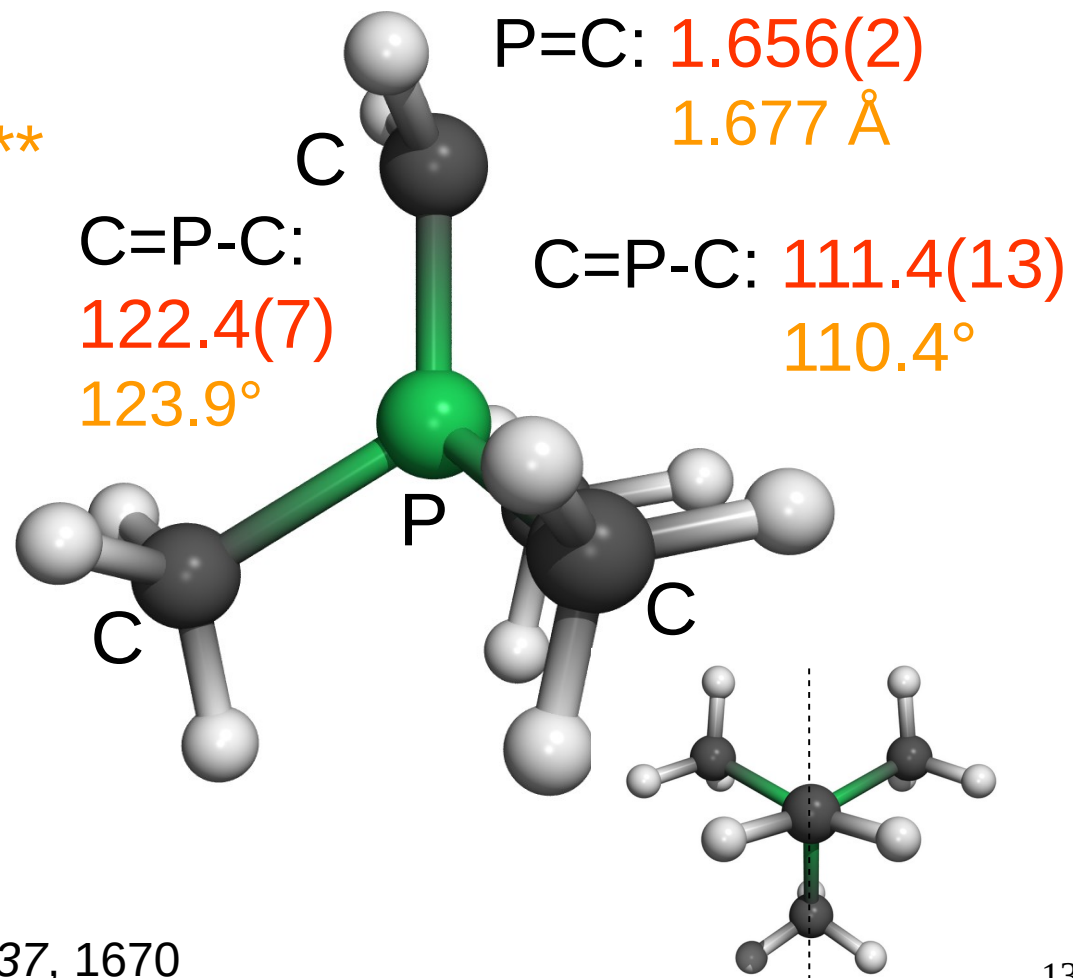
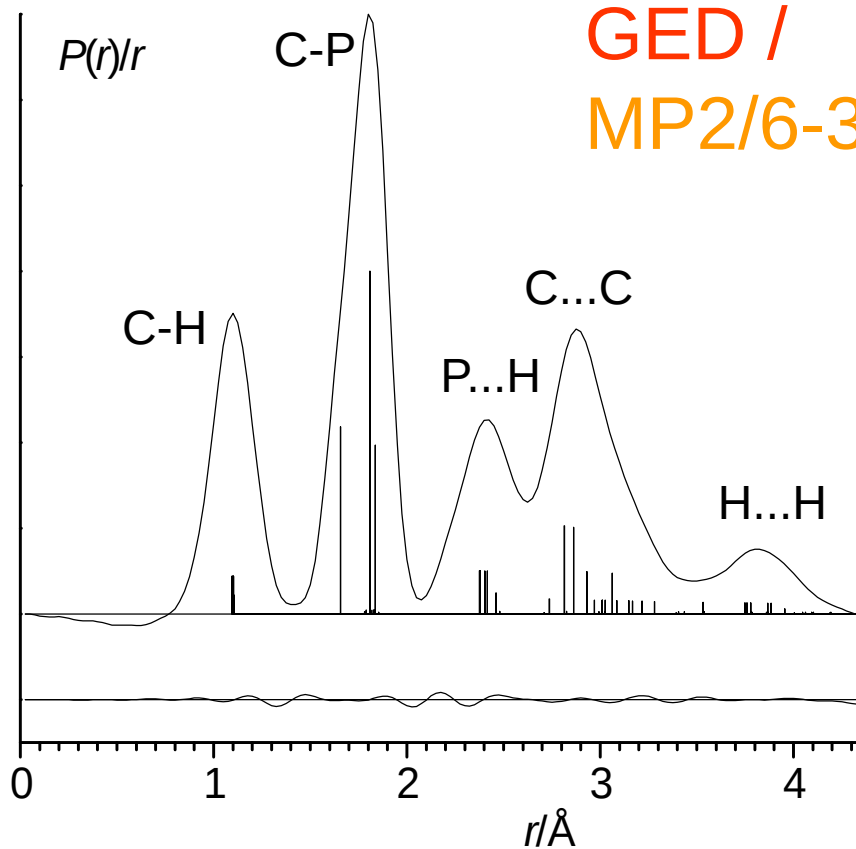
Modell:



