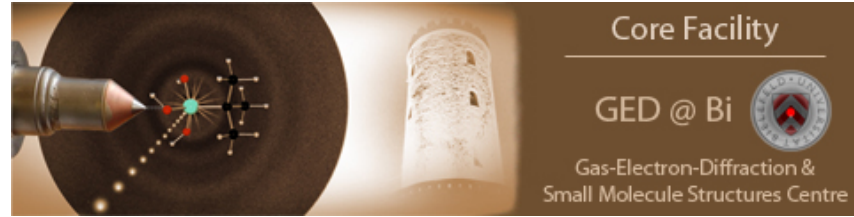


Struktur- und Elektrochemie von Pentafluorferrocen

AK-Seminar – 02.02.2015

Sebastian Blomeyer

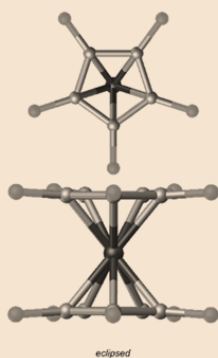
Rückblick – Vortrag 04/14



Fe(Cp^f)₂ – QM



Energetisches Minimum:

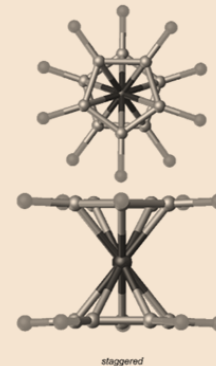


D_{5h} -Symmetrie

Fluoratome nicht in C_5 -Ebene

eclipsed

Maximum bei Rotation eines C_5 -Rings:



D_{5d} -Symmetrie

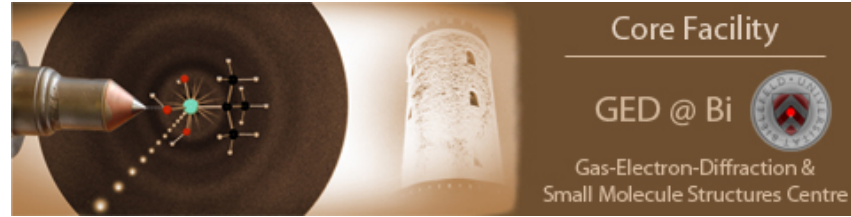
Fluoratome nicht in C_5 -Ebene

$\Delta E = 1.7$ kJ/mol

staggered

Gaussian 09/B3LYP/TZVPP+f

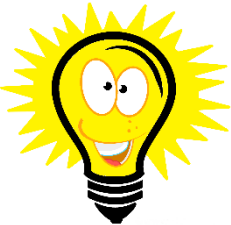
Rückblick – GED

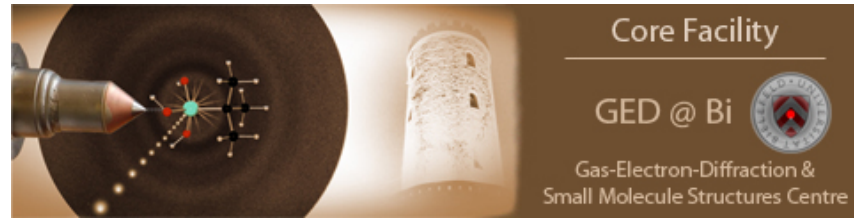
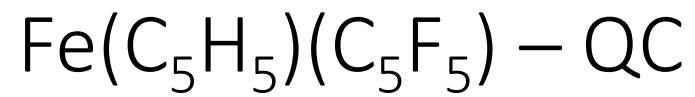


