Anorganische Chemie VI

Konzepte und Theorie an ausgewählten Stoffklassen (KTS)

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2026

PN-Chemie

- Inhalt

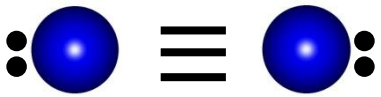
- PN Phosphazene
- Azaphosphole
- $GaCl_3$-assistierte Reaktionen
- Ausblick: Schwere Pnikogene (Azaarsole)

Alle Folien sind im Internet als pdf Dokument erhältlich:

http://www.schulz.chemie.uni-rostock.de/

Stickstoff *vs.* Kohlenstoff *vs.* Phosphor *vs.* Schwefel

Distickstoff: N_2



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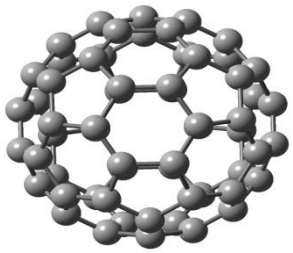
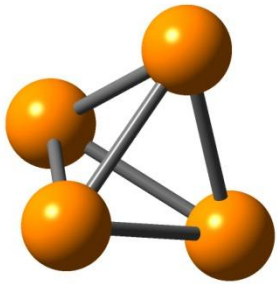
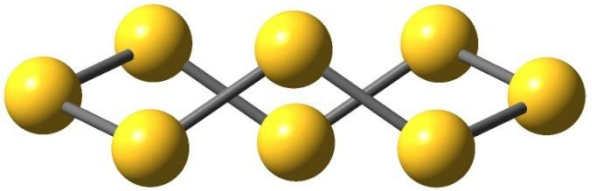


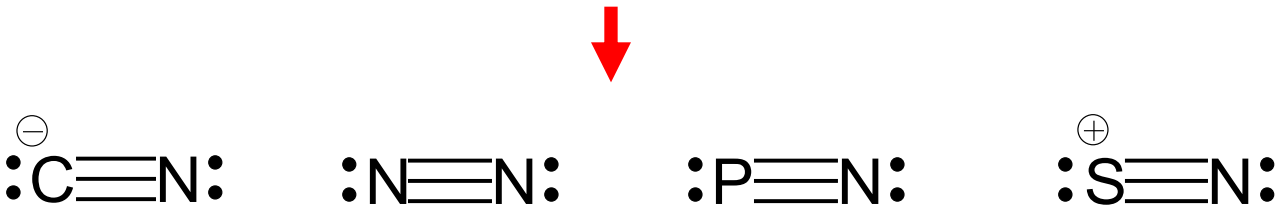
Kohlenstoff: C_{60}



Phosphor: P_4

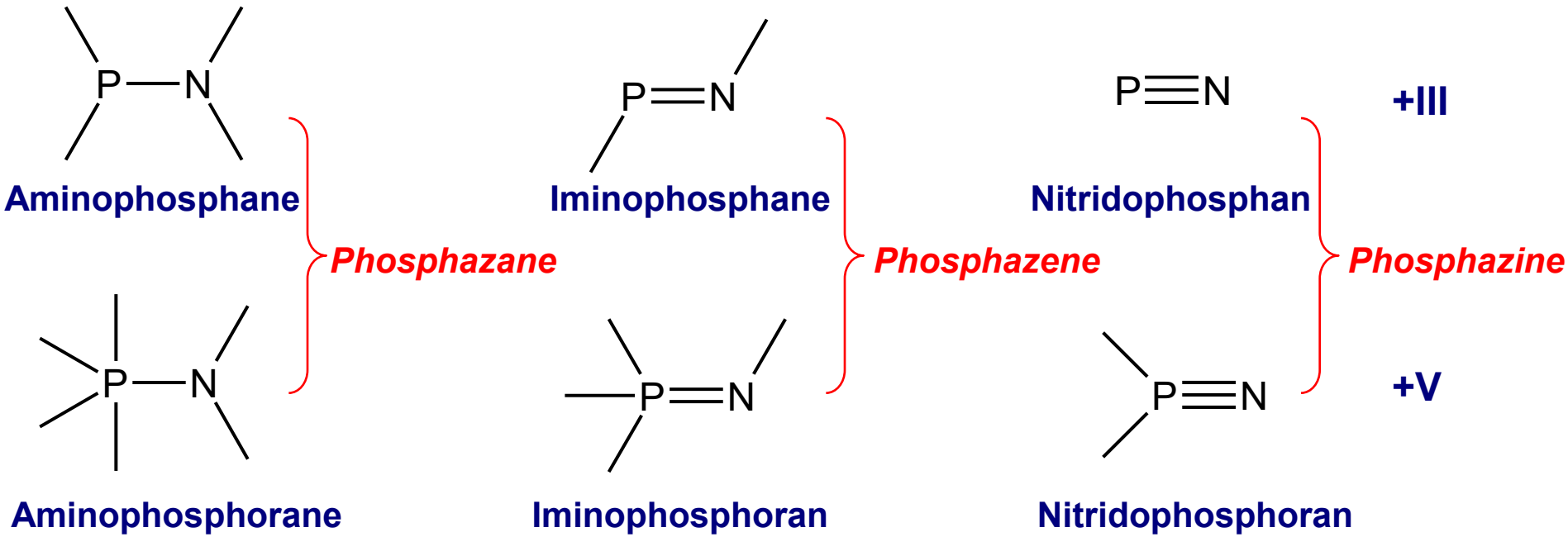


Schwefel: S_8



iso(valenz)elektronisch

Binäre PN Spezies



- Kationen: keine
- Neutralspezies: P_3N_5, $(PN)_n$, $P(N_3)_3$, $P(N_3)_5$, $P_3N_{21} = [PN(N_3)_2]_3$
- Anionen: formal PN_4^{7-}, $P_3N_9^{12-}$, $P_4N_{10}^{10-}$, $[PN_2^-]_n$ (polymeres Anion)

Anwendung - Phosphazene

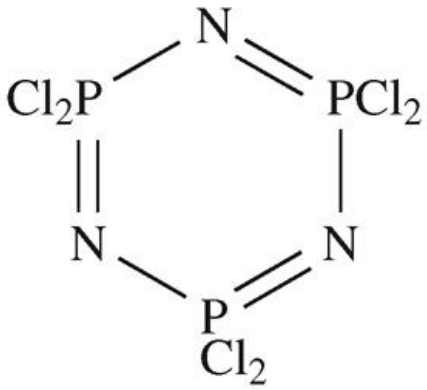
- phosphazane and phosphazene are important starting materials for polyphosphazene
- Exchange of Cl against OR, NR_2, R or chain linking groups
- hydrolysis stable material (from flexible to glass hard)
- fibers, tissues, plastic films, tubes, pipes…
- X = OCH_2CF_3 used for spare organs

Material for synthetic bones

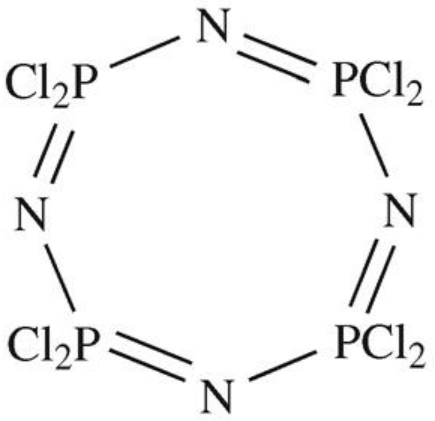
$(-N=PX_2-)_n$

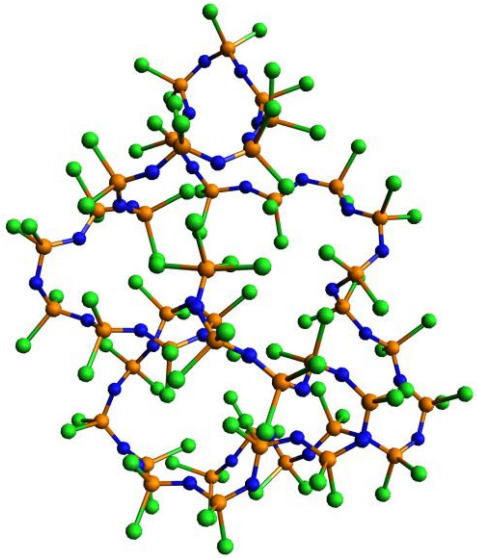
High elastic polymer

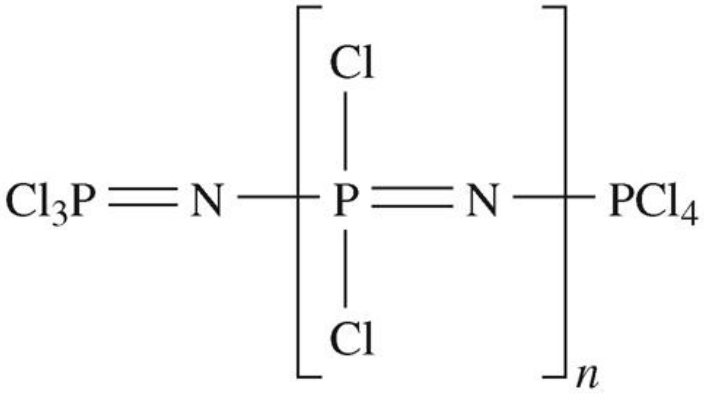
Phosphazene



cyclische







Lineare (Ketten) ?

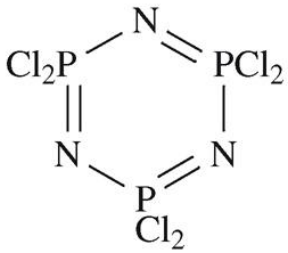
Phosphazene - Darstellung

$$3PCl_5 + NH_4Cl \xrightarrow{-4HCl} [Cl_3P{=}N{=}PCl_3]^+\,[PCl_6]^-$$

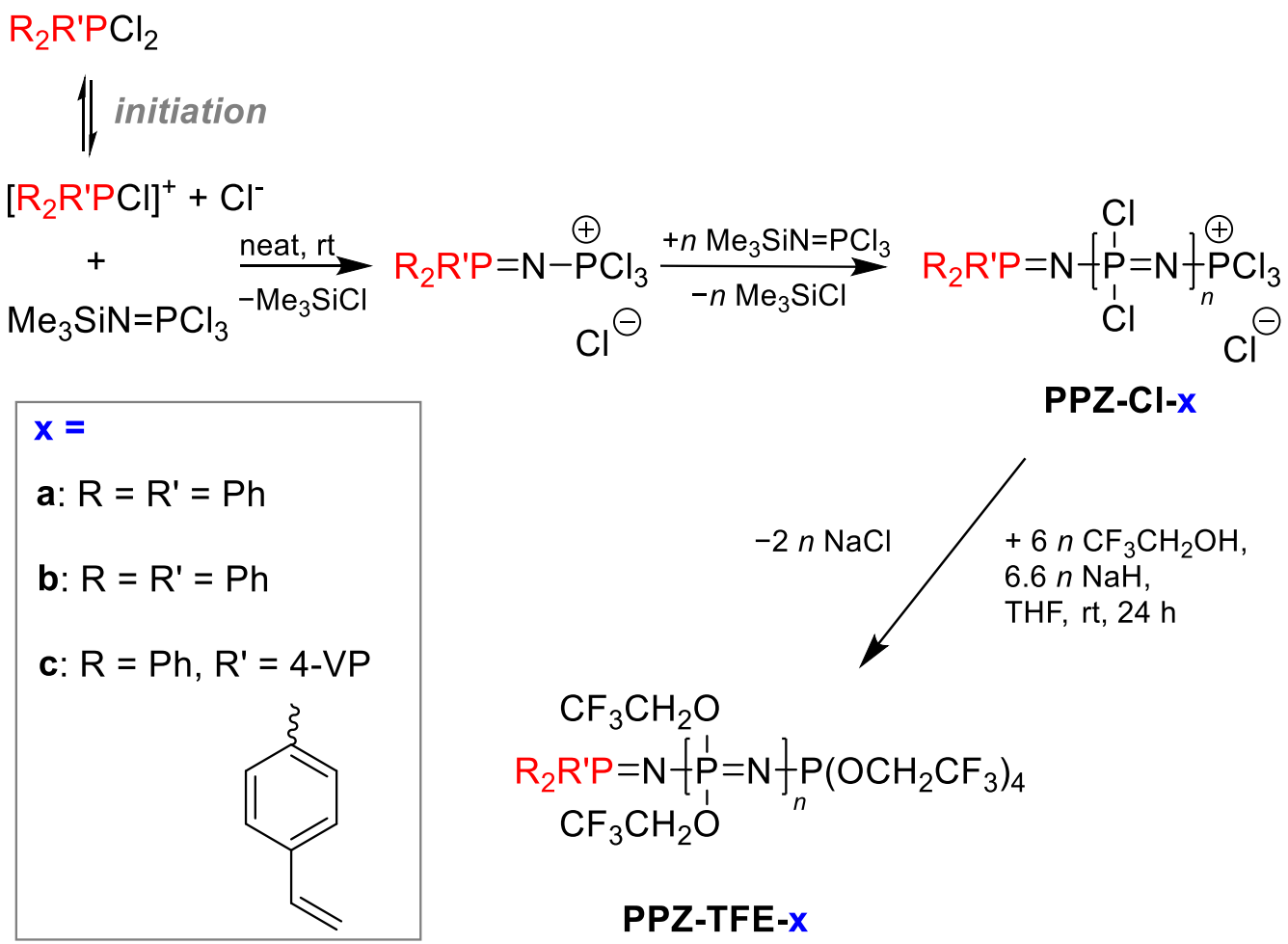
$$[NH_4]^+ + [PCl_6]^- \rightarrow Cl_3P{=}NH + 3HCl$$

$$[Cl_3P{=}N{=}PCl_3]^+ + Cl_3P{=}NH \xrightarrow{-HCl} [Cl_3P{=}N{-}PCl_2{=}N{=}PCl_3]^+$$