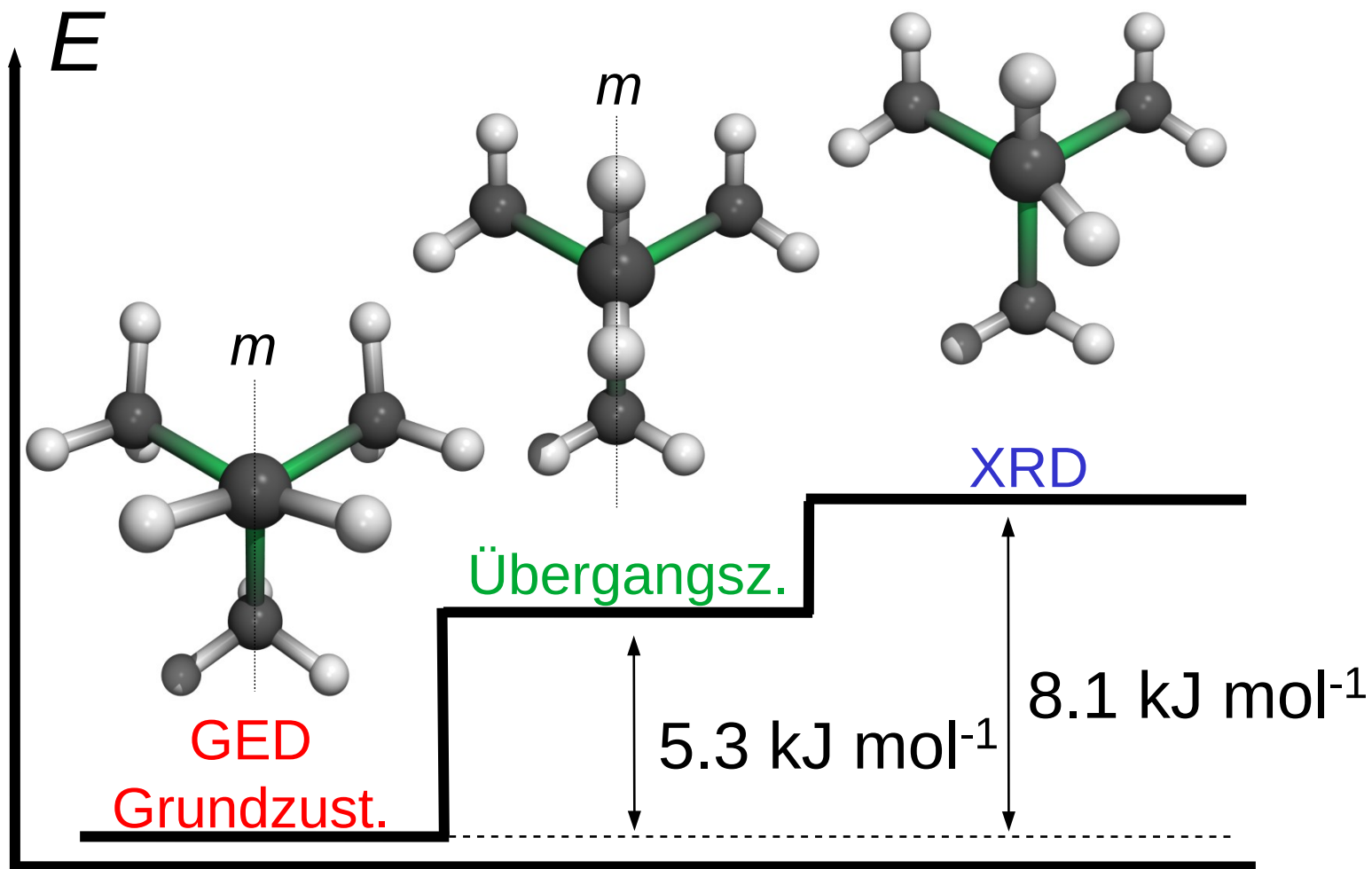
XRD: K. Vojinovic, N. W. Mitzel

GED: H. Oberhammer et al., *J. Am. Chem. Soc.* **1996**, *118*, 3720

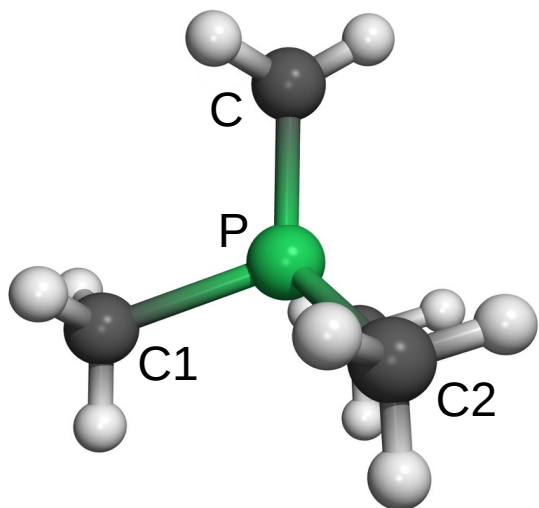
# Packungseffekte: $\text{Me}_3\text{P}=\text{CH}_2$



# Me<sub>3</sub>P=CH<sub>2</sub> (Rechnungen)



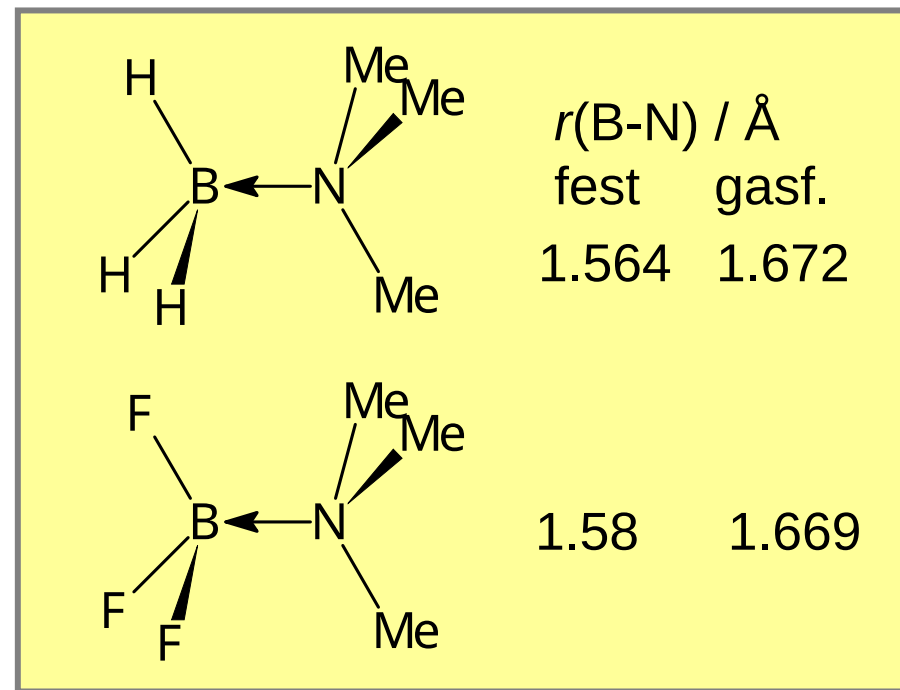
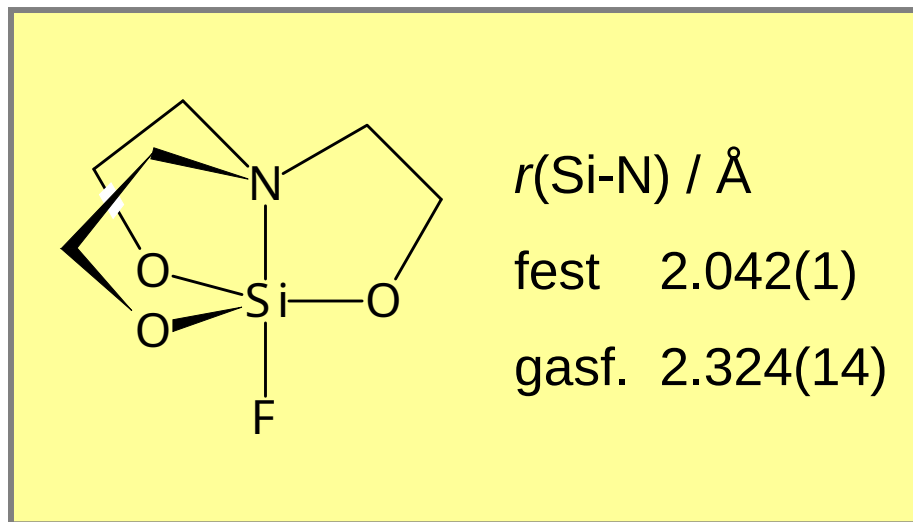
# Packungseffekte: $\text{Me}_3\text{P}=\text{CH}_2$ (XRD)



Die molekulare Geometrie im Festkörper ist ähnlich Derjenigen eines berechneten Übergangszustandes der Rotation der  $\text{CH}_2$ -Gruppe um die  $\text{P}=\text{C}$ -Bdg.

	XRD	Übergangsz. MP2/6-311G**	GED
$\text{C}=\text{P}-\text{C1}$	110.6(2)	110.3	111.4(13)
<u><math>\text{C}=\text{P}-\text{C2}</math></u>	<u>115.6(1)</u>	<u>117.5</u>	<u>122.4(7)</u>
$\text{C1}-\text{P}-\text{C2}$	105.6(1)	104.8	
$\text{C2}-\text{P}-\text{C2}'$	102.9(2)	100.5	

# Dative Bindungen / Polarität

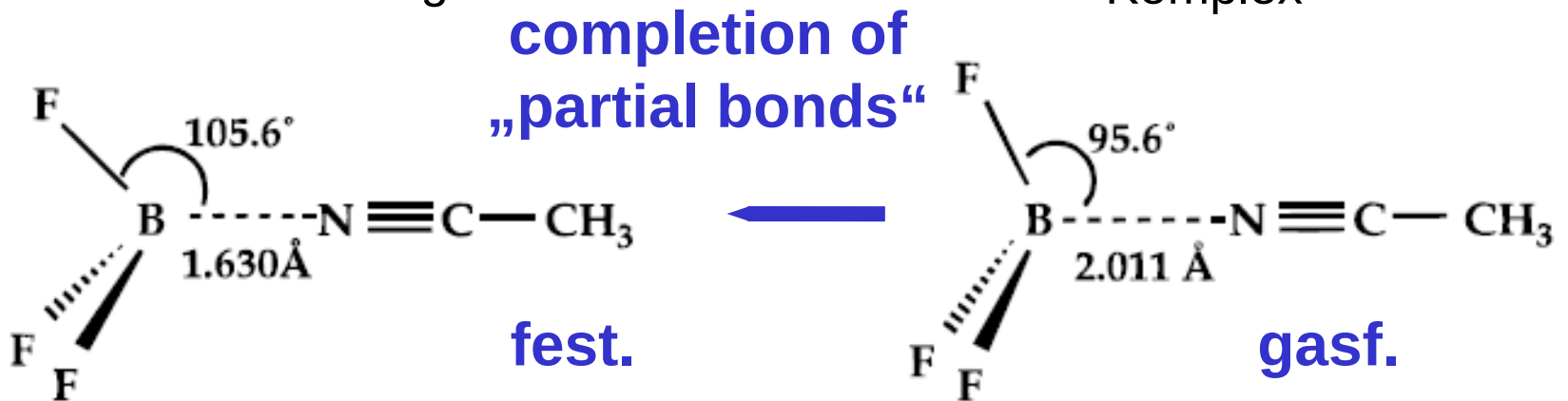
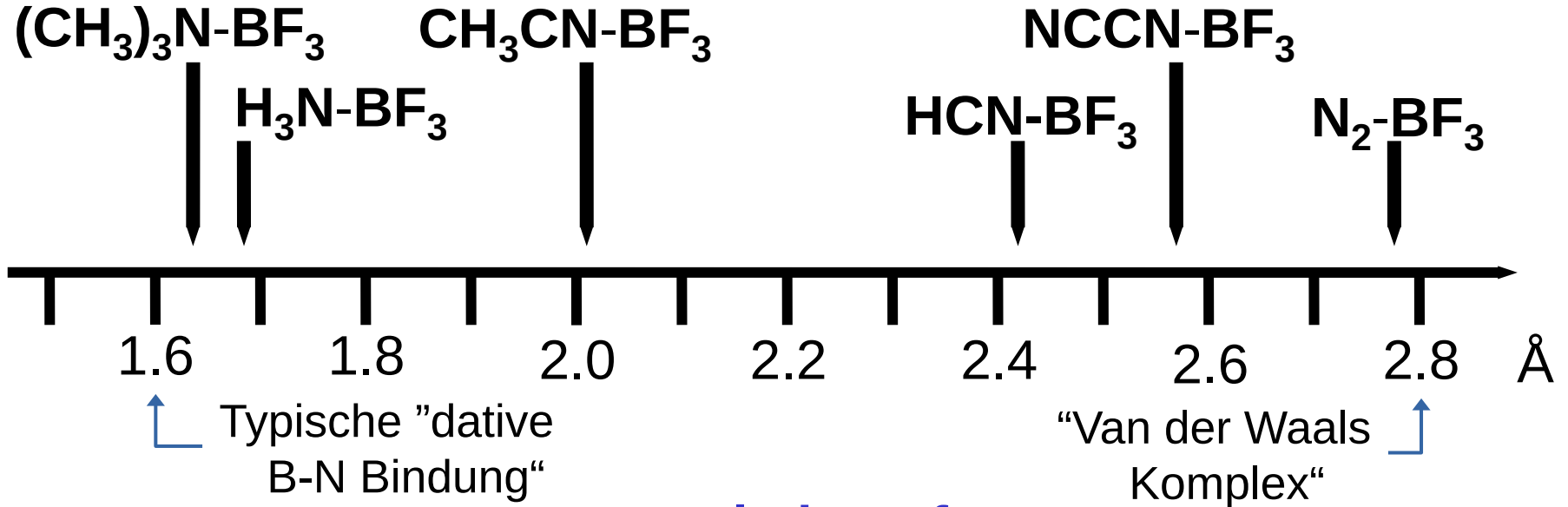