Bester R_f -Wert: 7.8 %

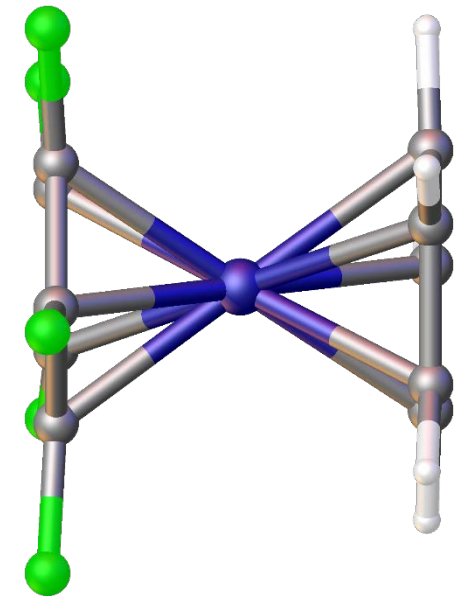
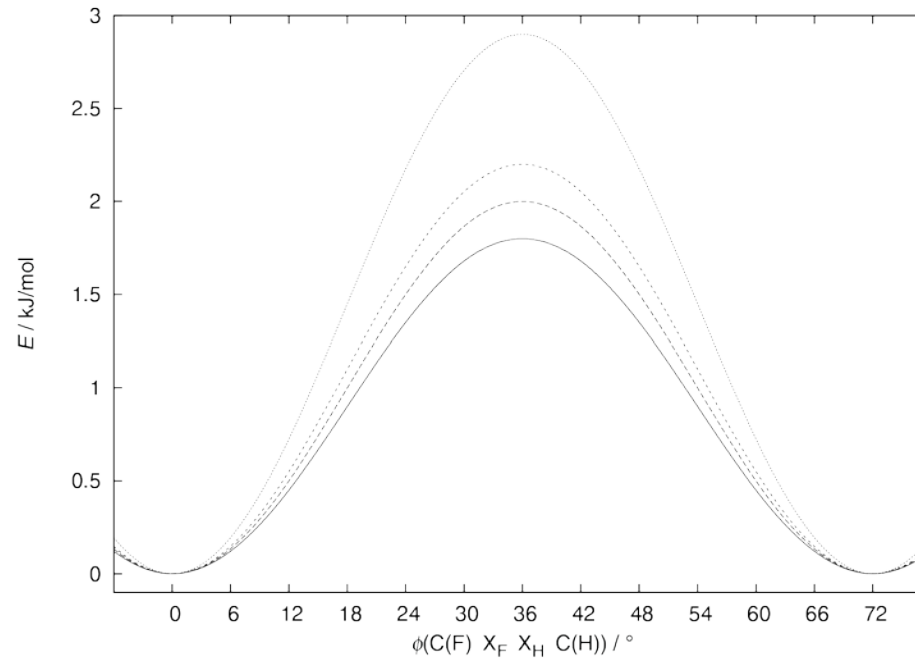
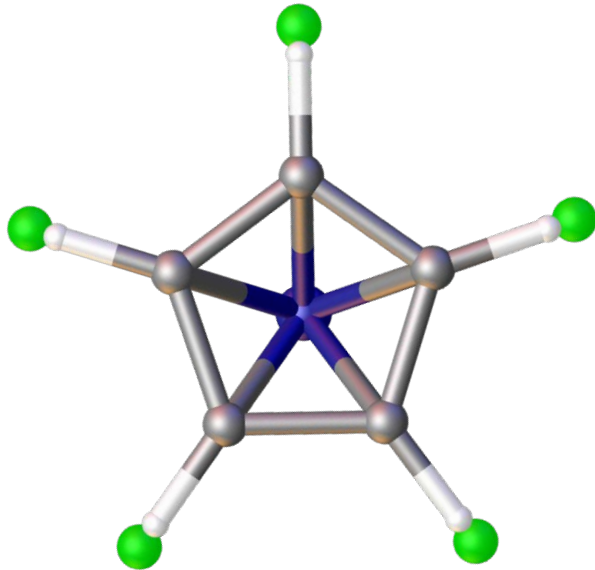
Probleme:

- hohe Korrelationen zwischen Parametern
- schlechte Übereinstimmung (exp. vs. theor.) für große Abstände
- R_f -Wert (eigentlich) zu schlecht für Publikation

→  → Penta nicht Deca!



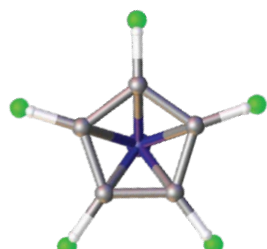
Quantenchemische Rechnungen (DFT¹ & Hybrid-DFT²):



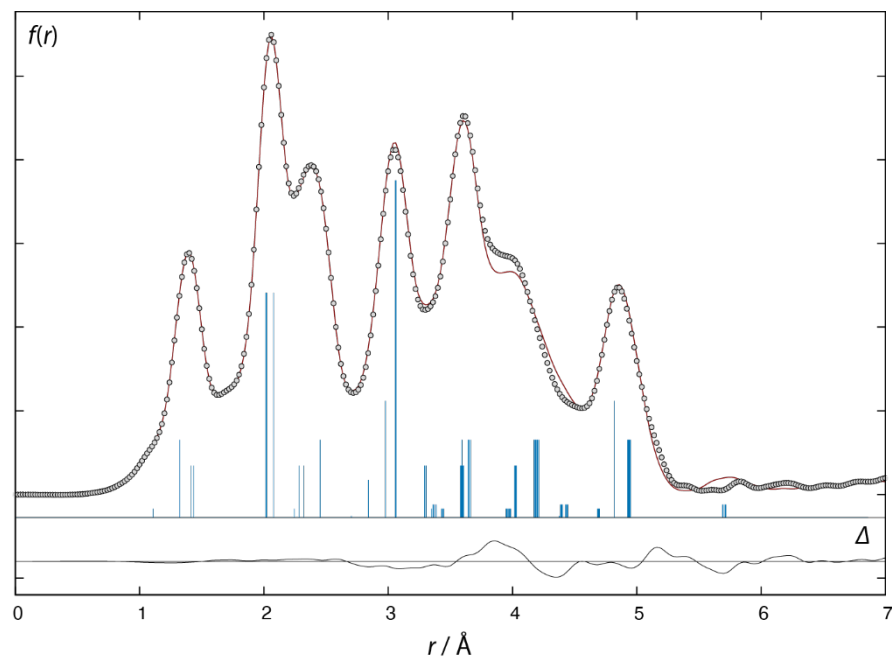
¹ PBE0, PBE0+D3, B3LYP, TPSSH, B3P86, B3PW91 – cc-pVTZ, TZV2P+f

² B2PLYP – cc-pVTZ

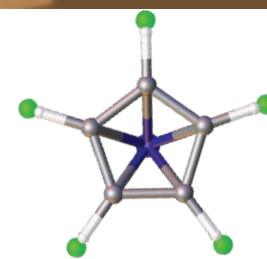
$\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_5\text{F}_5) - \text{GED}$