$$[Cl_3P{=}N{-}PCl_2{=}N{-}PCl_2{=}N{=}PCl_3]^+ \xrightarrow{-\,[PCl_4]^+}$$



Polymerisation von $Me_3Si\text{-}N{=}PCl_3$



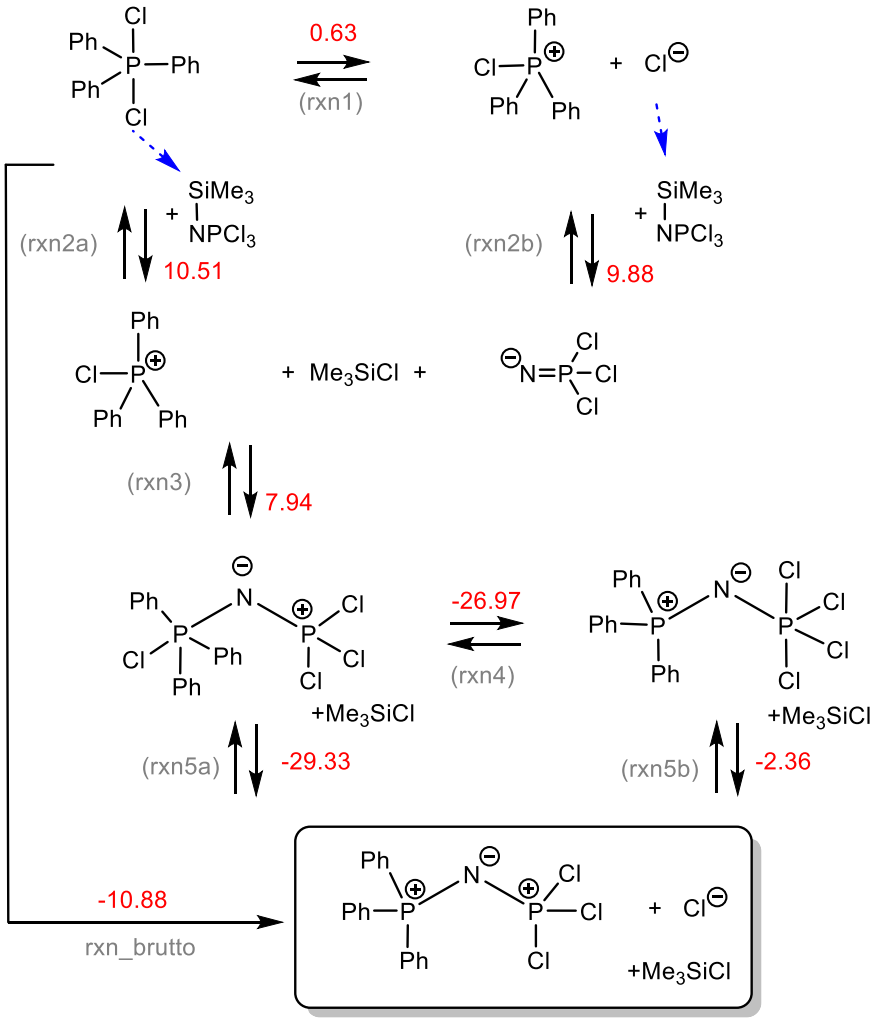
x =

a: R = R' = Ph

b: R = R' = Ph

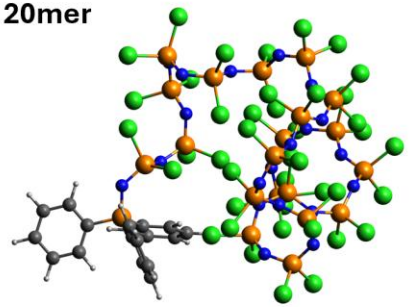
c: R = Ph, R' = 4-VP

Mechanismus

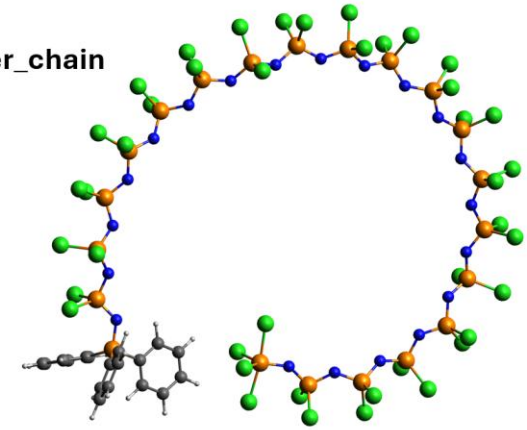


Strukturen

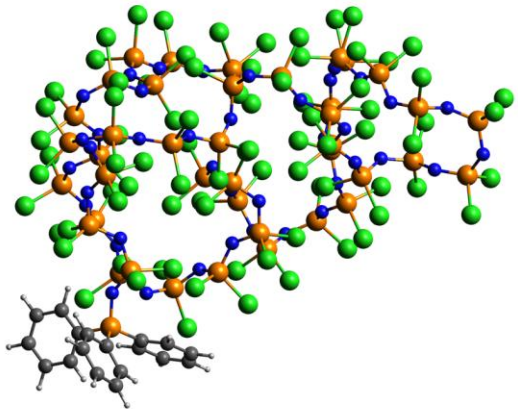
20mer



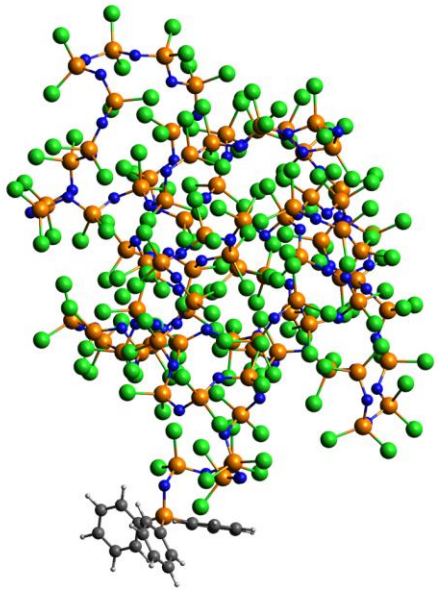
20mer_chain



40mer

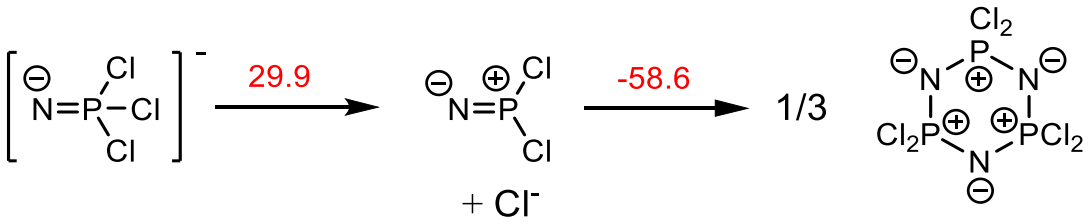


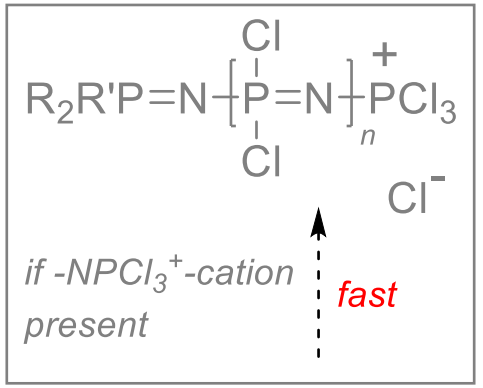
80mer



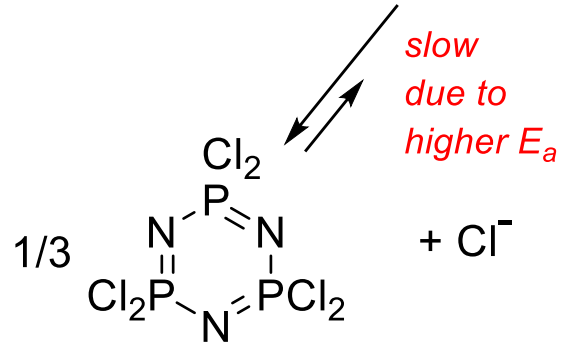
ΔE 47 kcal/mol

Mechanismus: Kette vs. Cyclus

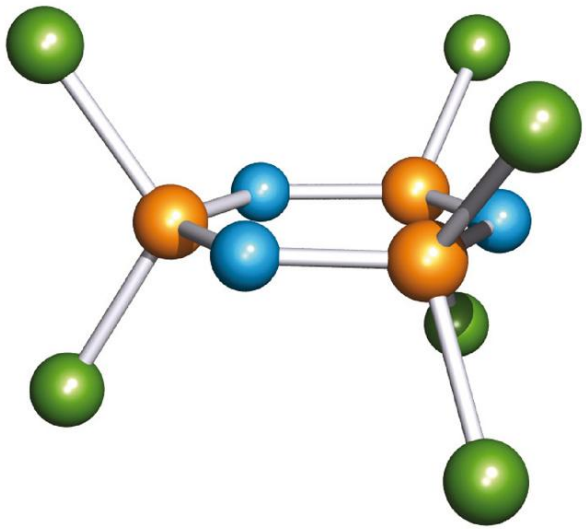




$$[Ph_4P]^+ + Cl^- + Me_3SiN{=}PCl_3 \xrightarrow[-Me_3SiCl]{CH_3CN,\ 25\ min,\ 40\ °C} [Ph_4P]^+ + [N{=}PCl_3]^-$$

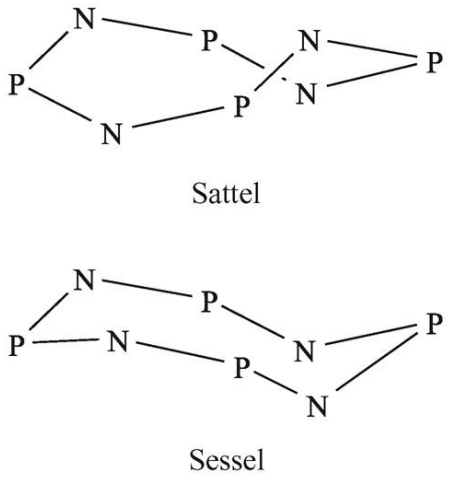


Phosphazene - Strukturen



(a)

	X = Cl	X = F
P—N / pm	158	156
P—X / pm	199	152
∠ P–N–P / Grad	121	120
∠ N–P–N / Grad	118	121
∠ X–P–X / Grad	102	99



(b)

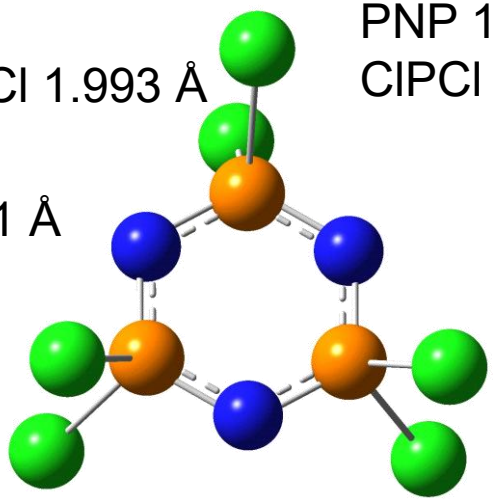
(a) Strukturparameter der Phosphazene $(NPX_2)_3$ (X = Cl oder F); Farbcode: P, orange; N, blau; X, grün. (b) Schematische Darstellungen der Konformationen der P_4N_4-Ringe in $(NPF_2)_4$ (nur Sattelkonformation) und $(NPCl_2)_4$ (Sattel- und Sesselkonformationen).

PN-Chemie: Phosphazene

NPN 118.4°
PNP 121.4°
ClPCl 101.4°

PCl 1.993 Å

PN 1.581 Å



Dewar-Inselmodell?

P: $sp^{2.09}d^{0.13}$

$\pi(p_N\text{-}d_P)$: NUR zu 5 % am P

1834 *Liebig und Wöhler*:

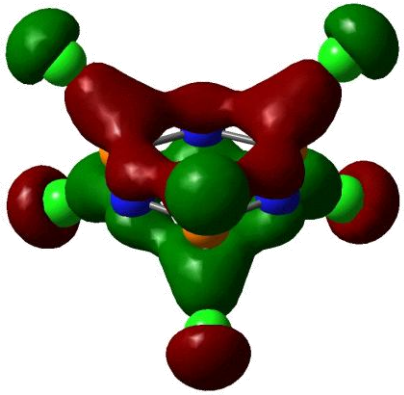
$$PCl_5 + NH_4Cl \longrightarrow 1/n\ (NPCl_2)_n + 4\ HCl$$