Review:

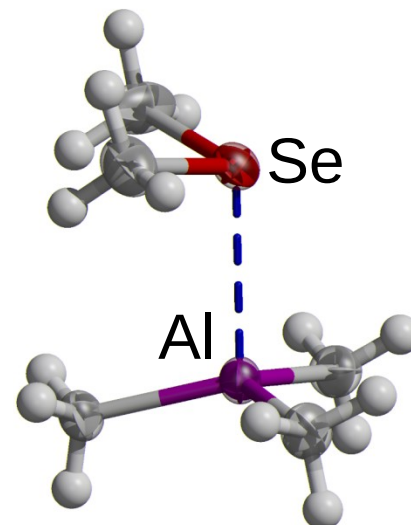
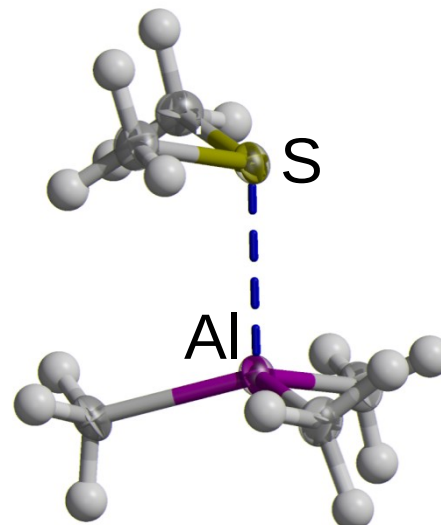
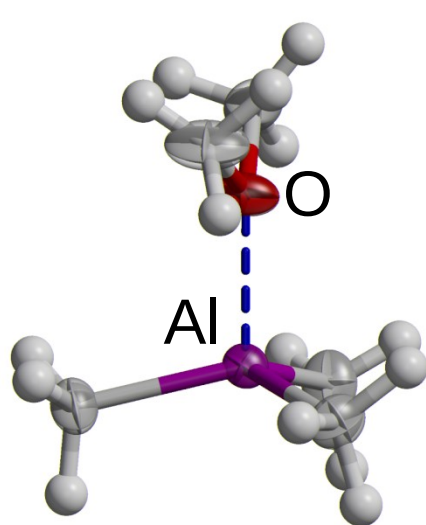
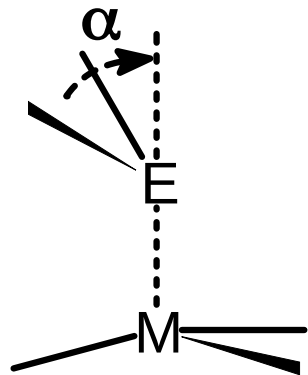
K. R. Leopold, M. Canagaratna, J. A. Phillips, *Acc. Chem. Res.* **1997**, 30, 57.



# Gasphasen-Werte für B-N



# Me<sub>2</sub>E-AlMe<sub>3</sub>-Addukte



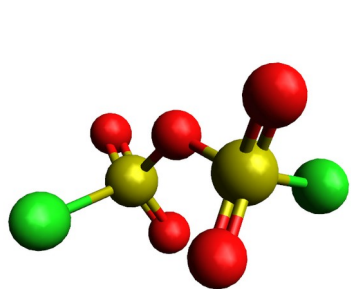
Al-E [Å]	1.940(2) 2.014(14)	2.461(av) 2.55(2)	2.605(av) [?]
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$\alpha$ [°]	12.5(1)° 5(4)°	69.2(av)° 31(5)°	73.6(av)° [?]
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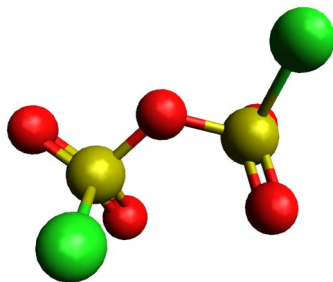
XRD  
GED

# Polymorphie: Cl(O)<sub>2</sub>SOS(O)<sub>2</sub>Cl

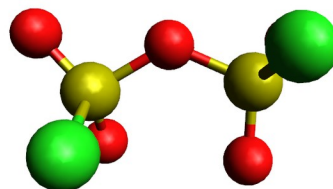
Gas:



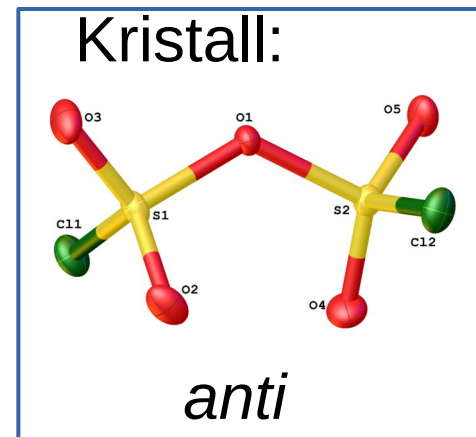
*anti*



*gauche*



*syn*



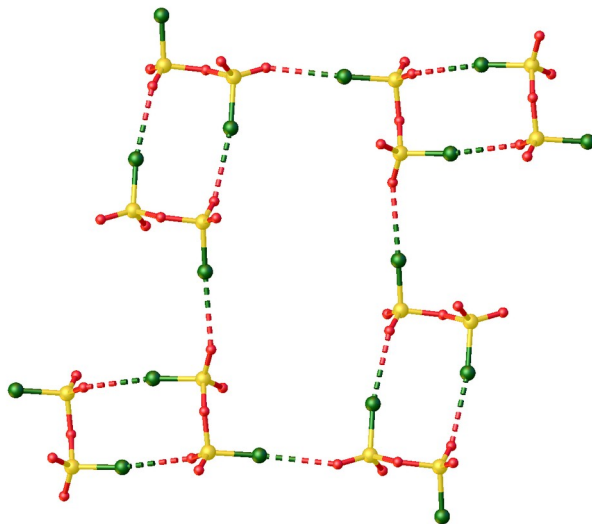
	Anteil	S-Cl	S-O	Cl-S-S-Cl
Gas <i>anti</i>	50 %	1.993(11)	1.642(10)	80.5(7)
Gas <i>gauche</i>	25 %	2.006(11), 2.004(11)	1.641(12) – 1.660(12)	163.0(15)
Gas <i>syn</i>	25 %	1.989(11)	1.639(13) – 1.640(13)	-110.9(15)

# Polymorphie: $\text{Cl}(\text{O})_2\text{SOS}(\text{O})_2\text{Cl}$ (XRD)

Phase 1

$P2_1/c$ ,  $Z = 4$

$\rho = 2.211 \text{ g/cm}^3$



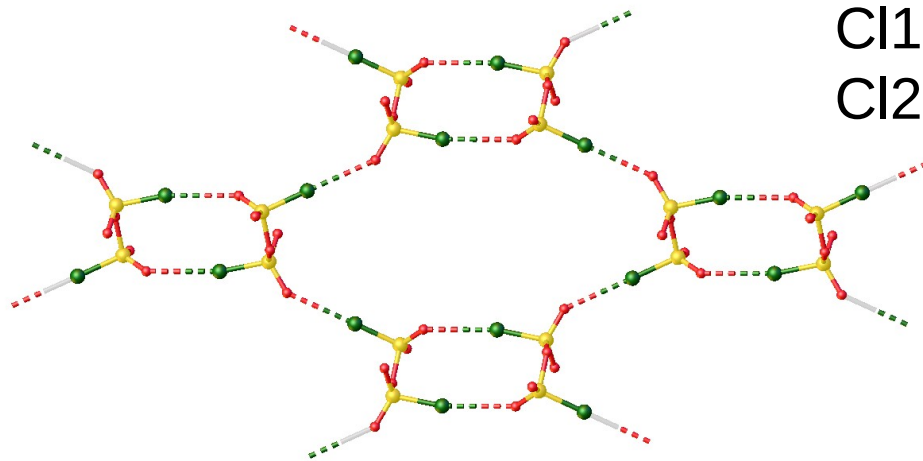
Cl1-S1 1.9729(2)