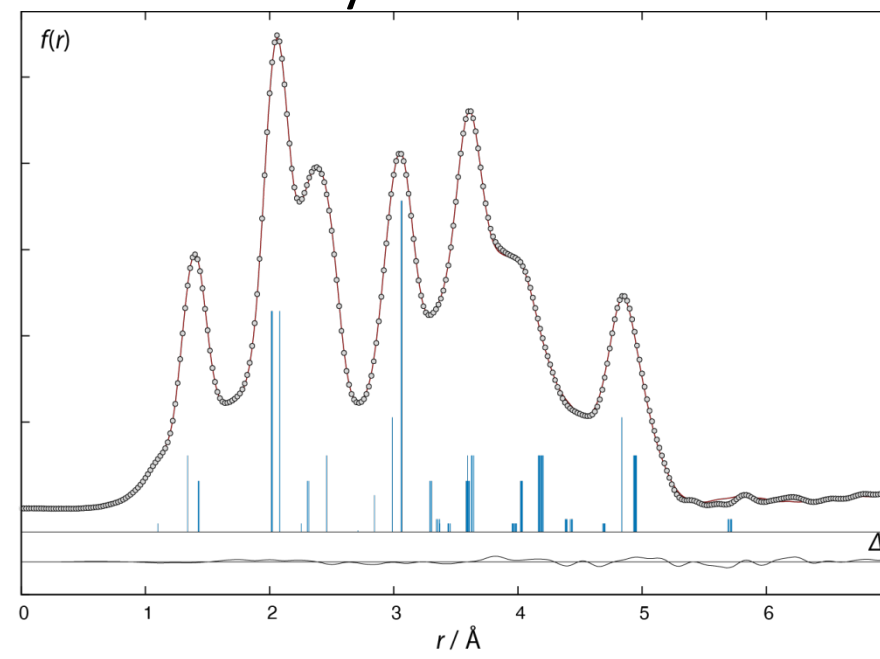
statisch



$R_f = 5.8 \%$

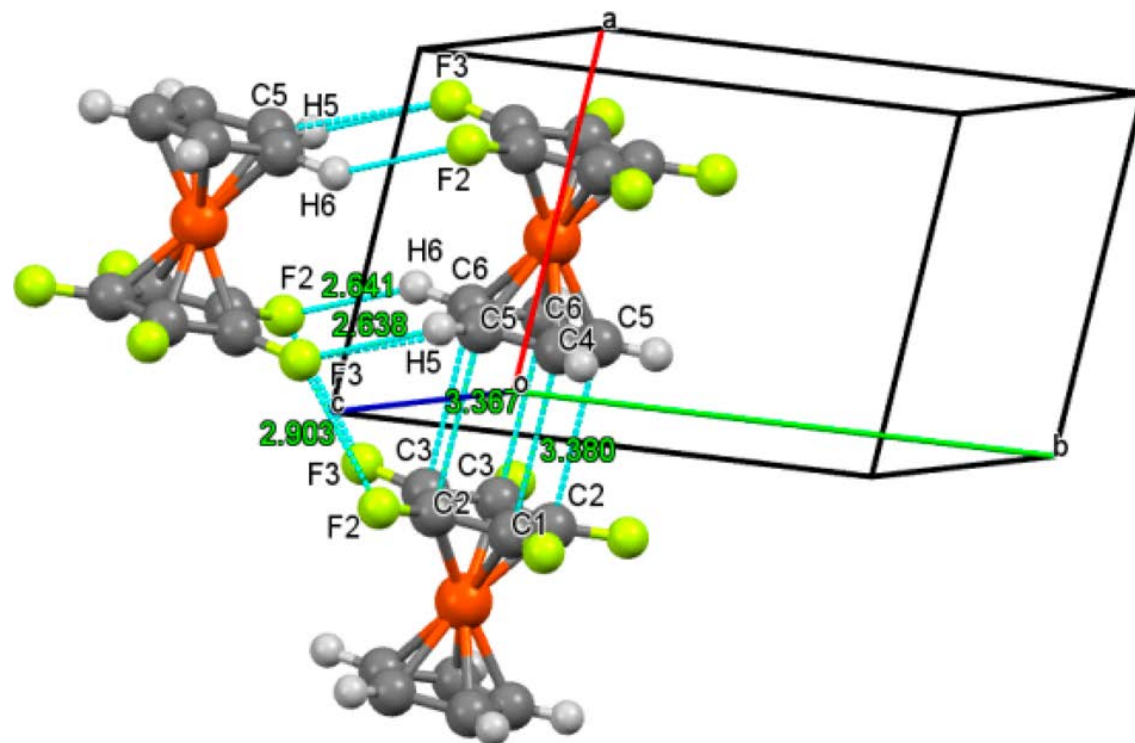


dynamisch



$R_f = 4.4 \%$

Fe(C₅H₅)(C₅F₅) – XRD



π-Stacking, $d(\text{Cp}^f\text{-Cp})$:
intermolekular: ca. 3.37 Å
intramolekular: 3.26 Å