Polymer vs. Makromolekül

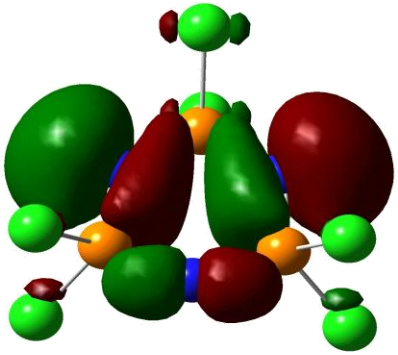
n = 3 Hexachlor-cyclotriphosphazen

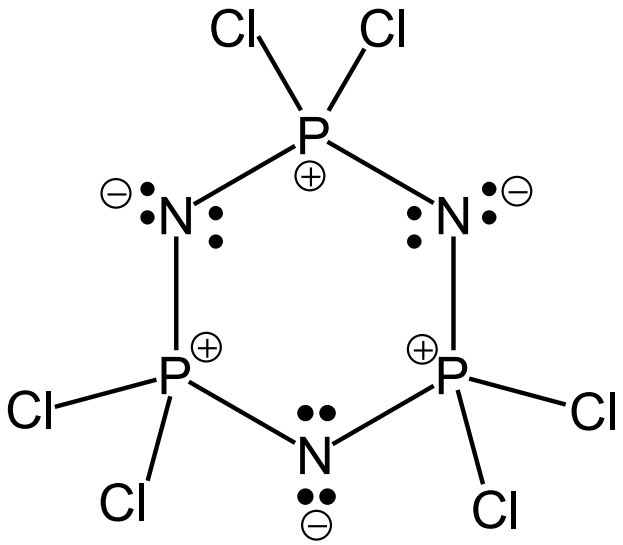
Doppelbindungen in $(NPCl_2)_3$: VB versus MO

out-of-plane

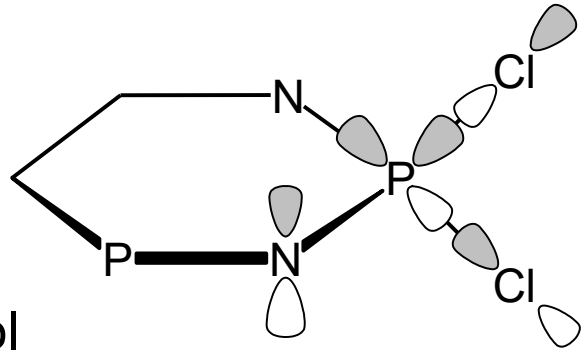


in-plane



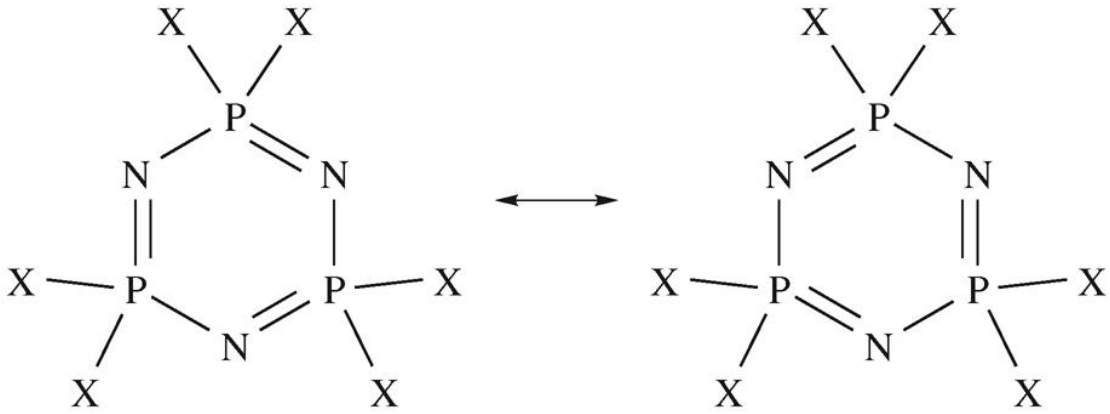


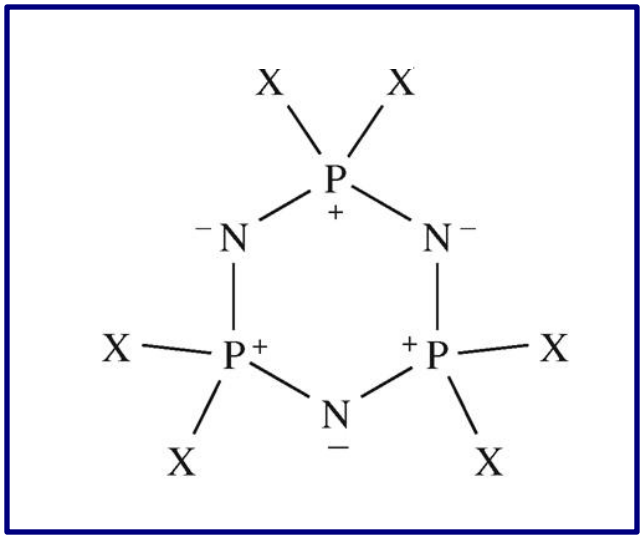
P: **+2.07**
N: **-1.61**
Cl: -0.24



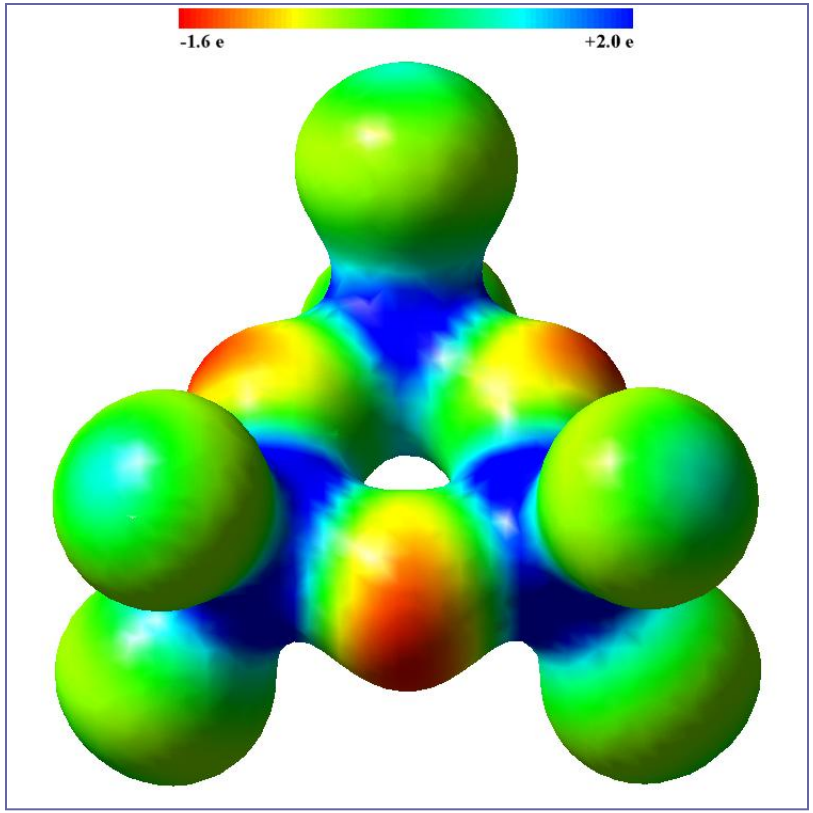
π-LP(N) $\rightarrow$ σ^*(P-Cl): 19 kcal/mol

Lewis-Formeln





Ladungsverteilung – Nukleophile Substitution



Internet Electronic Journal of Molecular Design **2003**, *2*, 653.

$$(NPCl_2)_3 + 6\ KX \longrightarrow [NP(X)_2]_3 + 6\ KCl$$

X = Pseudohalogen

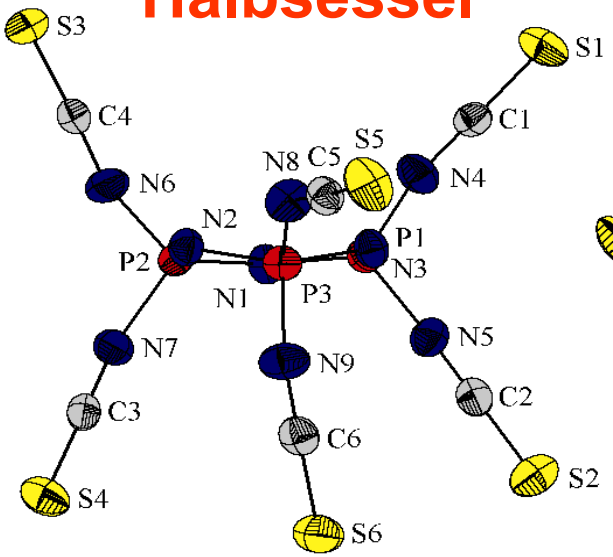
2,2,4,4,6,6-Hexaisothiocyanatocyclotriphosphazen

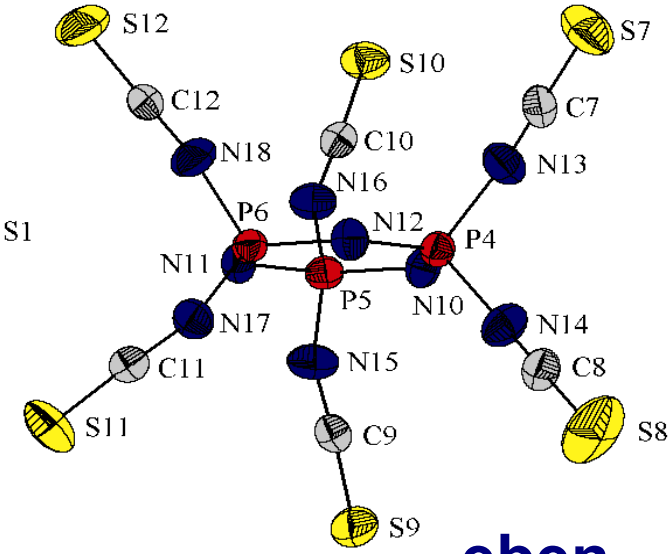
$P2_1/c$

Acta Cryst. **2002**, *E58*, i15–i16

d(P–N) = 1.56 - 1.58 Å

Halbsessel

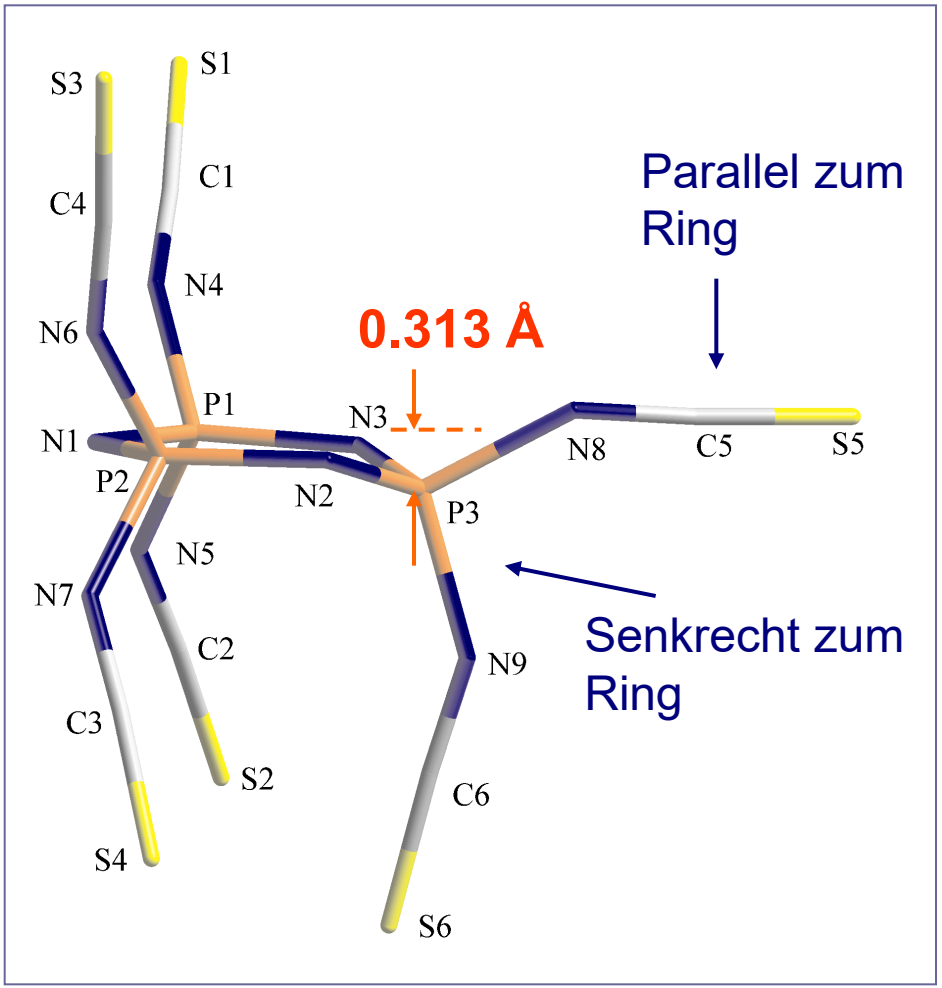




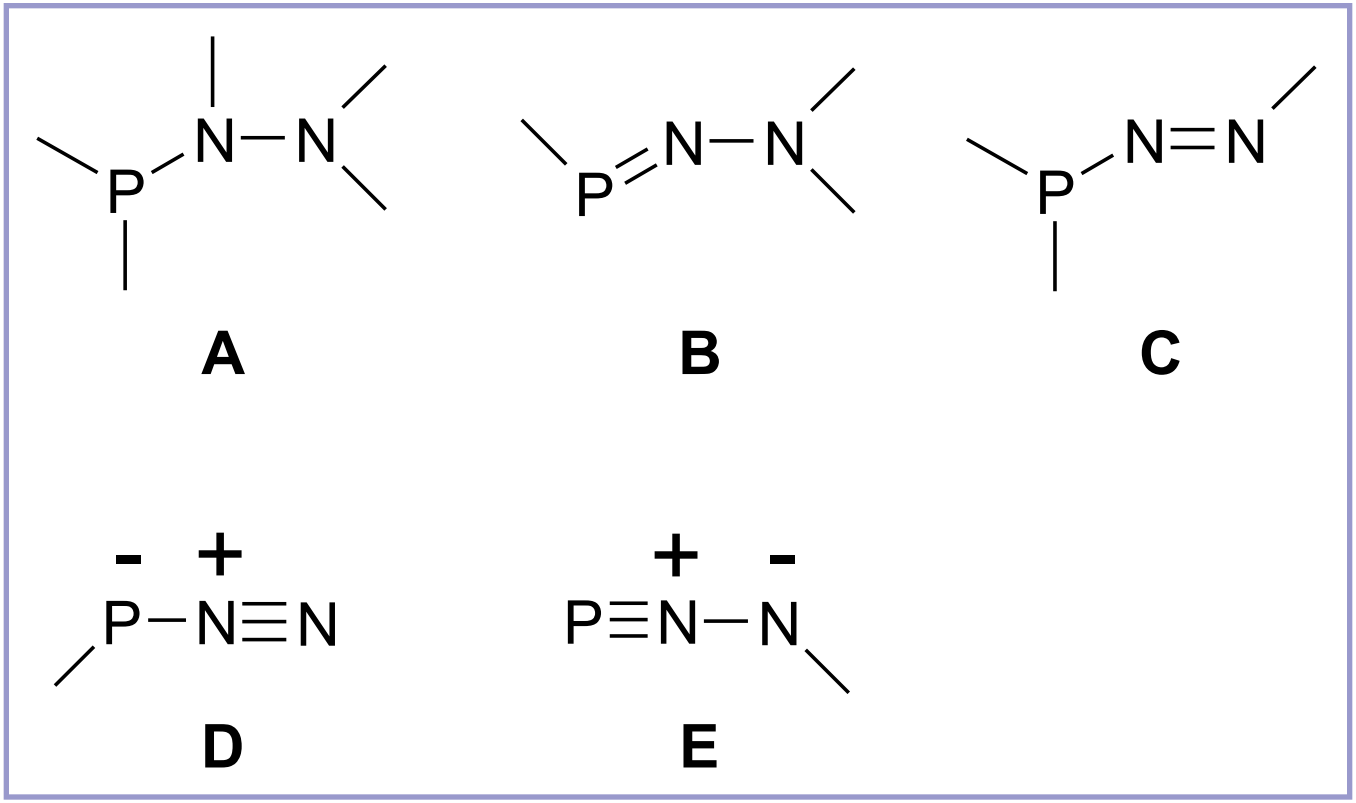
eben

$(NPCl_2)_3$ + 6 KSCN ⟶ $[NP(SCN)_2]_3$ + 6 KCl

Symmetrieerniedrigung erzwingt Abwinkelung



Phosphor-Azid-Analoga: NNP^- ?