Cl2-S2 1.9661(2)

Phase 2

$P2_1/c$ ,  $Z = 4$

$\rho = 2.234 \text{ g/cm}^3$



Cl1-S1 1.9724(1)

Cl2-S2 1.9714(1)

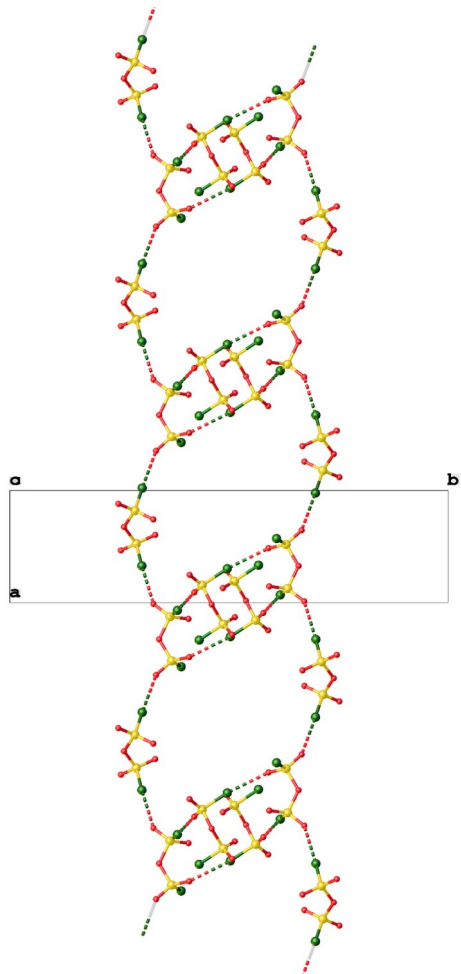
# Polymorphie: Cl(O)<sub>2</sub>SOS(O)<sub>2</sub>Cl (XRD)

Cl1-S1 1.9729(1)  
Cl2-S2 1.9661(1)

Phase 3

$P2_1/c$ ,  $Z = 4$

$\rho = 2.212 \text{ g/cm}^3$

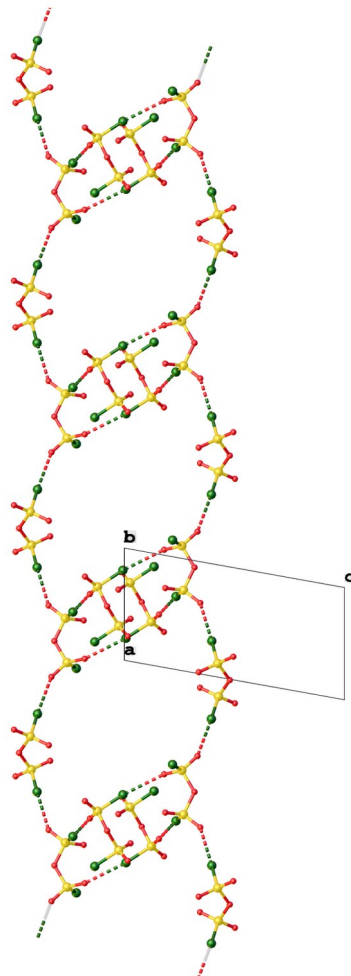


S1-Cl1 1.9708(2)  
S2-Cl2 1.9763(3)  
S3-Cl3 1.9786(3)  
S4-Cl4 1.9674(2)  
S5-Cl5 1.9715(2)  
S6-Cl6 1.9754(2)

Phase 4

$P\bar{1}$ ,  $Z = 12$

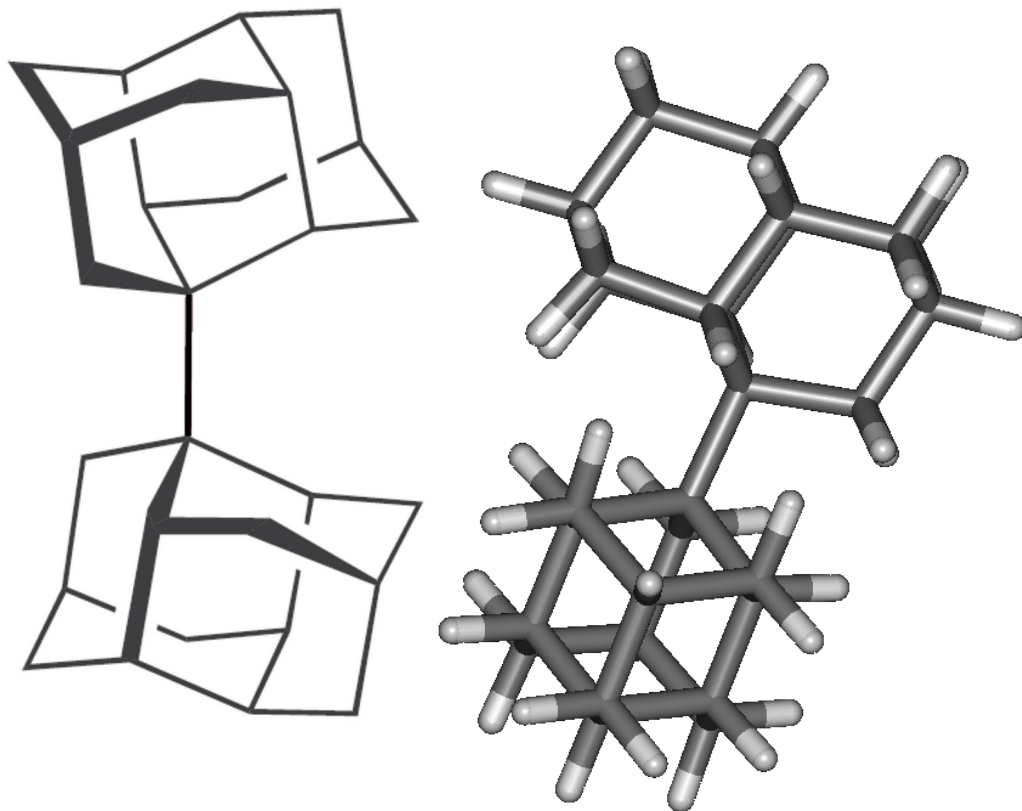
$\rho = 2.211 \text{ g/cm}^3$



# Dispersive Wechselwirkungen

Bis(diamantan)  $C_{28}H_{38}$

Zentral- $r(C-C)$ , Å

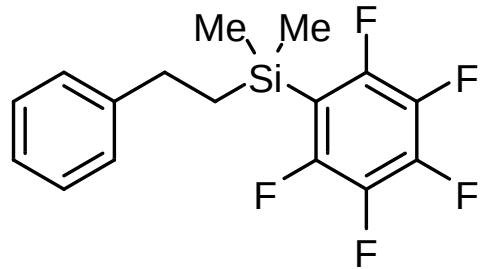
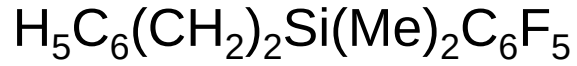


B3LYP/6-31G(d,p)	1.674
B3LYP-D3/6-31G(d,p)	1.653
B97D/6-31G(d,p)	1.668
M06-2X/6-31G(d,p)	1.648
<b>XRD, Einkristall</b>	<b>1.647(4)</b>
<b>GED, Gasphase</b>	<b>1.630(5)</b>