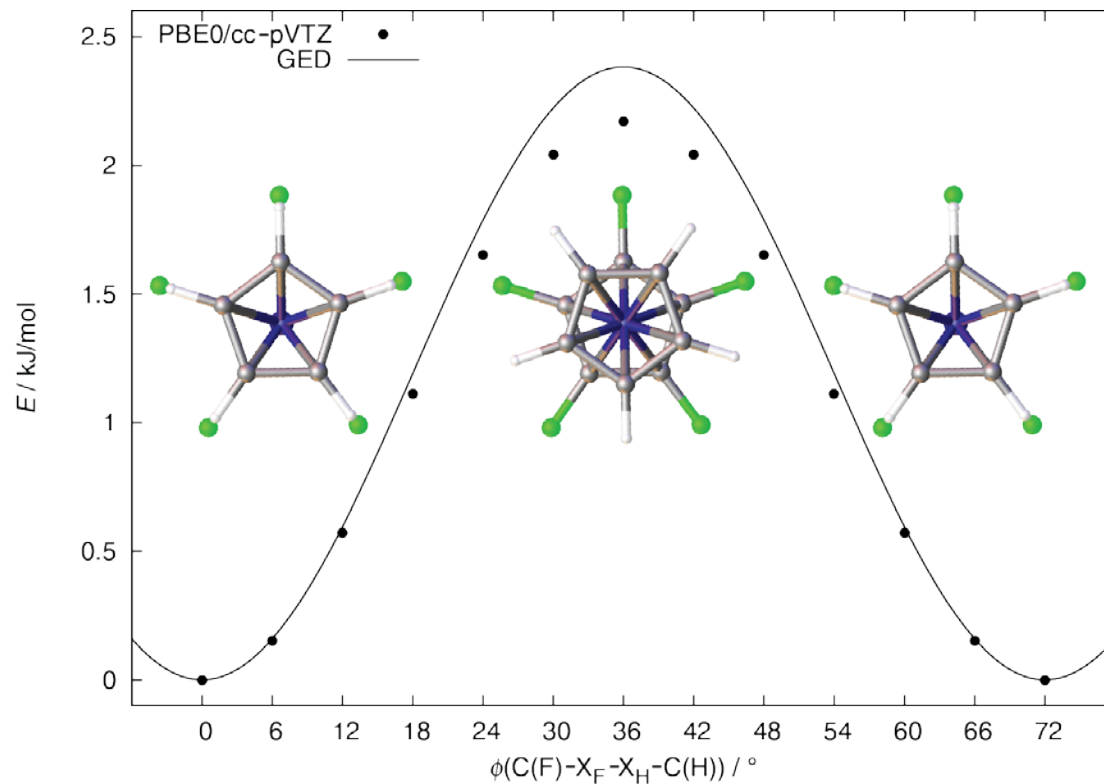
Fe(C₅H₅)(C₅F₅) – Parameter



Abstand/Winkel [Å/°]	GED	DFT	XRD
$d(\text{Fe}-\text{C}_\text{H})$	2.071(1)	2.054	2.048(3) – 2.054(3)
$d(\text{Fe}-\text{C}_\text{F})$	2.009(1)	2.012	1.997(3) – 2.005(3)
$d(\text{C}-\text{H})$	1.085(7)	1.079	0.96(3) – 1.13(2)
$d(\text{C}-\text{F})$	1.333(1)	1.323	1.331(4) – 1.341(4)
$d(\text{C}_\text{H}-\text{C}_\text{H})$	1.425(1)	1.420	1.417(3) – 1.427(3)
$d(\text{C}_\text{F}-\text{C}_\text{F})$	1.419(1)	1.420	1.410(3) – 1.416(3)
$\Phi(\text{C}_5\text{-F})$	-3.7(1)	-3.0	-3.5(3)
$\Phi(\text{C}_5\text{-H})$	+1.6(2)	+1.6	+2.1(4)

Fehler: 1 σ

Fe(C₅H₅)(C₅F₅) – GED

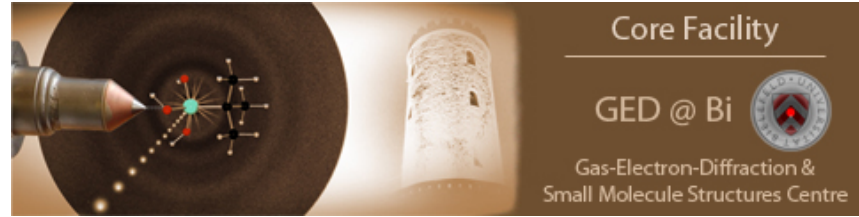


$$V(\Phi) = V_0(1 - \cos(5\Phi))/2$$

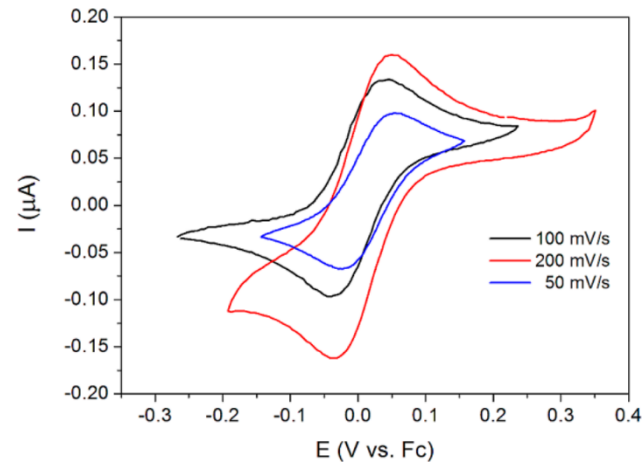
$$V_0 = 2.4(3) \text{ kJ mol}^{-1}$$

Verbindung	$V_0 = E_{\text{stag}} - E_{\text{ecl}} / \text{kJ mol}^{-1}$
Fe(C ₅ H ₅) ₂	3.8(3)
Fe(C ₅ Me ₅) ₂	-4.0(3)
Fe(C ₅ Cl ₅) ₂	-0.8(2)