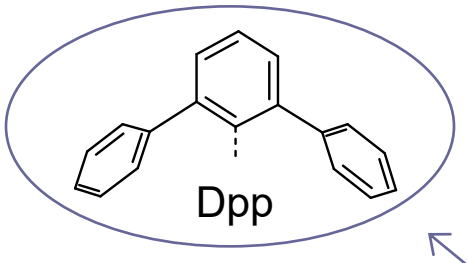


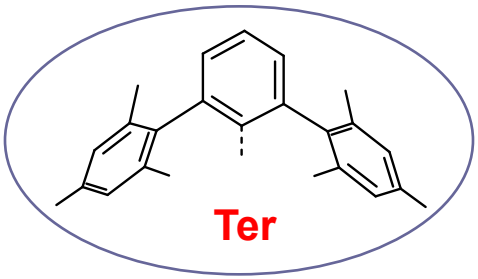
PN Chemie:

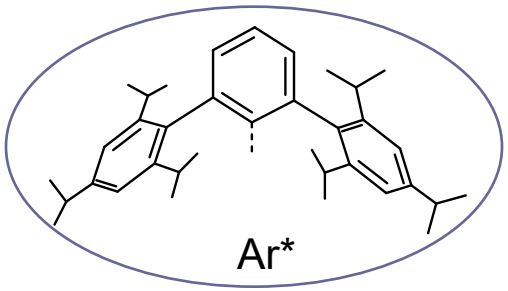
E. Niecke, D. Gudat, *Angew. Chem.* **1991**, *103*, 251 – 270.
Multiple Bonds and Low Coordination in Phosphorus Chemistry, ed. M. Regitz, O. J. Scherer, Weinheim, 1990.

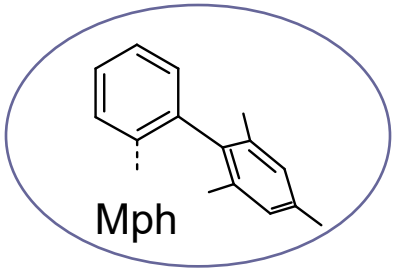
Tolman Cone Angle für einige sterisch anspruchsvolle Liganden

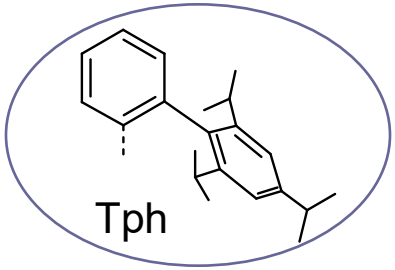
Ligand R		Θ_{max}
t-Bu	$-CMe_3$	124
Mes	$-C_6H_2Me_3$-2,4,6	165
Trip	$-C_6H_2i\text{-}Pr_3$-2,4,6	178
Tph	$-C_6H_3$Trip-2	180
Hyp	$-Si(SiMe_3)_3$	192
Dpp	$-C_6H_3Ph_2$-2,6	200
Ter	$-C_6H_3Mes_2$-2,6	206
Tris	$-C(SiMe_3)_3$	215
Mes*	$-C_6H_3$ *t*-Bu_3-2,4,6	228
Ar*	$-C_6H_3Trip_2$-2,6	310

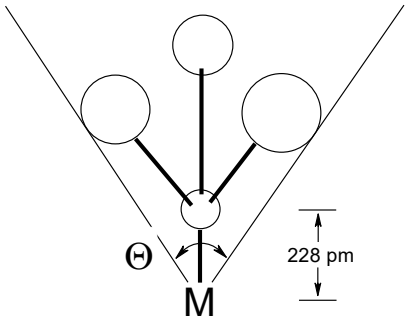




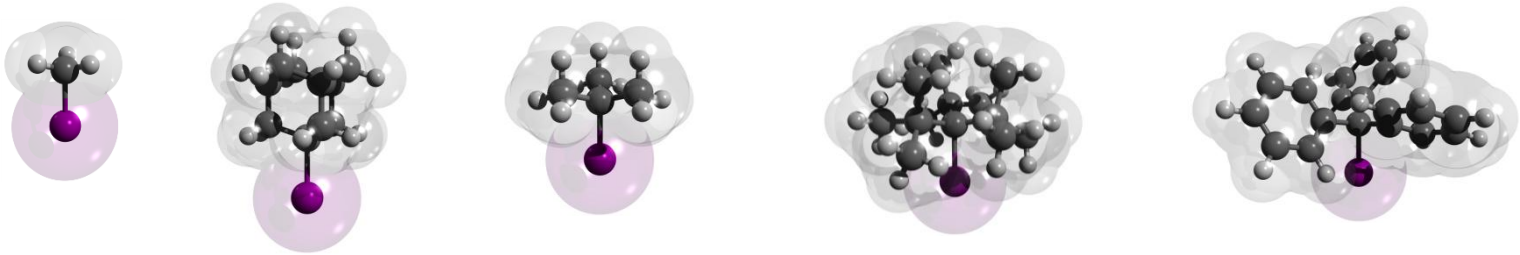


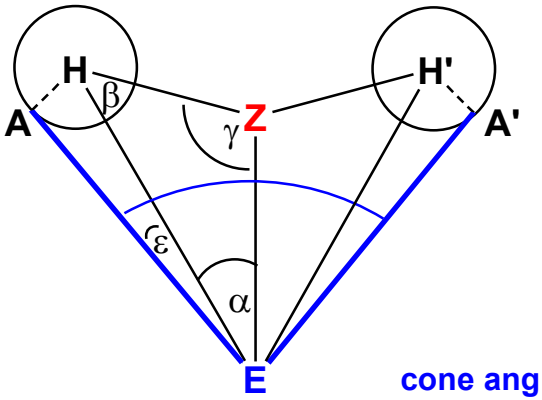




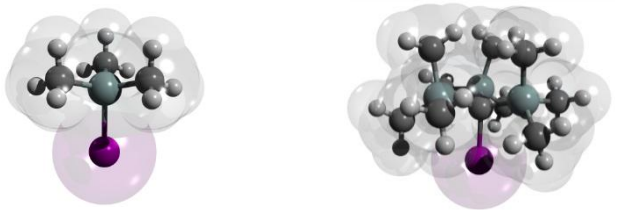


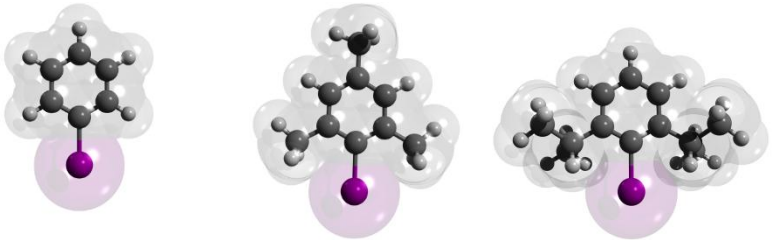
Cone Angles

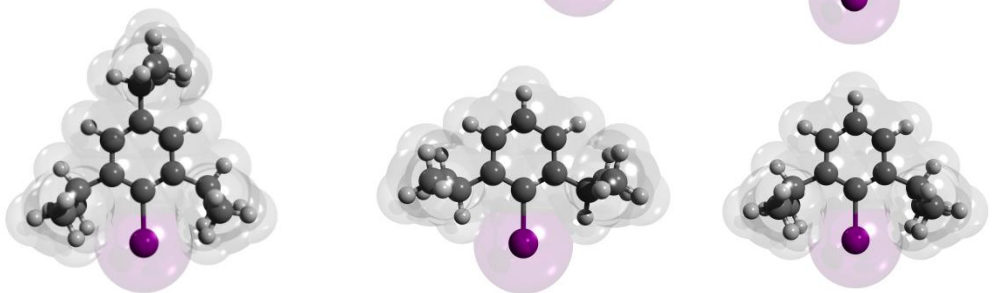




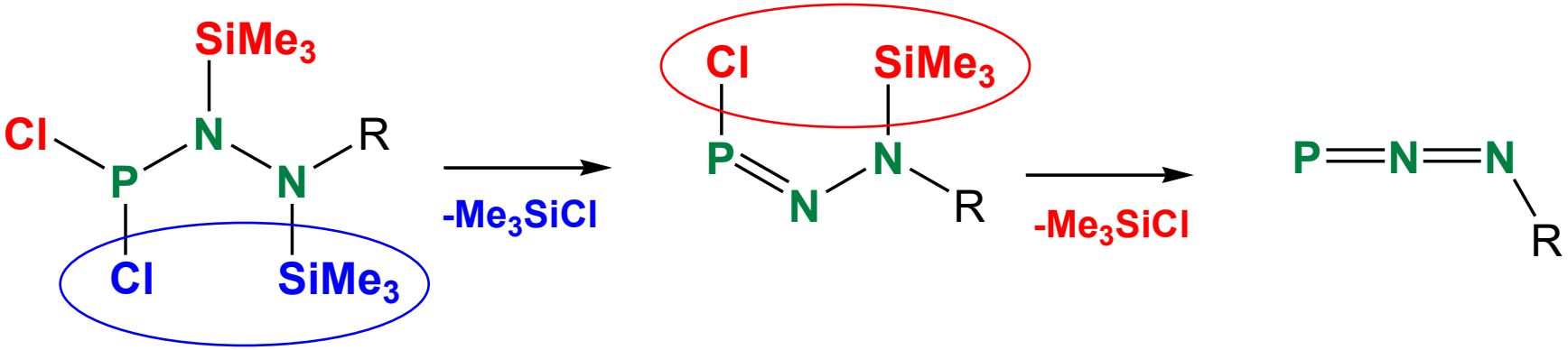
cone angle = $\Theta = 2\,(\alpha + \varepsilon)$

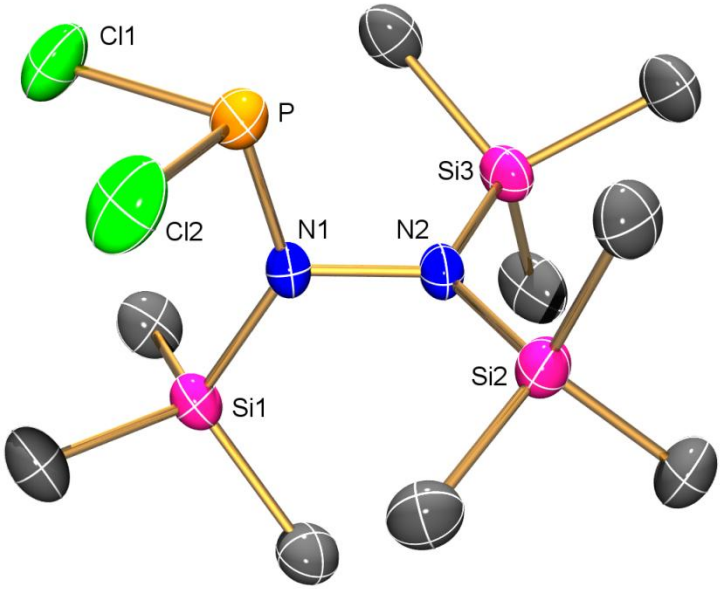






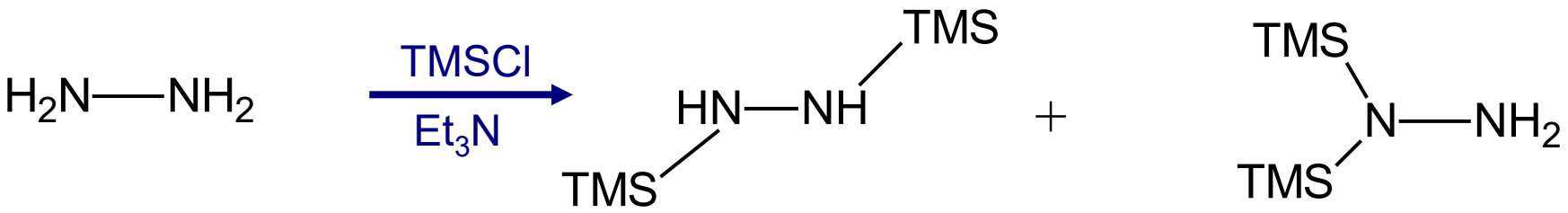
$(Me_3Si)_2N$-$(Me_3Si)N$-PCl_2: Ein „NNP-Precursor“ ?



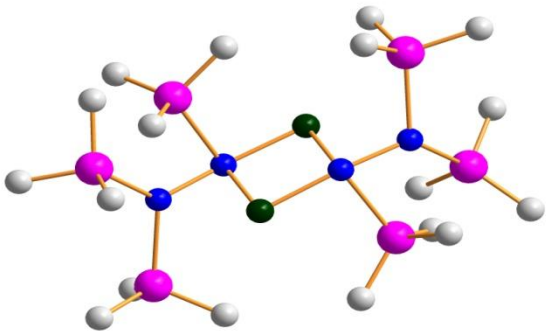


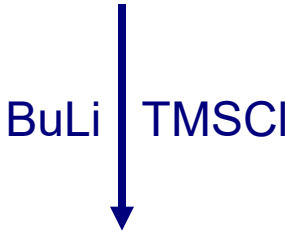
E. Niecke, O. Altmeyer, M. Nieger, F. Knoll *Angew. Chem.* **1987**, *99*, 1299.