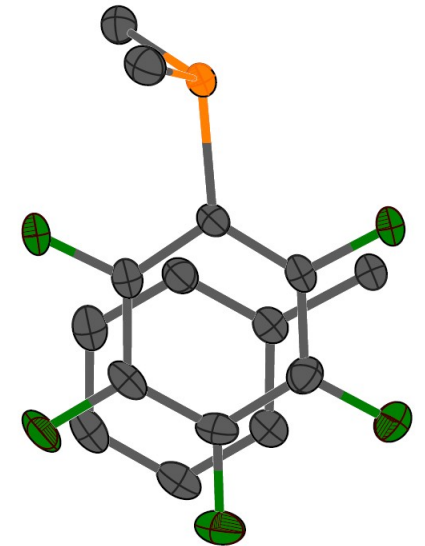
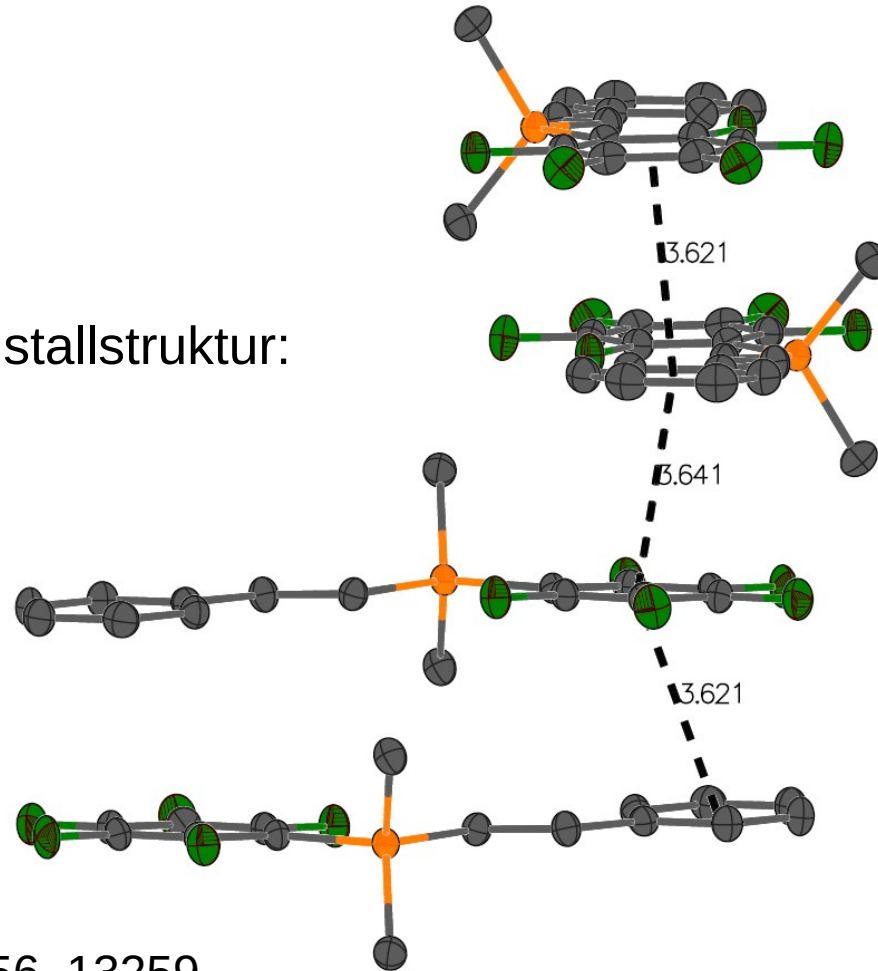
A. A. Fokin et al., *J. Am. Chem. Soc.*,  
2017, 139, 16696.

Übersichtsartikel:  
N. W. Mitzel, J.-H. Lamm,  
*Acc. Chem. Res.*, 2023, 56, 3379.

# Dispersion + Polarität

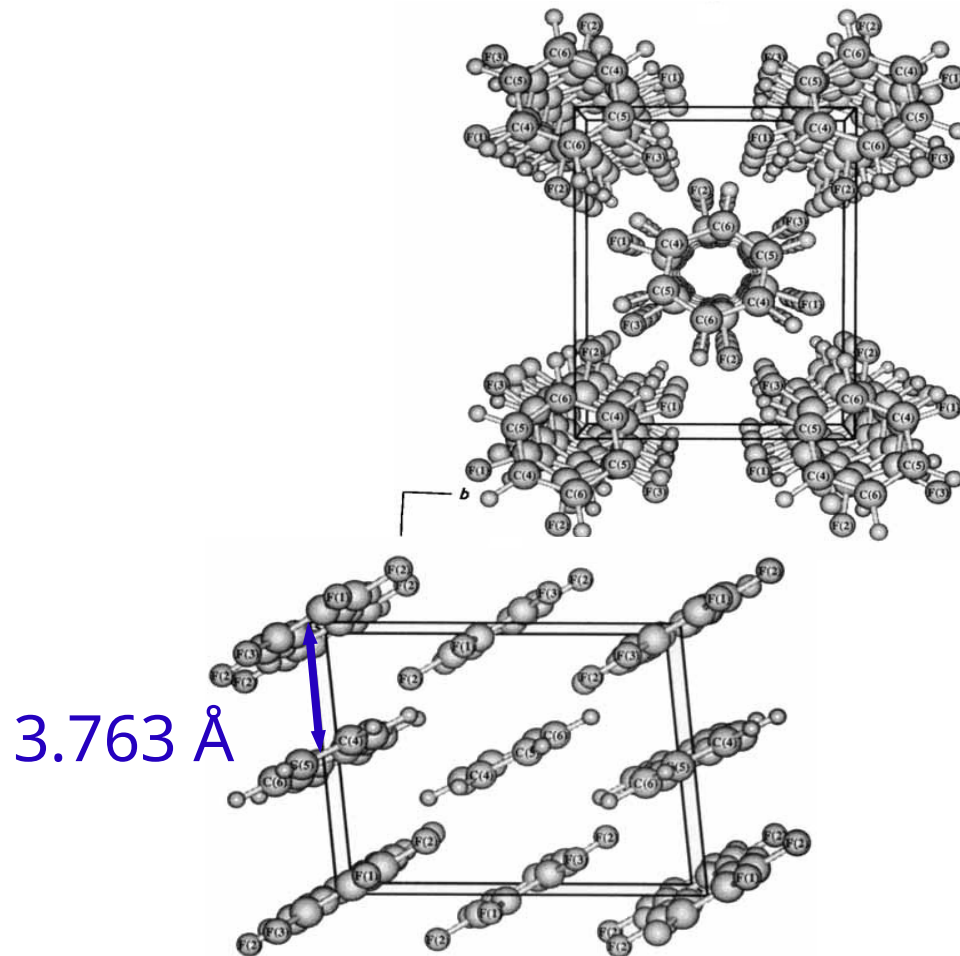
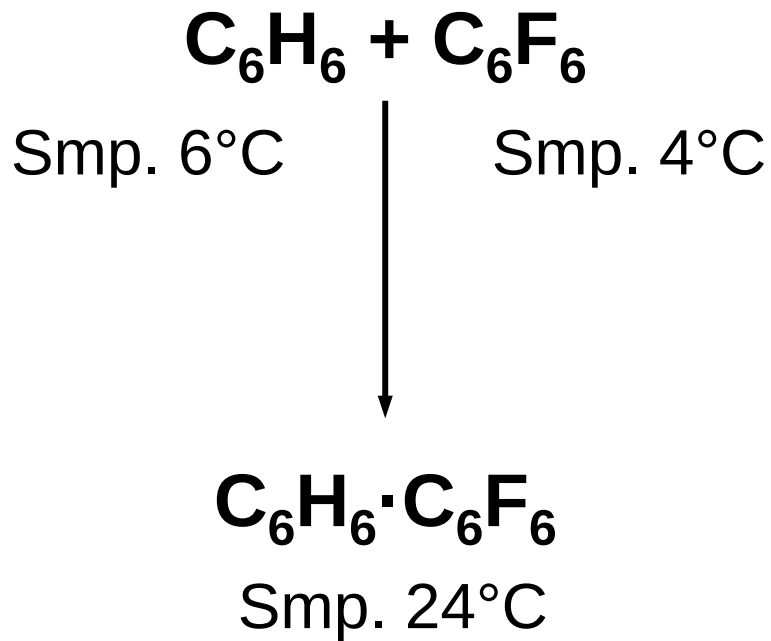


Kristallstruktur:



S. Blomeyer et al.,  
*Angew. Chem. Int. Ed.* 2017, 56, 13259.

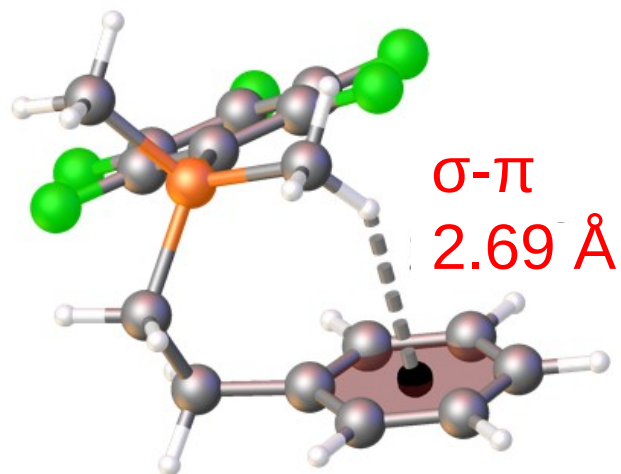
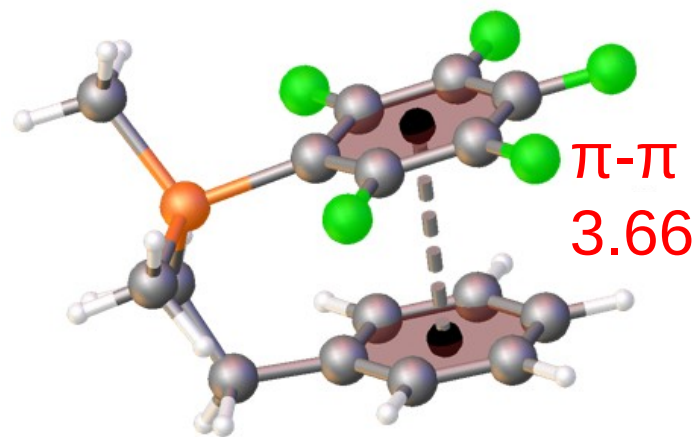
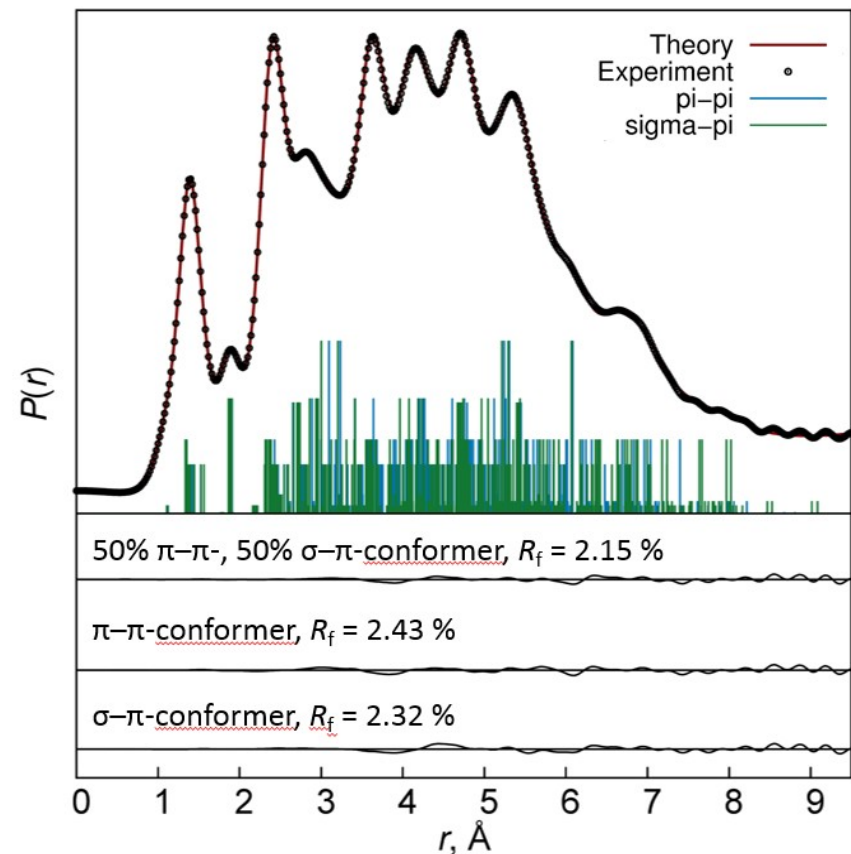
# Vgl: $C_6H_6 \cdot C_6F_6$ – Kristallstruktur