$\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_5\text{F}_5) - \text{CV}$

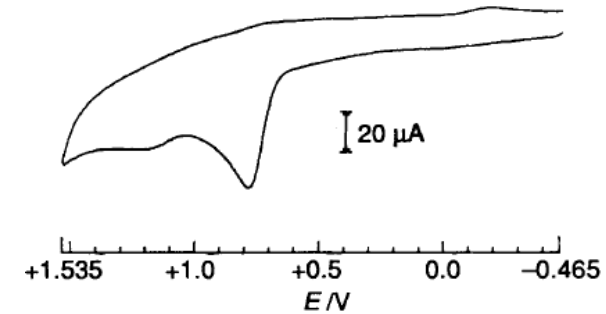


$\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_5\text{F}_5)$



$E^0 = 0.01 \text{ V}$ (reversible Welle)^[1]

$\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_5\text{Cl}_5)$



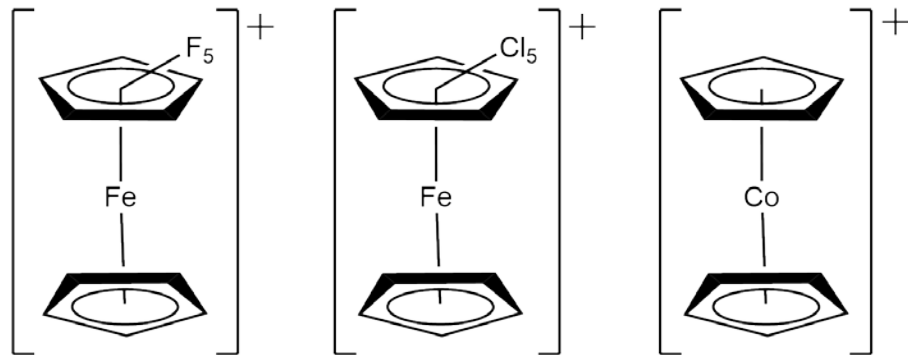
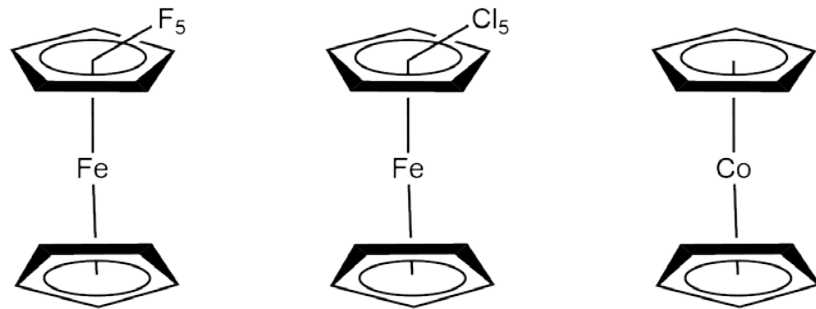
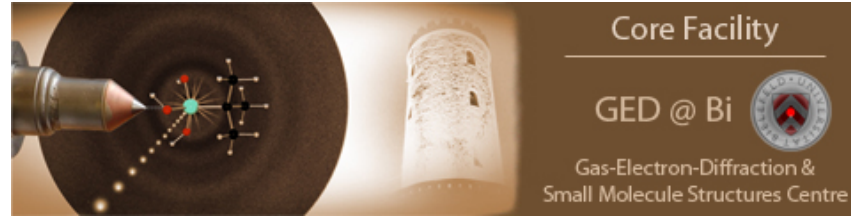
$E^0 = 0.77 \text{ V}$ (irreversible Welle)^[2]

Reviewer: „Kann man das rechnen?“

[1] Sünkel, K.; Weigand, S.; Hoffmann, A.; Blomeyer, S.; Reuter, C. G.; Vishnevskiy, Yu. V.; Mitzel, N. W.; *J. Am. Chem. Soc.* **2015**, *137*, 126.

[2] Phillips, L.; Lacey, A. R.; Cooper, M. K. *J. Chem. Soc., Dalton Trans.* **1988**, 1383.