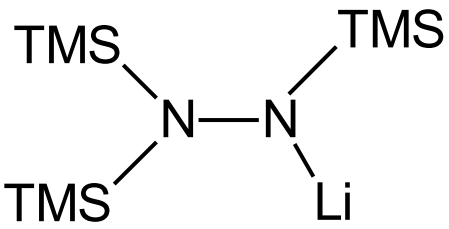
Bis[lithium-tris(trimethylsilyl)hydrazid]

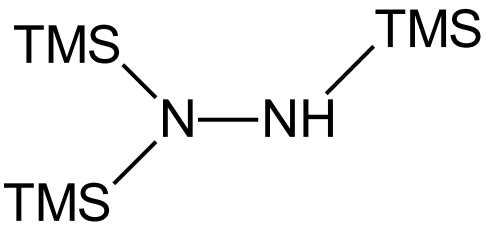


TMS = Me_3Si





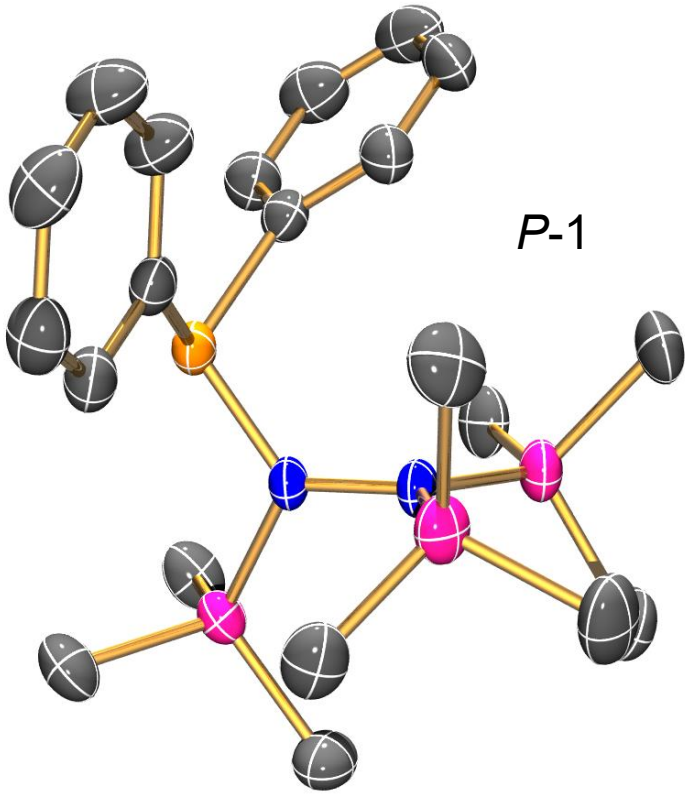


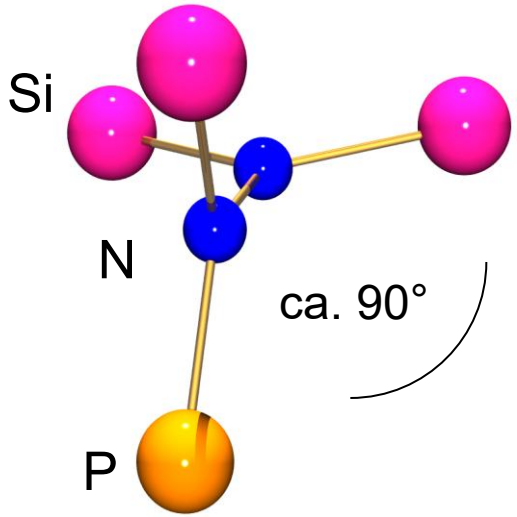


Nöth et al. *Angew. Chem*. **1994**, *106*, 1837-1839;
Klingebiel et al. *Z. Anorg. Allg. Chem*. **1995**, *621*, 500-505.

Umsetzung mit Ph_2PCl

$$Li[N(TMS)N(TMS)_2] + Ph_2PCl \longrightarrow Ph_2PN(TMS)N(TMS)_2 + LiCl$$





d(NN) = 1.476 Å
d(PN) = 1.704 Å

r_{kov}(N) = 0.7
r_{kov}(P) = 1.1
Σ = 1.8 Å

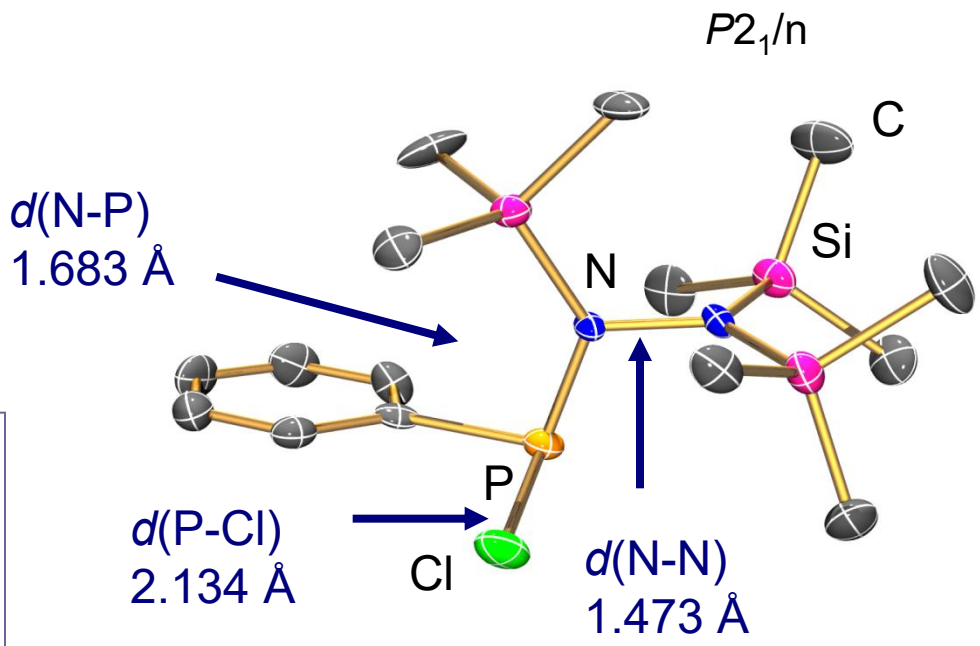
TMS = Me_3Si

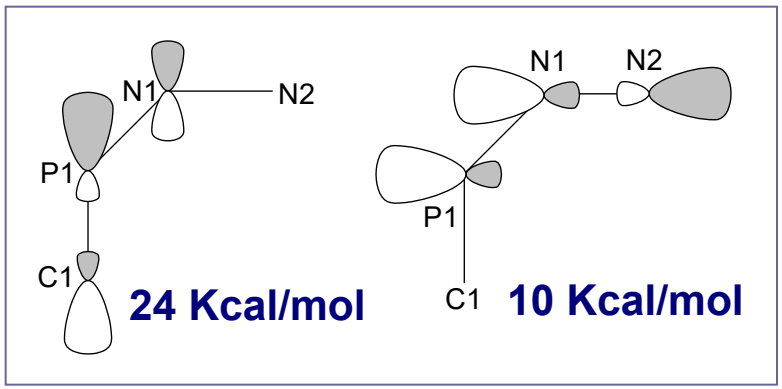
Inorg. Chem. **2005**, *44*, 1740 – 1751.

Umsetzung mit $PhPCl_2$

$$Li[N(TMS)N(TMS)_2] + PhPCl_2 \longrightarrow PhP(Cl)N(TMS)N(TMS)_2 + LiCl$$

TMS = Me_3Si



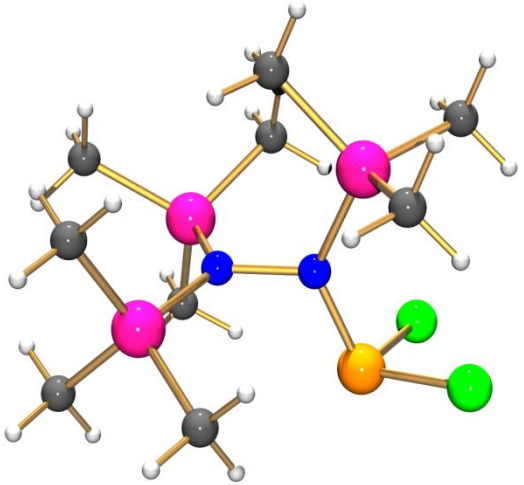


Inorg. Chem. **2005**, *44*, 1740 – 1751.

Umsetzung mit PCl_3

$$Li[N(TMS)N(TMS)_2] + PCl_3 \xrightarrow{RT,\ THF} Cl_2PN(TMS)N(TMS)_2 + LiCl$$

TMS = Me_3Si



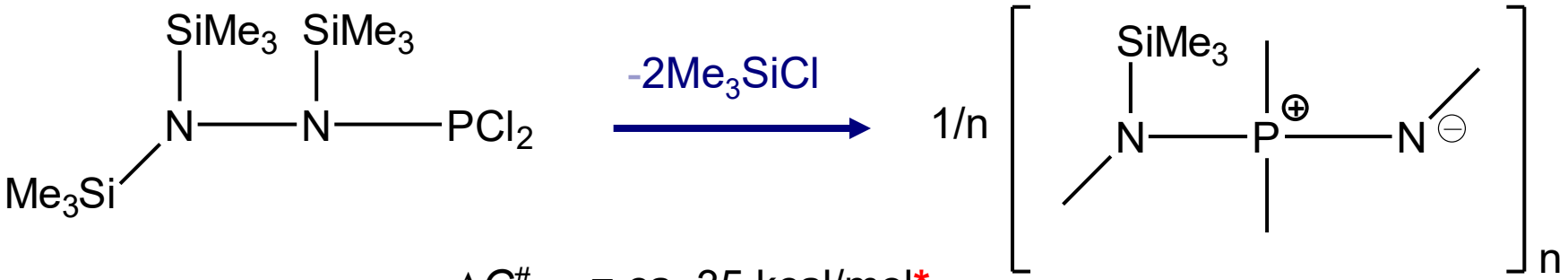
4 Wochen Rückfluß kochen!

Rückfluß | Benzol

$$\text{„ClPNN(TMS)}_2\text{“} + \text{TMS-Cl} \xrightarrow[\text{Benzol}]{\text{Rückfluß}} \text{„PNN(TMS)“} + \text{TMS-Cl}$$

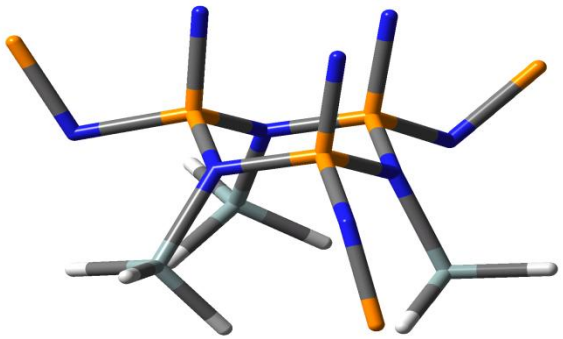
HCNP-Analyse, Raman

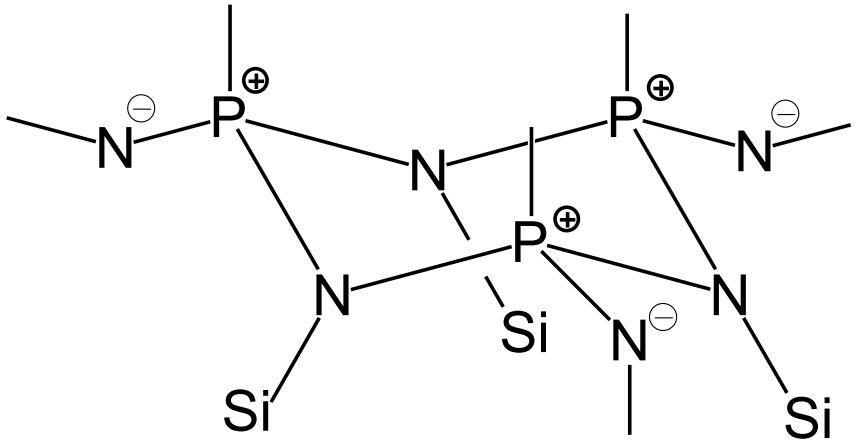
Me_3Si-Derivat vom Phospham $(HPN_2)_n$



$\Delta G^{\#}_{298}$ = ca. 35 kcal/mol*

Formal polymeres Strukturelement: PN_2^-

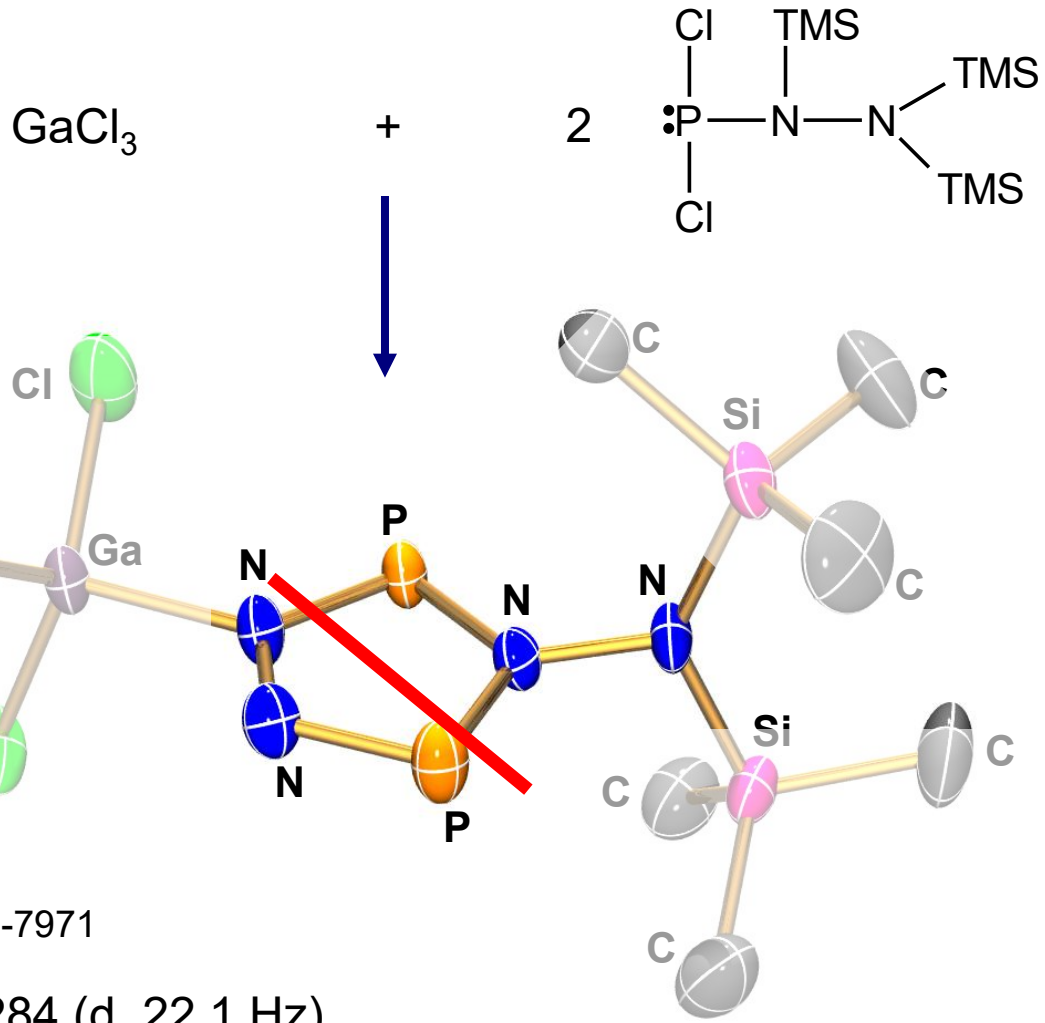




*B3LYP/6-311+G(3df,2p)