J. H. Williams, J. K. Cockcroft, N. Fitch,  
*Angew. Chem. Int. Ed.* **1992**, 31, 1655

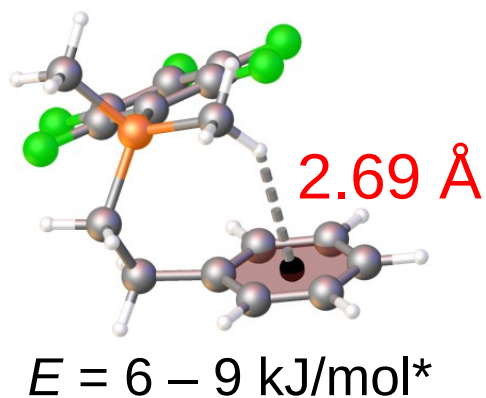
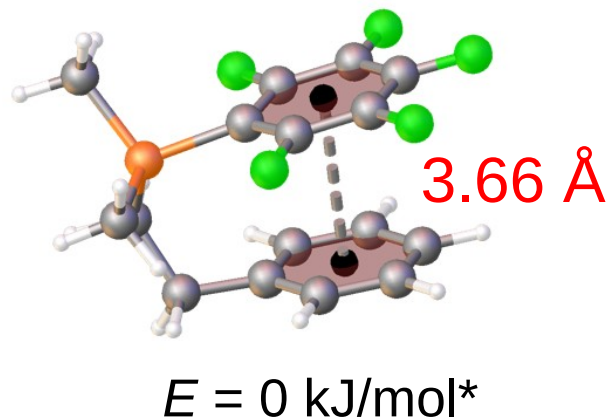


# $\text{H}_5\text{C}_6(\text{CH}_2)_2\text{Si}(\text{Me})_2\text{C}_6\text{F}_5$ – GED



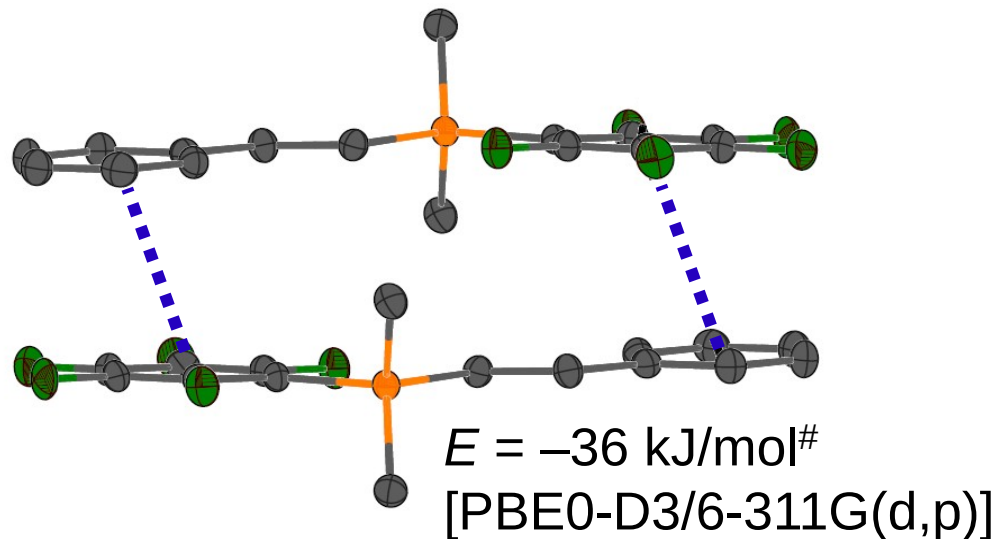
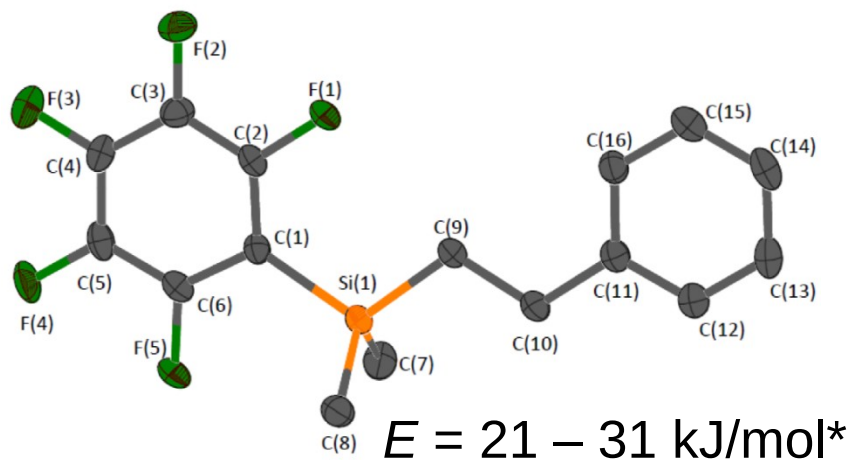
S. Blomeyer et al.,  
*Angew. Chem. Int. Ed.* 2017, 56, 13259.

# Gasphase/Festkörper



\* Einzelmolekül mit  
B97D/  
TPSS-D3/  
PBE0-D3/  
B3LYP-D3/  
B2PLYP-D3

Vgl. Kristall:



# Molekül(e) des Tages

## Decamethylsilicocene – The First Stable Silicon(II) Compound: Synthesis, Structure, and Bonding

Peter Jutzi<sup>\* a</sup>, Udo Holtmann<sup>a</sup>, Dieter Kanne<sup>a</sup>, Carl Krüger<sup>b</sup>, Richard Blom<sup>c</sup>, Rolf Gleiter<sup>d</sup>, and Isabella Hyla-Kryspin<sup>d</sup>

Fakultät für Chemie der Universität Bielefeld<sup>a</sup>,  
Universitätsstraße, D-4800 Bielefeld, F. R. G.

Max-Planck-Institut für Kohlenforschung<sup>b</sup>,  
Kaiser-Wilhelm-Platz 1, D-4330 Mülheim-Ruhr, F. R. G.

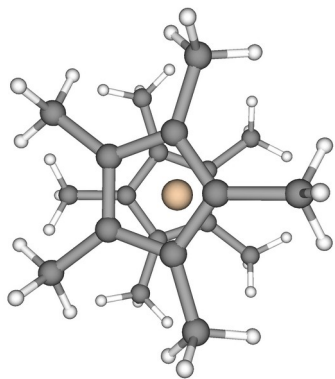
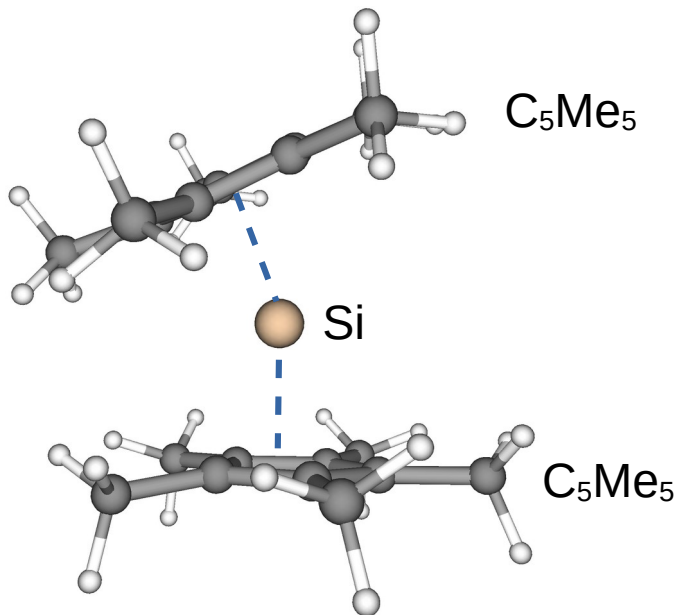
Department of Chemistry, University of Oslo<sup>c</sup>,  
Blindern, N-0315 Oslo 3, Norway

Organisch-Chemisches Institut der Universität Heidelberg<sup>d</sup>,  
Im Neuenheimer Feld 270, D-6900 Heidelberg, F. R. G.