Fe(C₅H₅)(C₅F₅) – CV/QC



+ ZPE

+ thermische Korrekturen

+ Solvatationsenthalpien (IEFPCM)

→ ΔG⁰

Verb. / ΔG ⁰ [eV] rel. zu Fc/Fc ⁺	exp.	calcd.
Fe(C ₅ H ₅)(C ₅ F ₅) ^{0/+} (in ACN)	+0.01 ^[1]	-0.04 ^[1]
Fe(C ₅ H ₅)(C ₅ Cl ₅) ^{0/+} (in ACN)	+0.77 ^[2]	-0.02 ^[1]
Co(C ₅ H ₅) ₂ ^{0/+} (in DMF)	-1.17 ^[3]	-1.22 ^[1]

Diskrepanz bei Fe(C₅H₅)(C₅Cl₅):

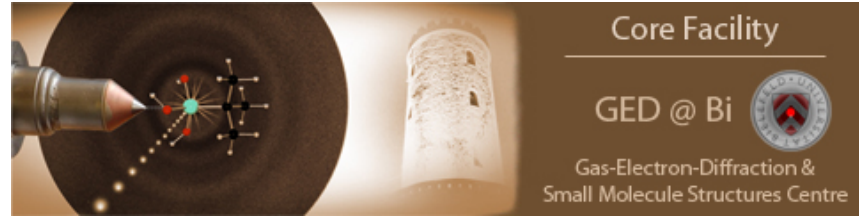
- (Rechnungen versagen)
- 2e⁻-Oxidationsprozesse

[1] Sünkel, K.; Weigand, S.; Hoffmann, A.; Blomeyer, S.; Reuter, C. G.; Vishnevskiy, Yu. V.; Mitzel, N. W.; *J. Am. Chem. Soc.* **2015**, *137*, 126.

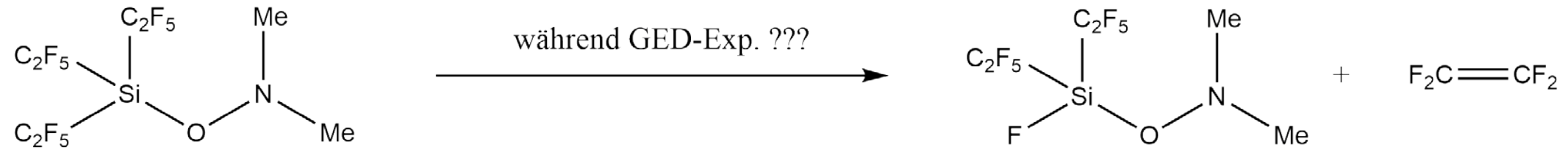
[2] Phillips, L.; Lacey, A. R.; Cooper, M. K. *J. Chem. Soc., Dalton Trans.* **1988**, 1383.

[3] Friesner, R. A.; Baik, M.-H. *J. Phys. Chem. A* **2002**, *106*, 7407.

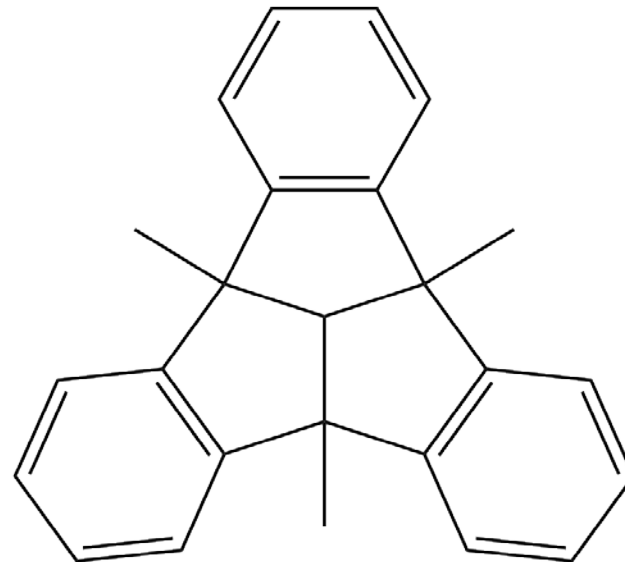
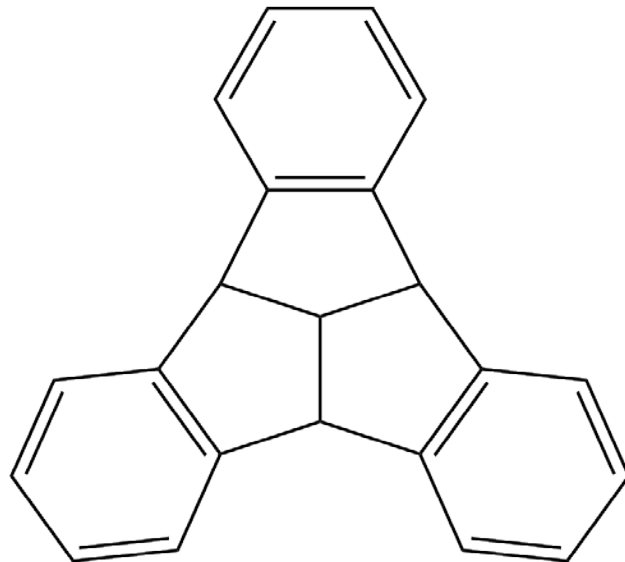
GED – weitere Projekte



Bene:



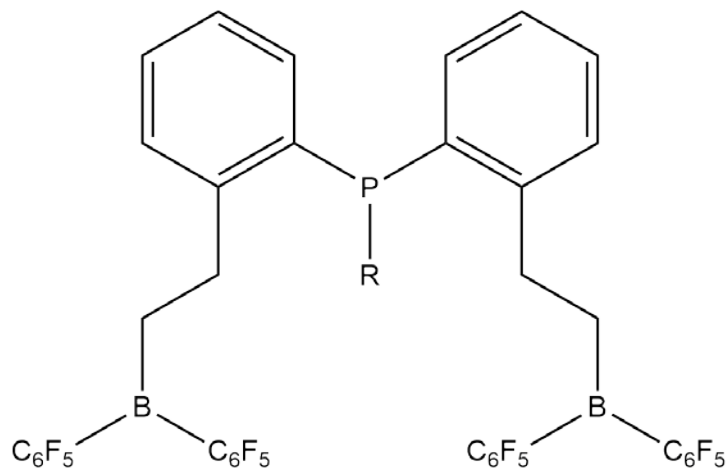
Janek:



QC – weitere Projekte



Leif:



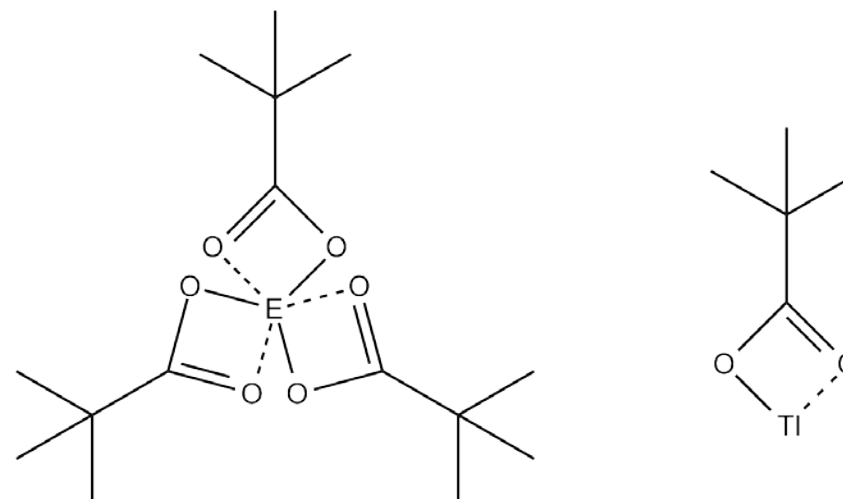
R = Ph, ^tBu, Mes, Tipp

Vergleich Stabilität von offen- und geschlossenkettiger Form

FLP

Dynamik

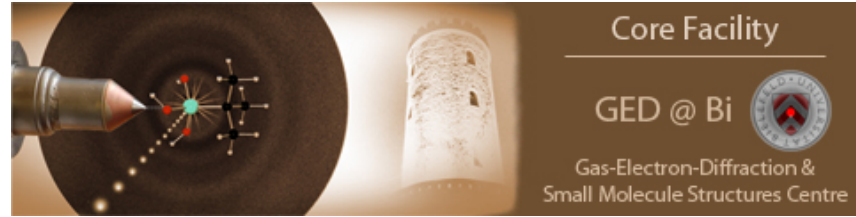
Oleg & Yura:



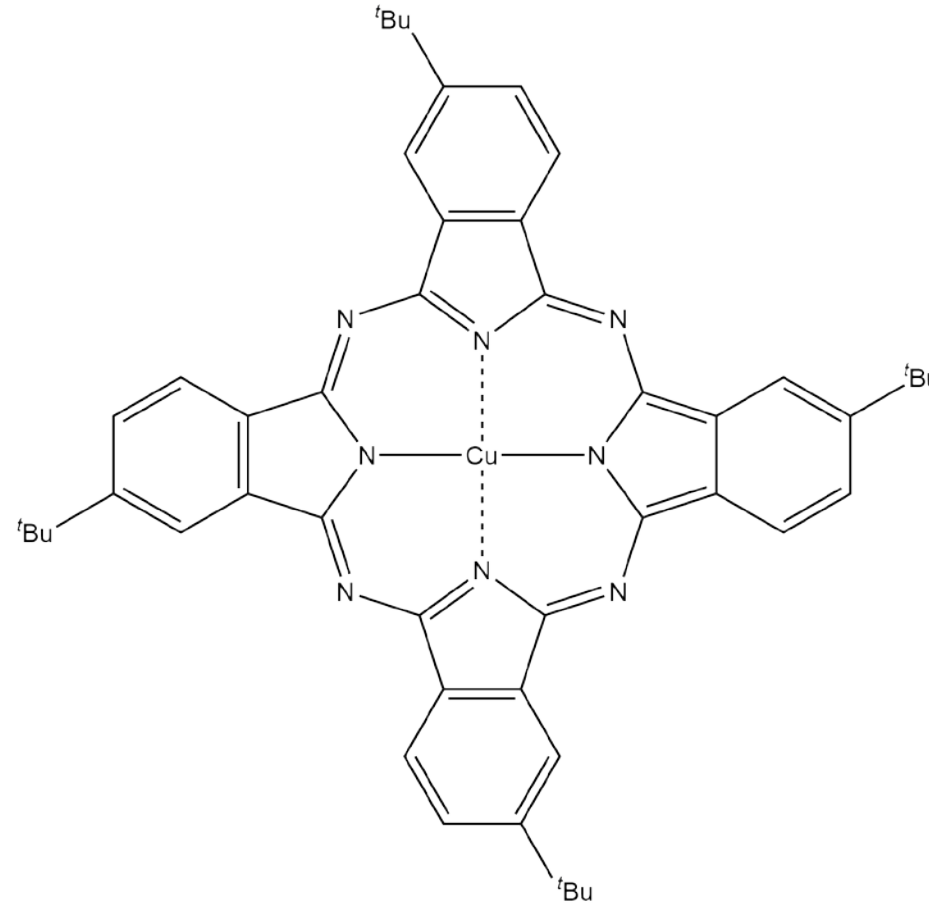
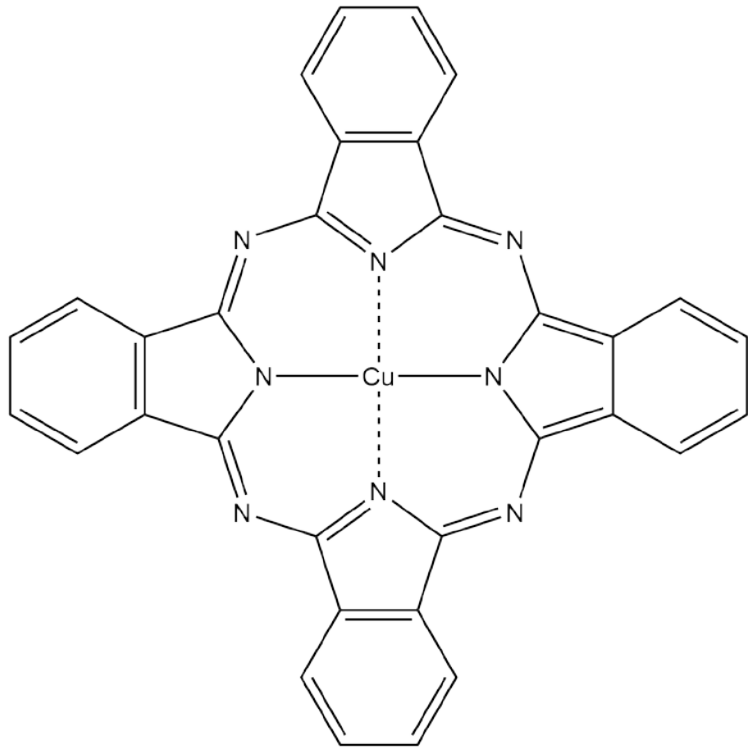
E = Al, Ga, In, (Tl)

Abhängigkeit elektronischer Struktur und Bindungsverhältnisse vom Zentralatom E

QC – weitere Projekte



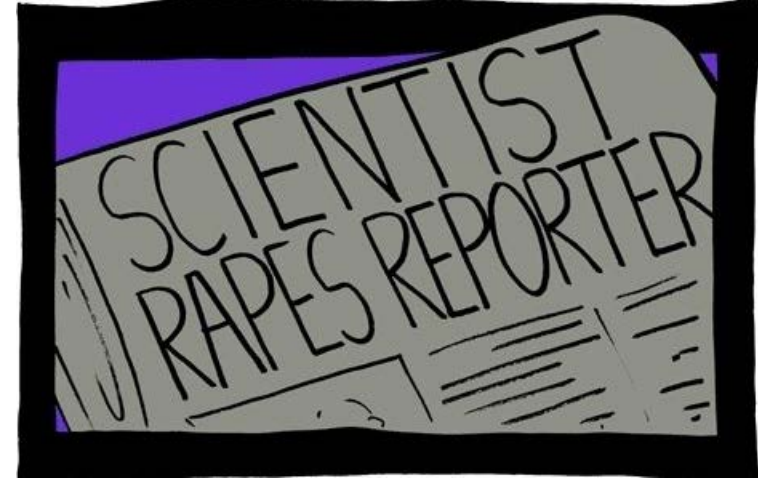
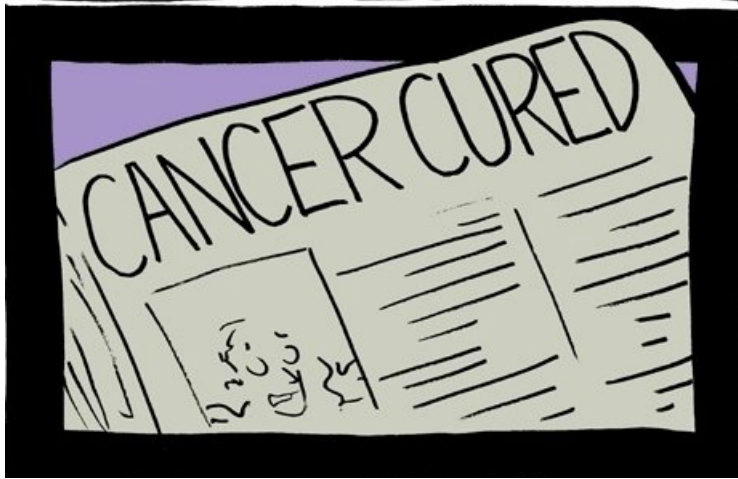
Oleg:



Substituenteneinfluss auf elektronische Struktur und Bindungsverhältnisse der Koordinationskavität

ENDE

HOW SCIENCE REPORTING WORKS:



NOCH FRAGEN?