Das erste Triazadiphosphol

TMS = Me_3Si

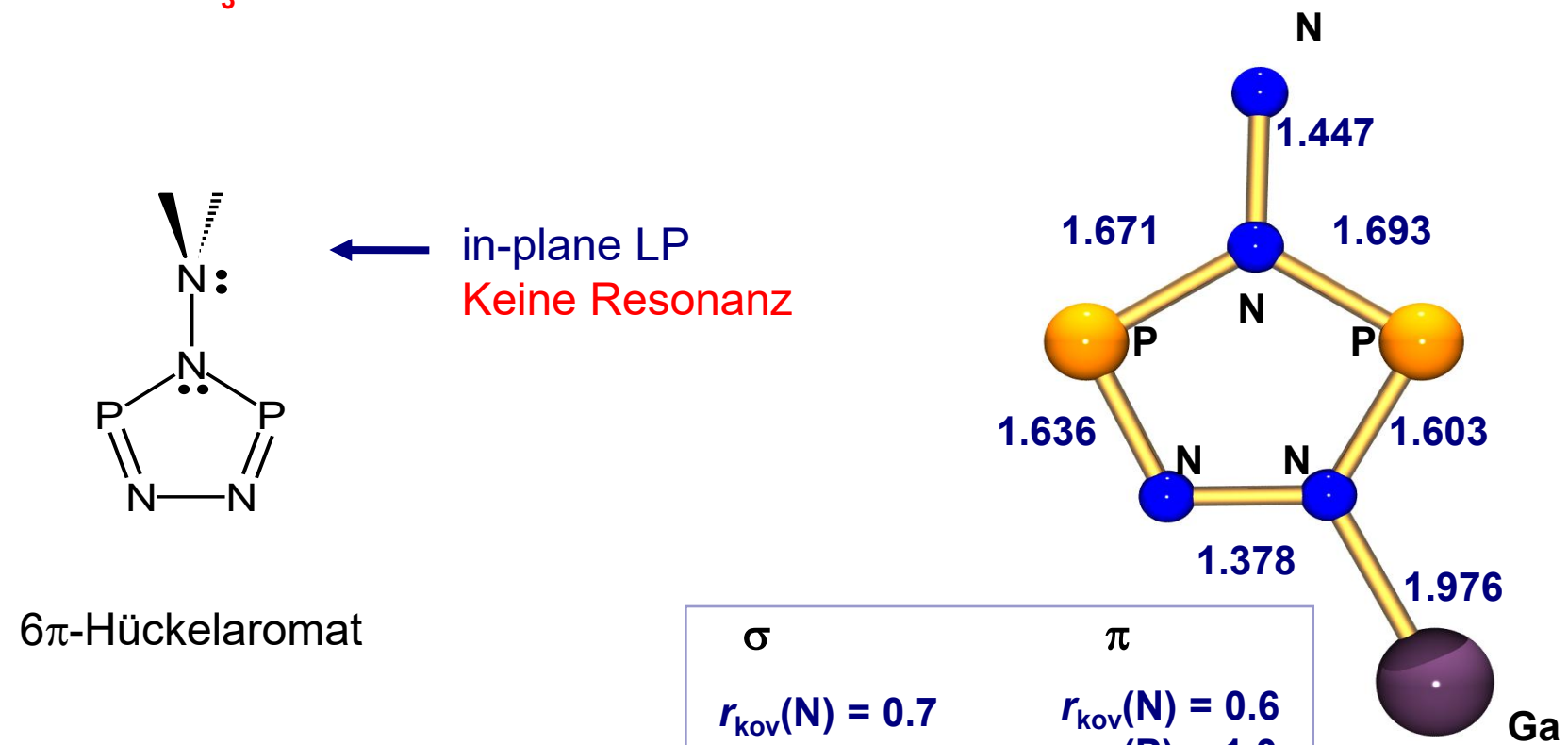


P-1

Angew. Chem. **2005**, *117*, 7968-7971

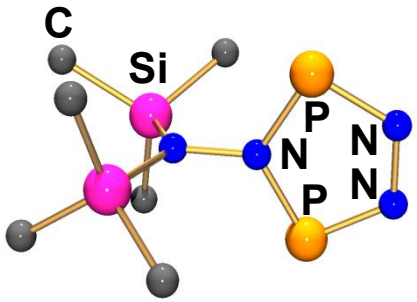
^{31}P: δ= 312 (d, 22.1 Hz), 284 (d, 22.1 Hz)

P_2N_3: Struktur und Bindung

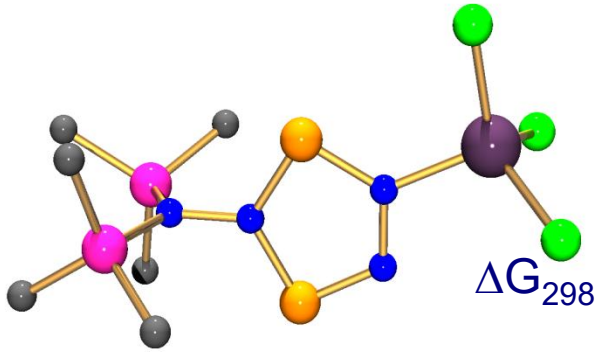


Angew. Chem. **2005**, *117*, 7968-7971.

$GaCl_3$ - Addukt - Gleichgewichte



$+GaCl_3$ ⇌ $-GaCl_3$



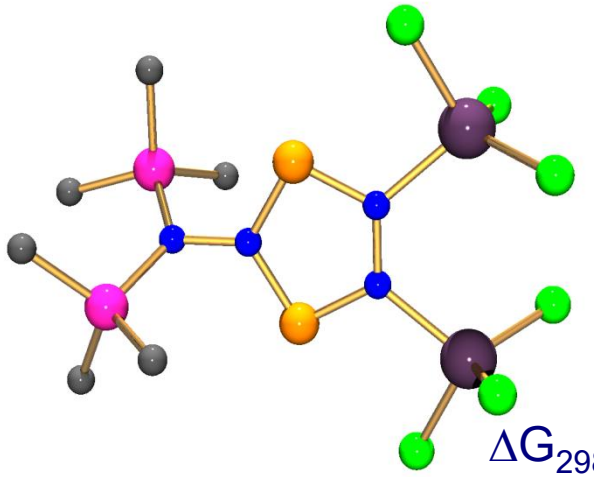
Q_{CT} = 0.16 *e*

ΔG_{298} = -7.8 kcal/mol*

Monoaddukt: $\delta(^{31}P)$= 312 (d, 22.1 Hz), 284 (d, 22.1 Hz)