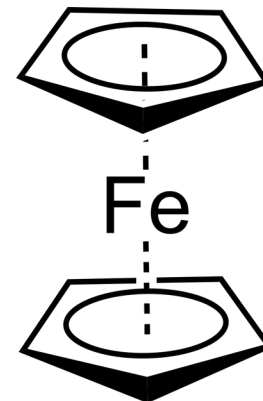
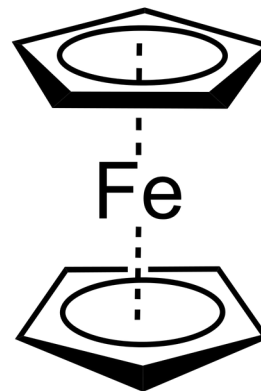
P. Jutzi, U. Holtmann, D. Kanne, C. Krüger, R. Blom, R. Gleiter, I. Hyla-Kryspin,  
*Chem. Ber.* 1989, 122, 1629.

# Rechnungen



Vgl. Ferrocen:

gestreckt

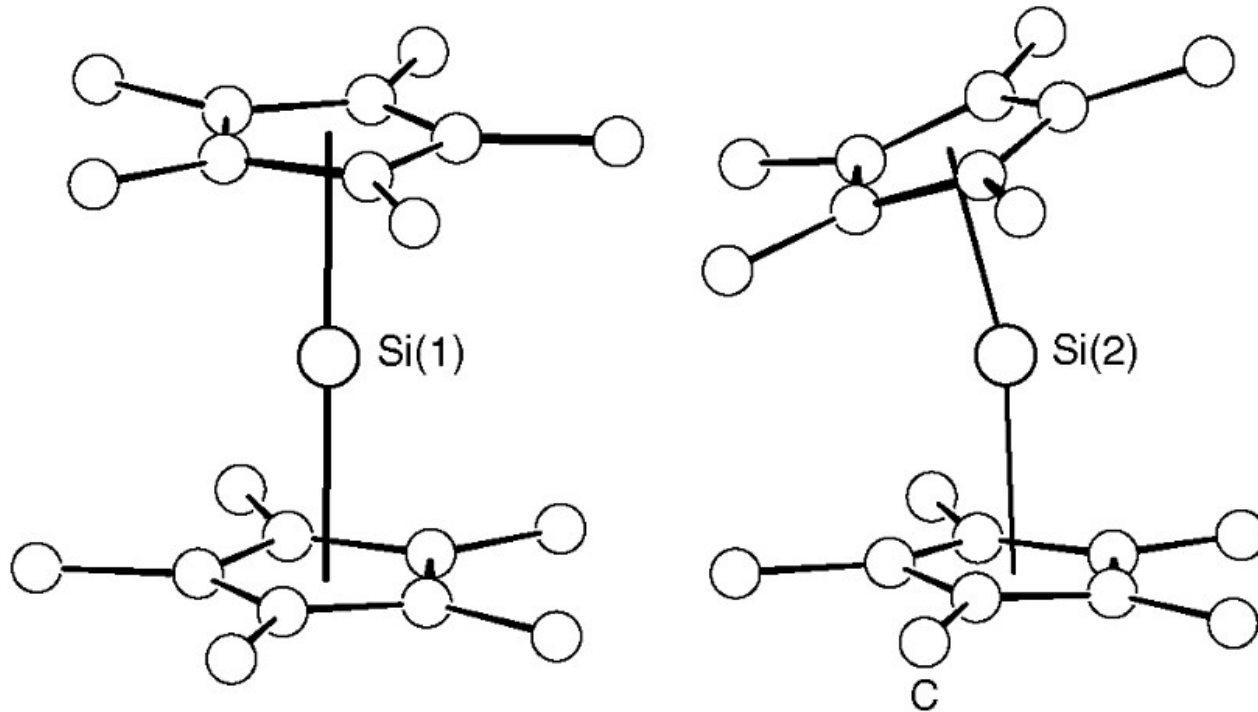


~Gestaffelt  
im Kristall  
(**ND**, Brock, 1997

Eklptisch  
in der Gasphase  
(**GED**, Haaland,  
1968)

T-abh!  
Fehlordnung!)

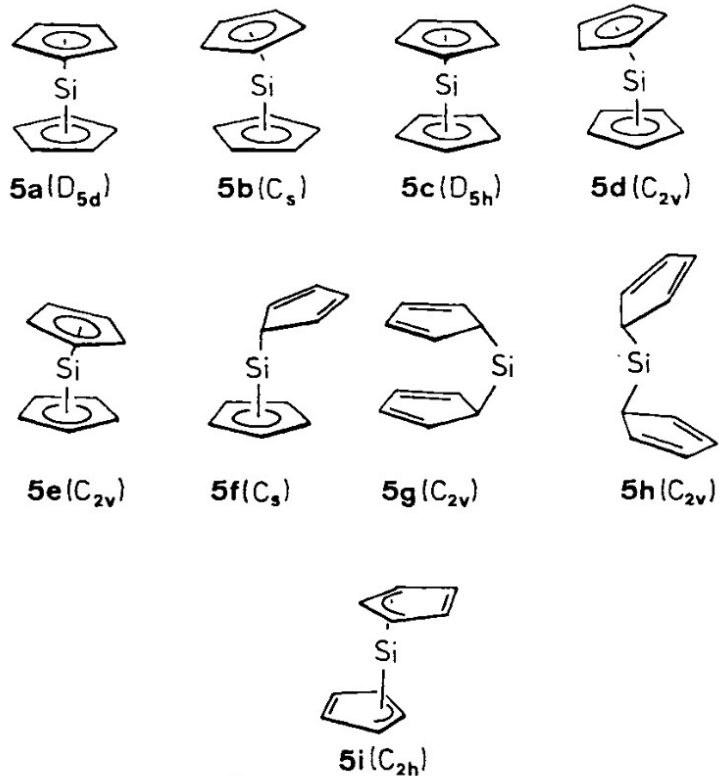
# Kristallstruktur



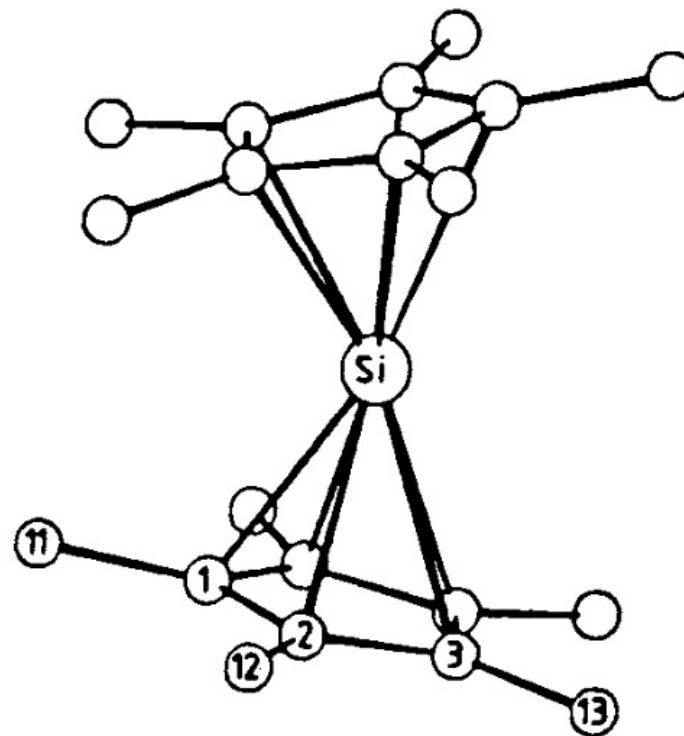
Gestaffelt, gestreckt **und** gewinkelt!

# Gasphase: GED

Getestete Modelle



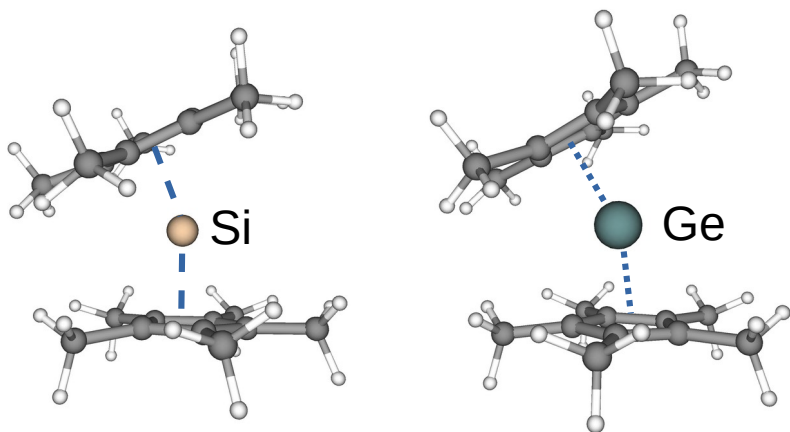
Das beste Modell (5b) ist gestaffelt und gewinkelt



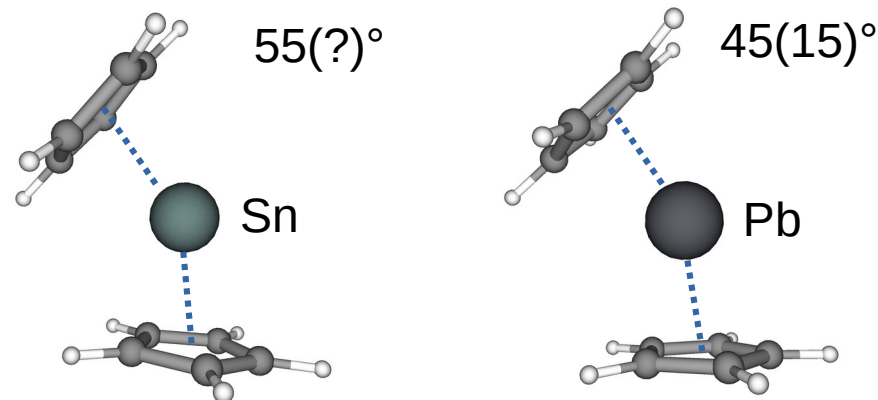
# Gasphase / Festkörper

Method <sup>a)</sup>	$d$ <sup>b)</sup> [Å]	$r(M-C)$ <sup>c)</sup> [Å]	$\delta$ <sup>d)</sup> [Å]	$\angle C_5C_5$ [°]	Ref.	
(Me <sub>5</sub> C <sub>5</sub> ) <sub>2</sub> Si <b>4a</b>	X	2.11	2.42(1)	0	0	this work
(Me <sub>5</sub> C <sub>5</sub> ) <sub>2</sub> Si <b>4b</b>	X	2.12	2.42(6)	0.023	25.3	this work
(Me <sub>5</sub> C <sub>5</sub> ) <sub>2</sub> Si <b>4</b>	GED	2.129(12)	2.45(2)	0.021	22.4(12)	this work
(Me <sub>5</sub> C <sub>5</sub> ) <sub>2</sub> Ge <b>6</b>	GED	2.21(3)	2.52(3)	0.015	23(3)	14)
(Me <sub>5</sub> C <sub>5</sub> ) <sub>2</sub> Sn <b>7</b>	X	2.39	2.68	0.023	36	26)
(Me <sub>5</sub> C <sub>5</sub> ) <sub>2</sub> Pb <b>8</b>	X	2.48	2.79	0.029	43	27)

a) X = X-ray crystallography, GED = gas-phase electron diffraction. — b) The distance from the central atom to the ring centroid. — c) Mean distances. — d) Mean values of the distances from the center of mass of each C<sub>5</sub> ring to the projection of the group 14 element into the ring plane.



Vgl. GED f. Sn(Cp)<sub>2</sub> und Pb(Cp)<sub>2</sub>:



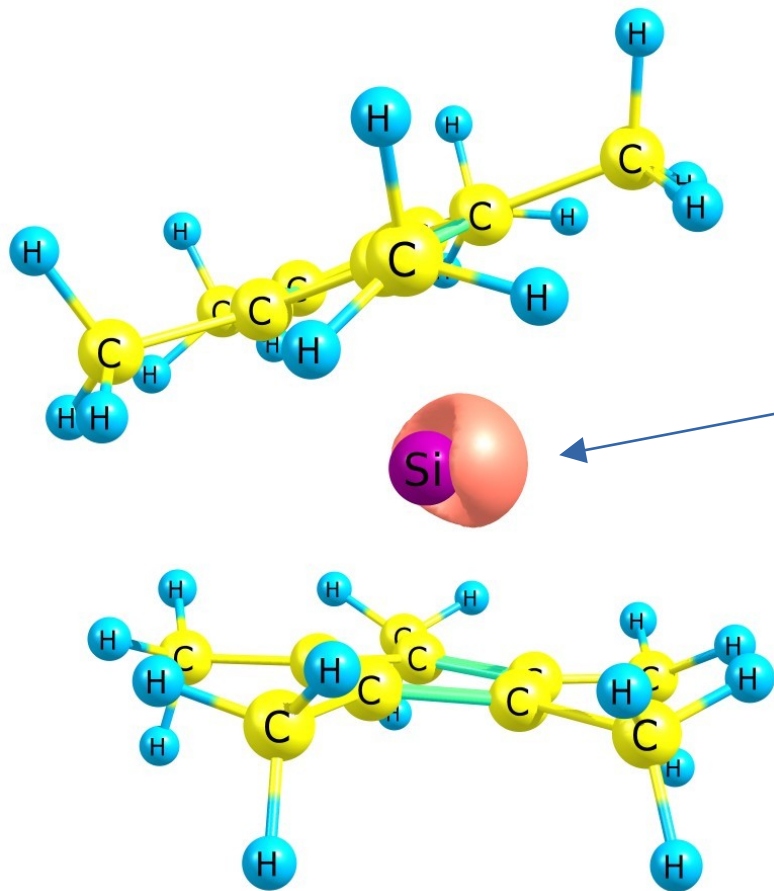
# Si(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>: NBO

NBO: **N**atural **B**ond **O**rbitals  
(F. Weinhold)

[PBE0-D3BJ/def2-TZVPP]

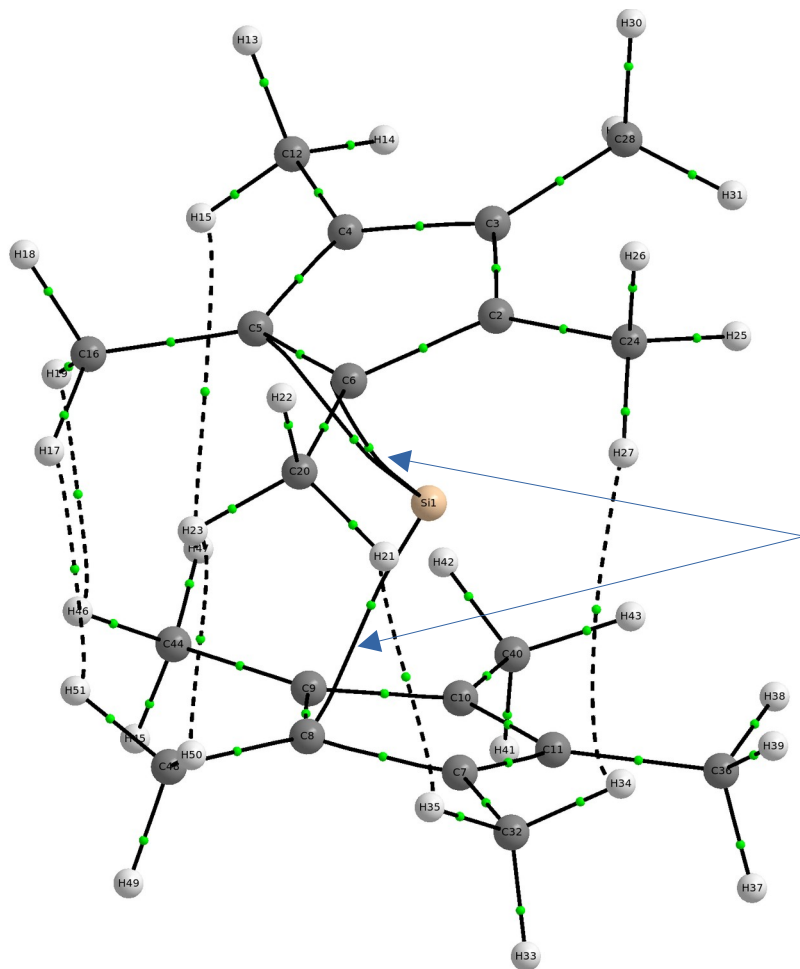
NBO #26: freies Elektronenpaar an Si,  
 $n = 1.98 e$ ,  
keine WWs mit anderen NBOs!

Stereochemisch aktiv!





# Si(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>: QTAIM



QTAIM:  
Quantum Theory of Atoms In Molecules  
(R. Bader)

Bindungspfad für Si-C

# Quellen / Literatur

- D. W. H. Rankin, N. W. Mitzel, C. A. Morrison, *Structural Methods in Molecular Inorganic Chemistry*, John Wiley & Sons, Chichester, 2013.
- K. R. Leopold, M. Canagaratna, J. A. Phillips, *Acc. Chem. Res.*, 1997, 30, 57
- N. W. Mitzel, J.-H. Lamm, *Acc. Chem. Res.* 2023, 56, 3379–3391.
- P. Jutzi, U. Holtmann, D. Kanne, C. Krüger, R. Blom, R. Gleiter, I. Hyla-Kryspin, *Chem. Ber.* 1989, 122, 1629–1639.