Diaddukt: $\delta(^{31}P)$= 305

$-GaCl_3$ ⇅ $+GaCl_3$



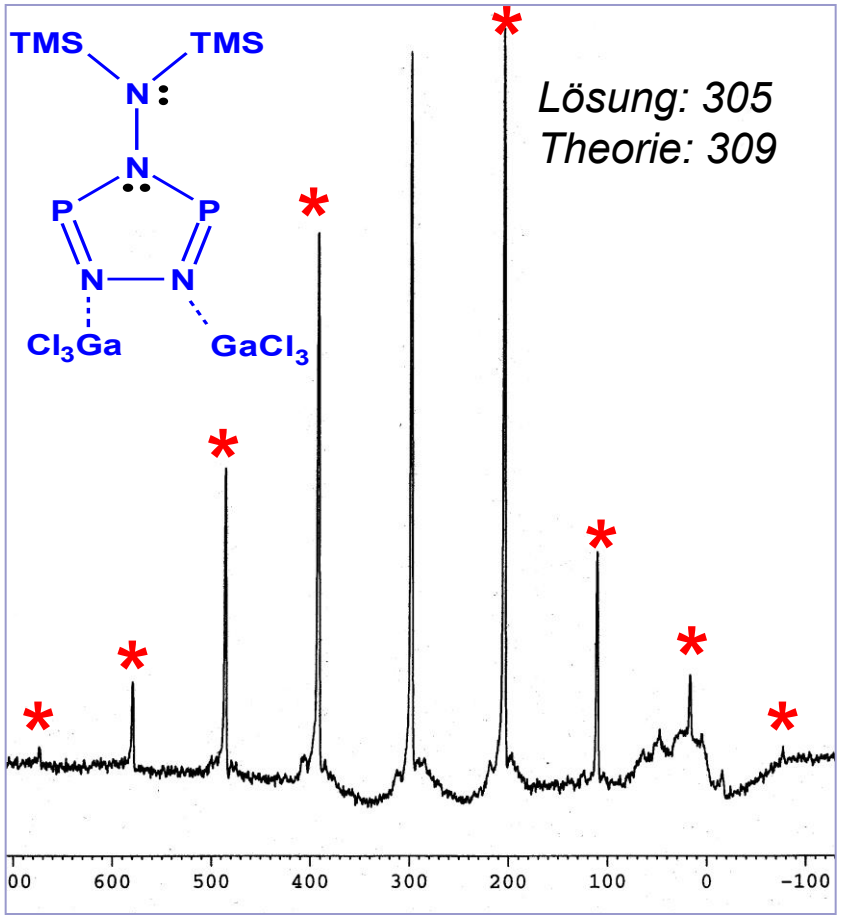
$2 \cdot Q_{CT}$ = 0.11 *e*

ΔG_{298} = 0.6 kcal/mol*

*B3LYP/6-31G(d,p), Ga: SDD+d

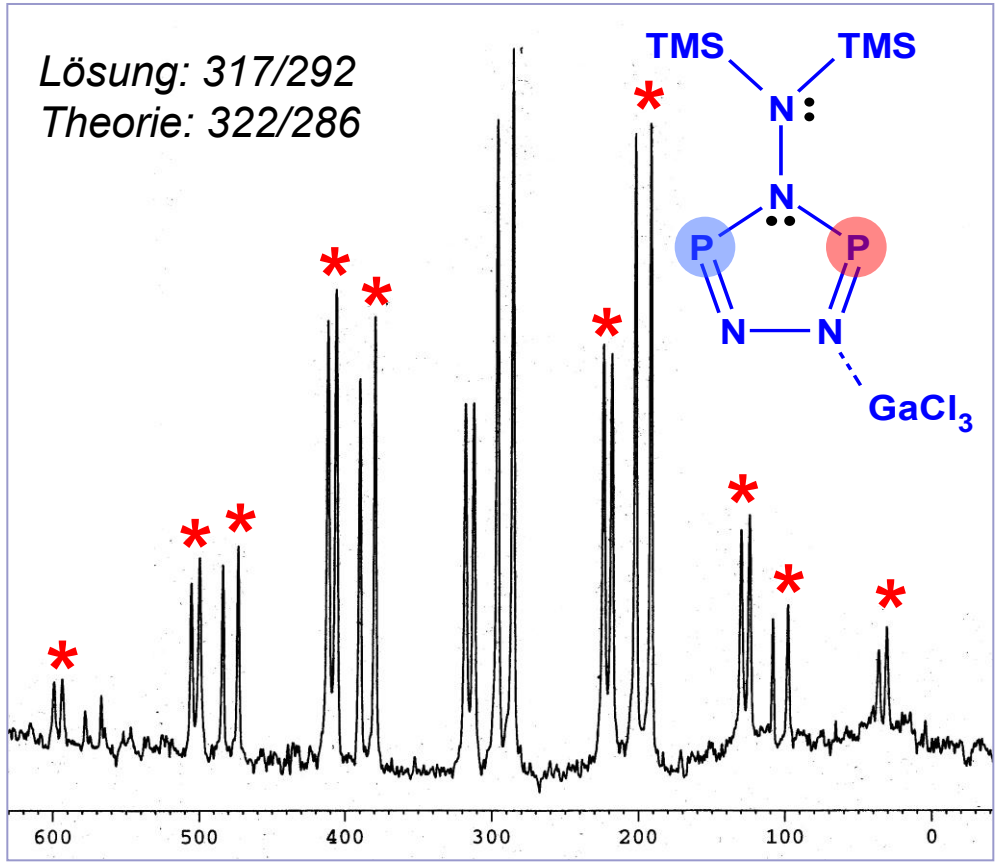
^{31}P-MAS-NMR-Studie

299 ppm



Diaddukt

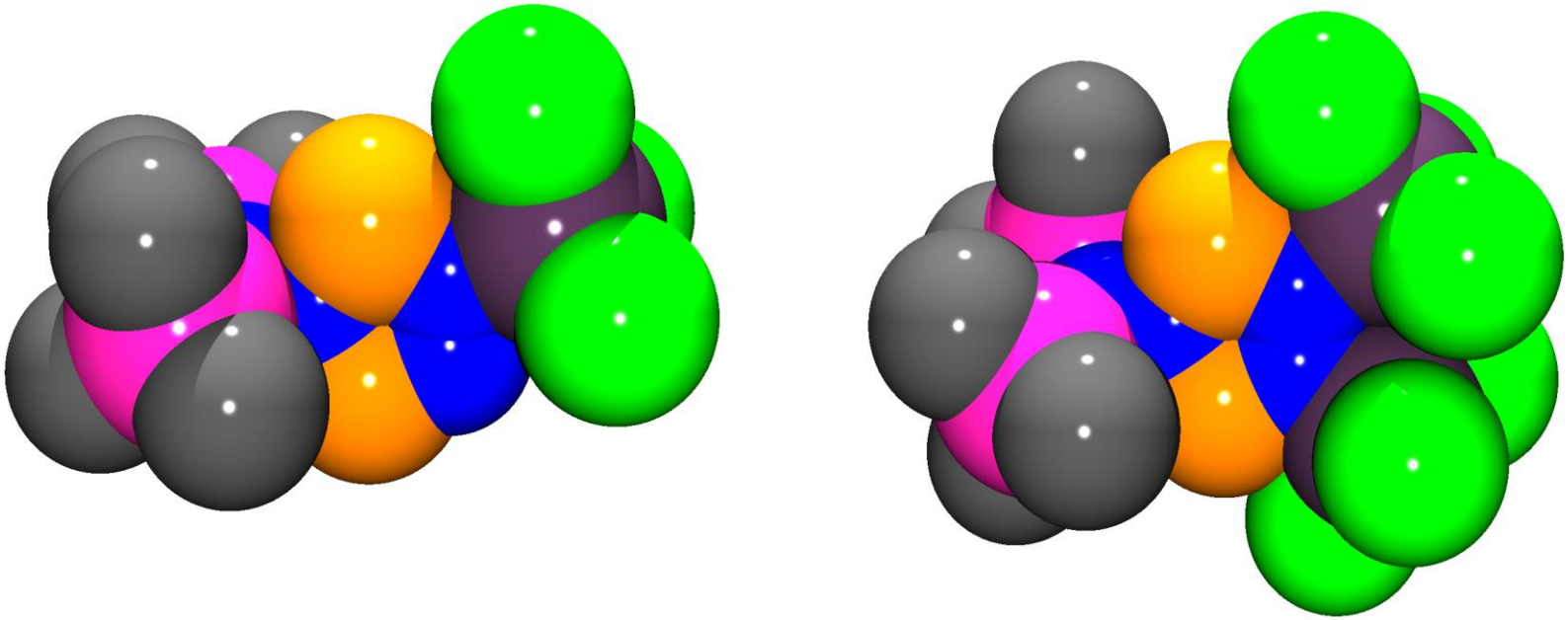
317/312 **296/285** **ppm**



Monoaddukt

Kinetische Stabilisierung - Eigenschaften

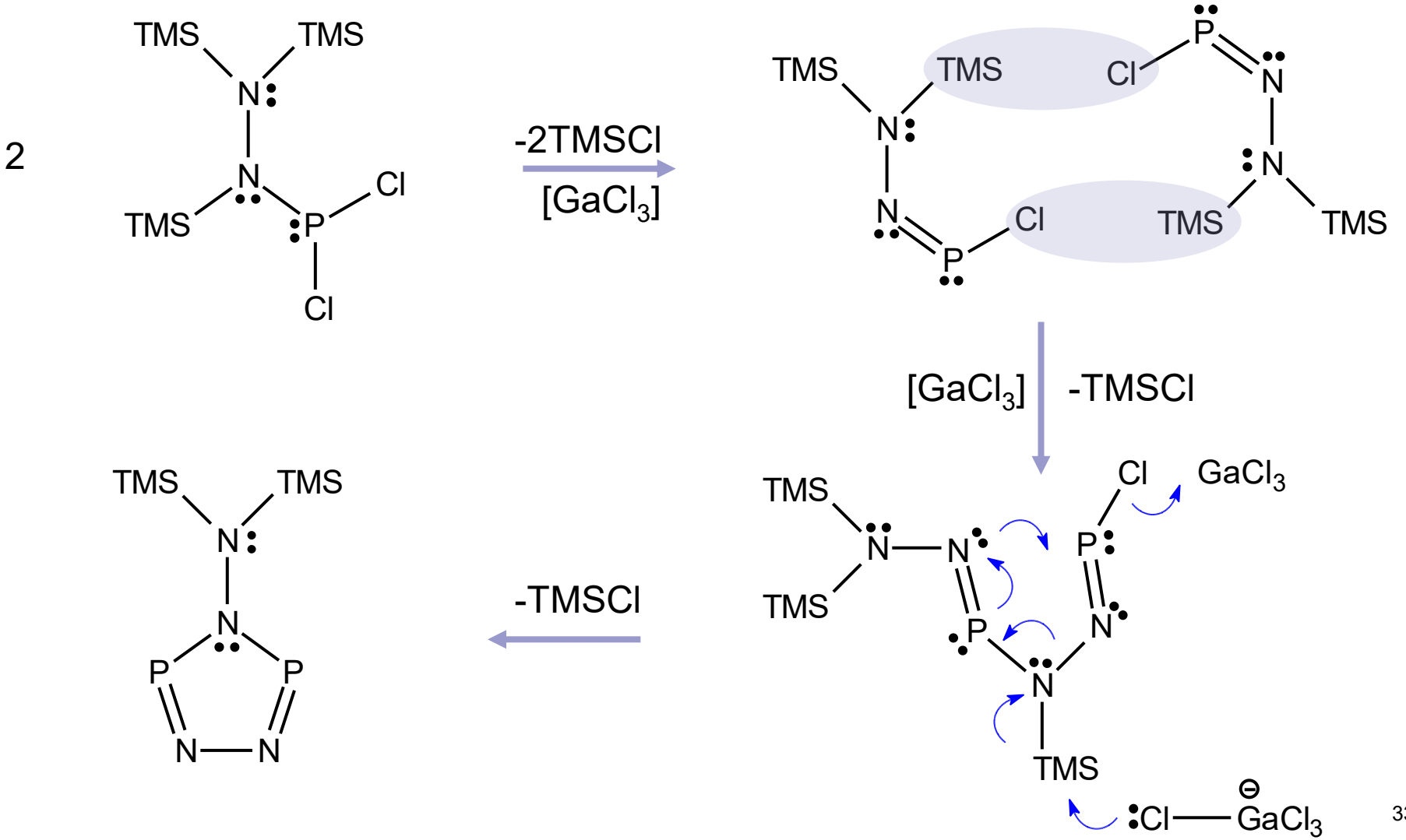
•Thermisch stabil
bis: **96°C** **130°C**



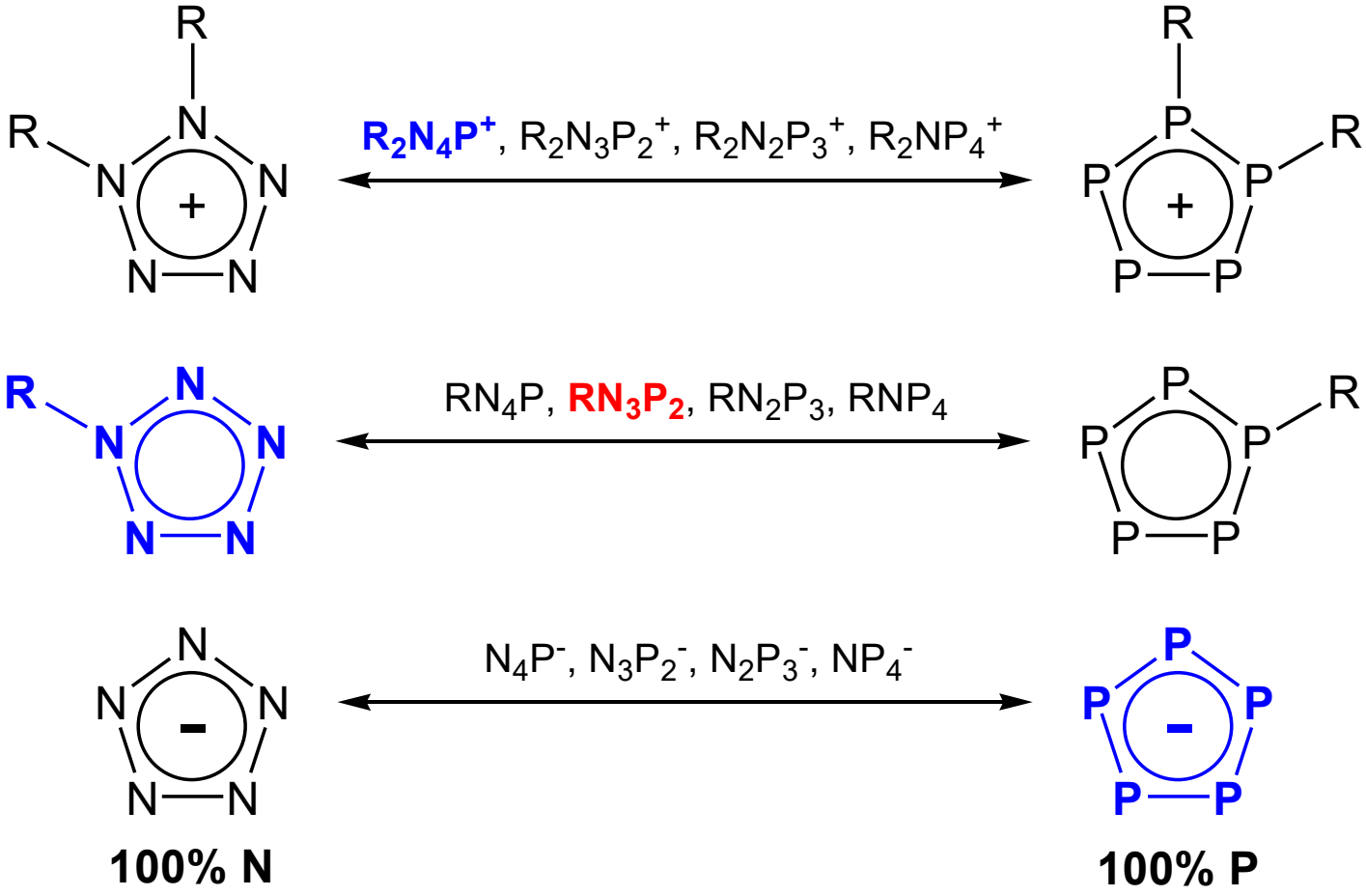
•Löslich in CH_2Cl_2, Benzol, Ether
•Extrem hydrolyseempfindlich
•Ausbeuten > **95%**

Angew. Chem. **2005**, *117*, 7968-7971.

P_2N_3: Mechanismus der Bildung

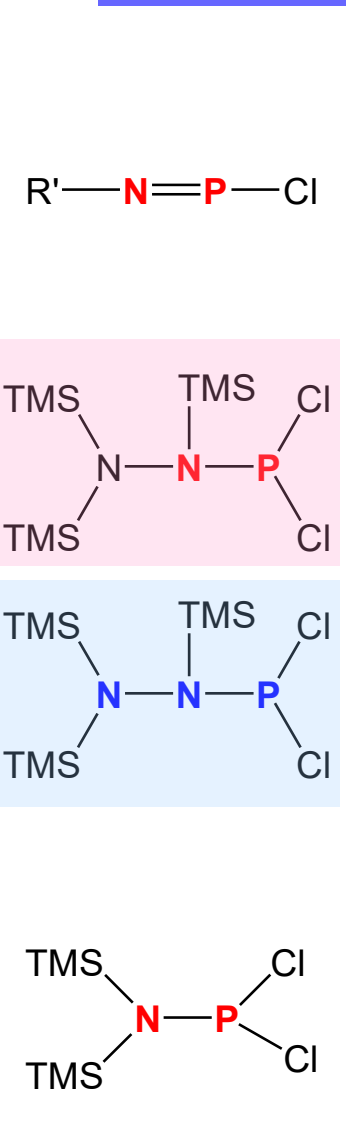


Drei Klassen binärer PN-Ringe (fünfgliedrig)

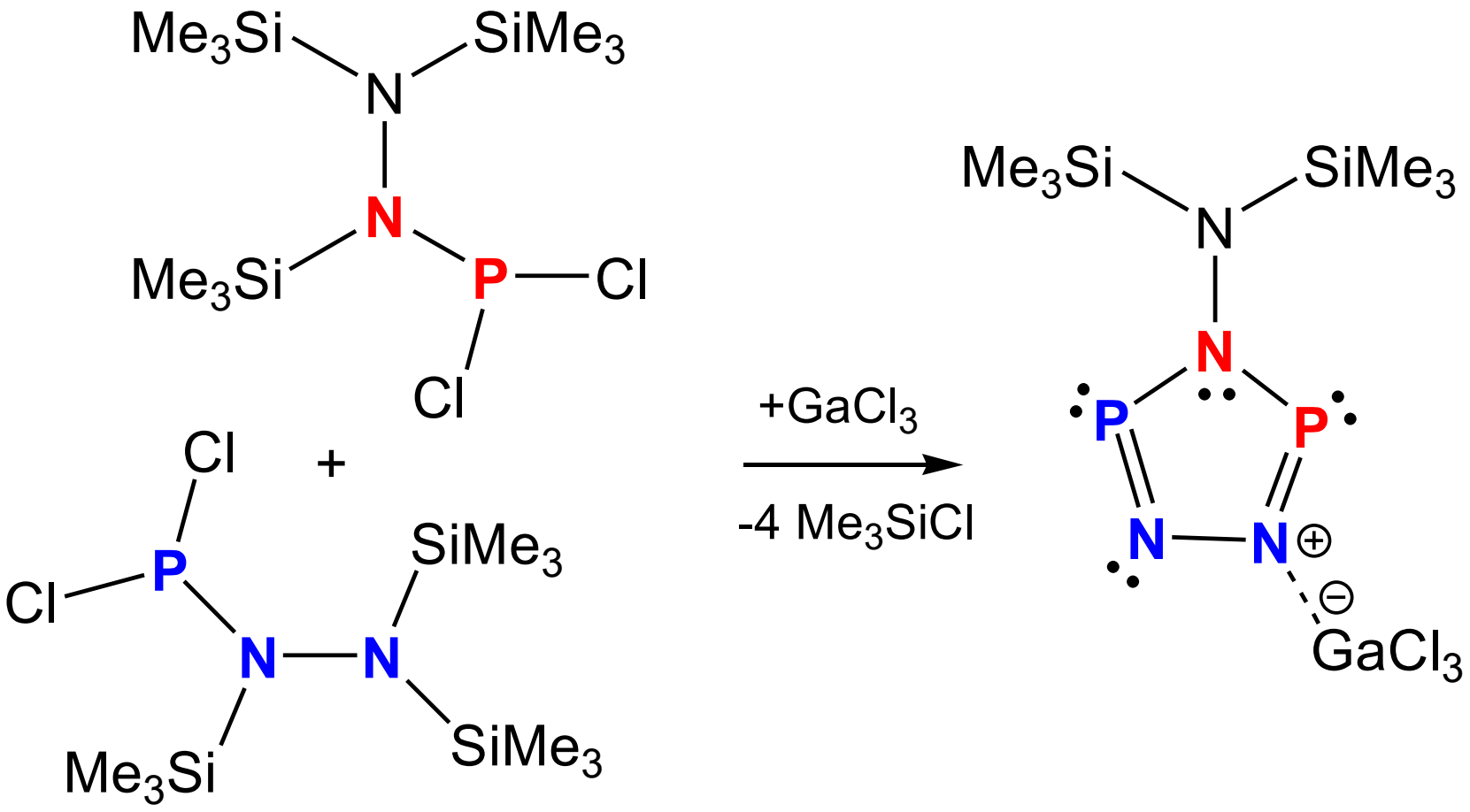


R. Huisgen, I. Ugi, *Chem. Ber.* **1957**, *90*, 2914;
M. Baudler, D. Düster, D.Z. Ouzounis, *Z. Anorg. Allg. Chem.* **1987**, *544*, 87;
G. David, E. Niecke, M. Nieger, V. van der Goenna, W. W. Schöller, *Chem. Ber.* **1993**, *126(7)*, 1513.

[3+2] Baukasten für P,N-Heterocyclen

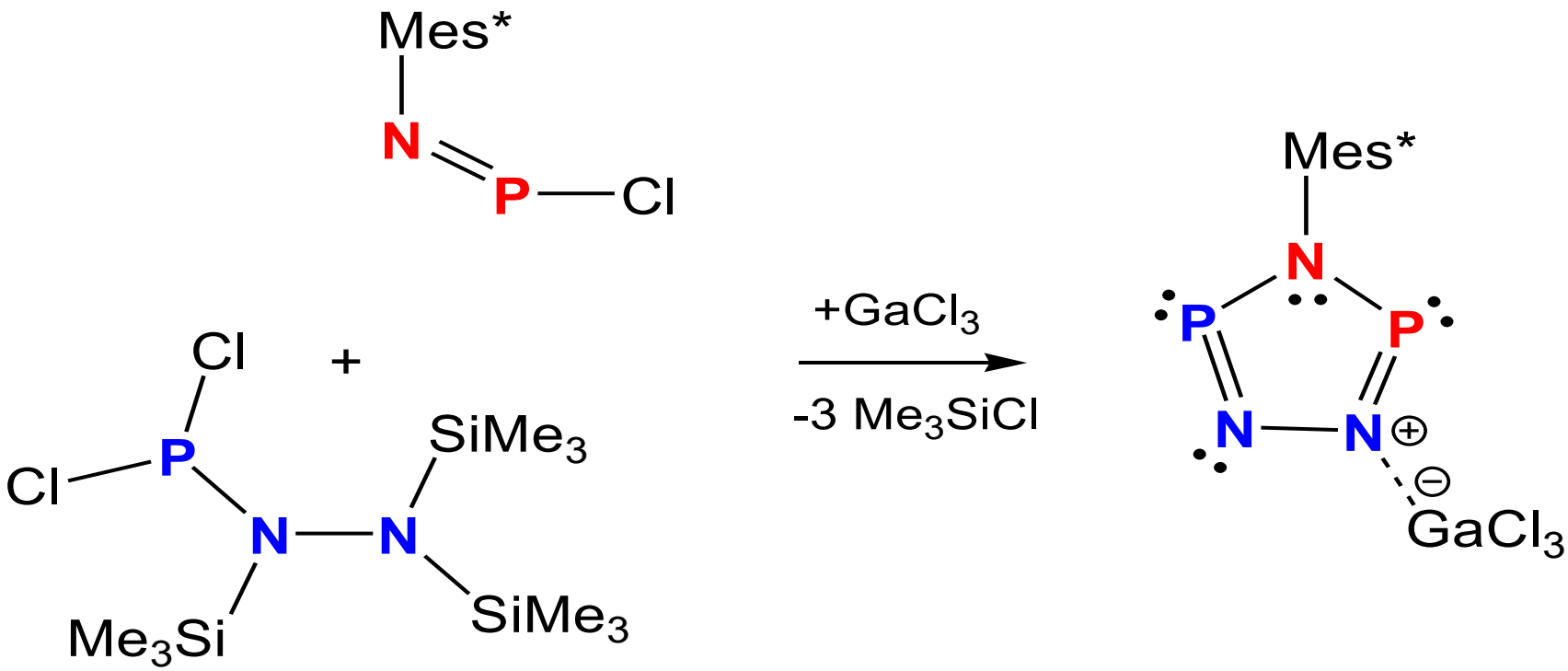


[3+2] zum Ersten



Angew. Chem. **2005**, *117*, 7968-7971.

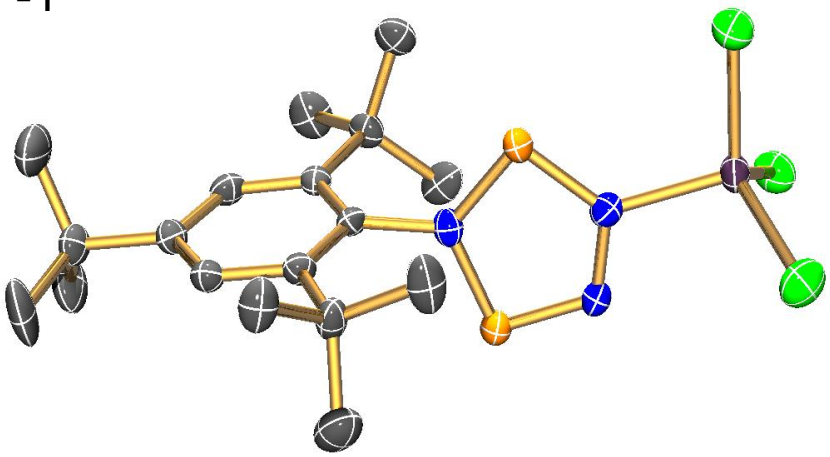
[3+2] zum Zweiten

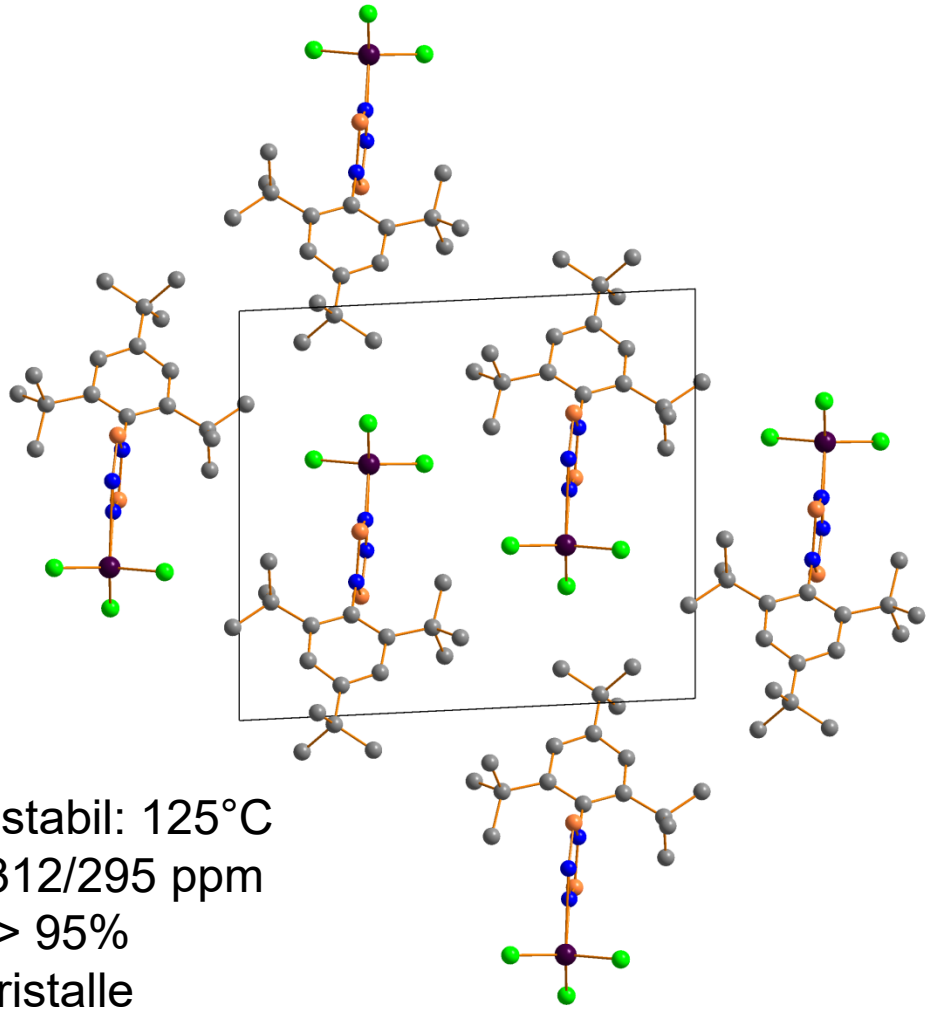


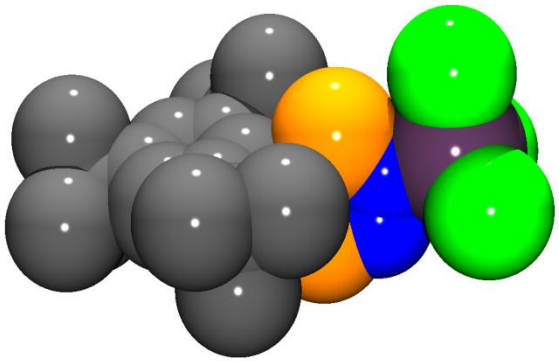
Eur. J. Inorg. Chem. **2006**, *2051*
J. Organomet. Chem. **2007**, *692*, 2839

Das Zweite Triazadiphosphol: Struktur, Bindung, Eigenschaften

P-1





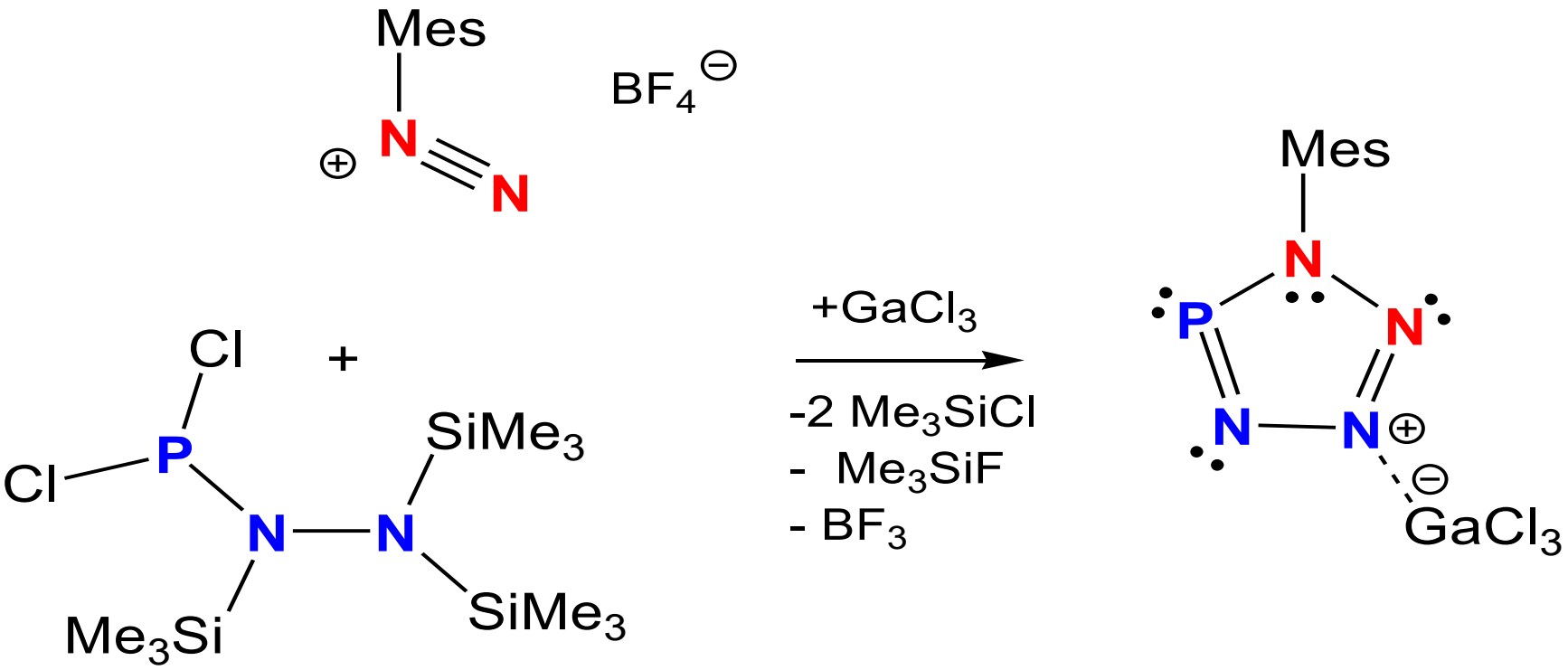


- Thermisch stabil: 125°C
- ^{31}P-NMR: 312/295 ppm
- Ausbeute: > 95%
- Farblose Kristalle

Eur. J. Inorg. Chem. **2006**, 2051.
J. Organomet. Chem. **2007**, *692*, 2839.

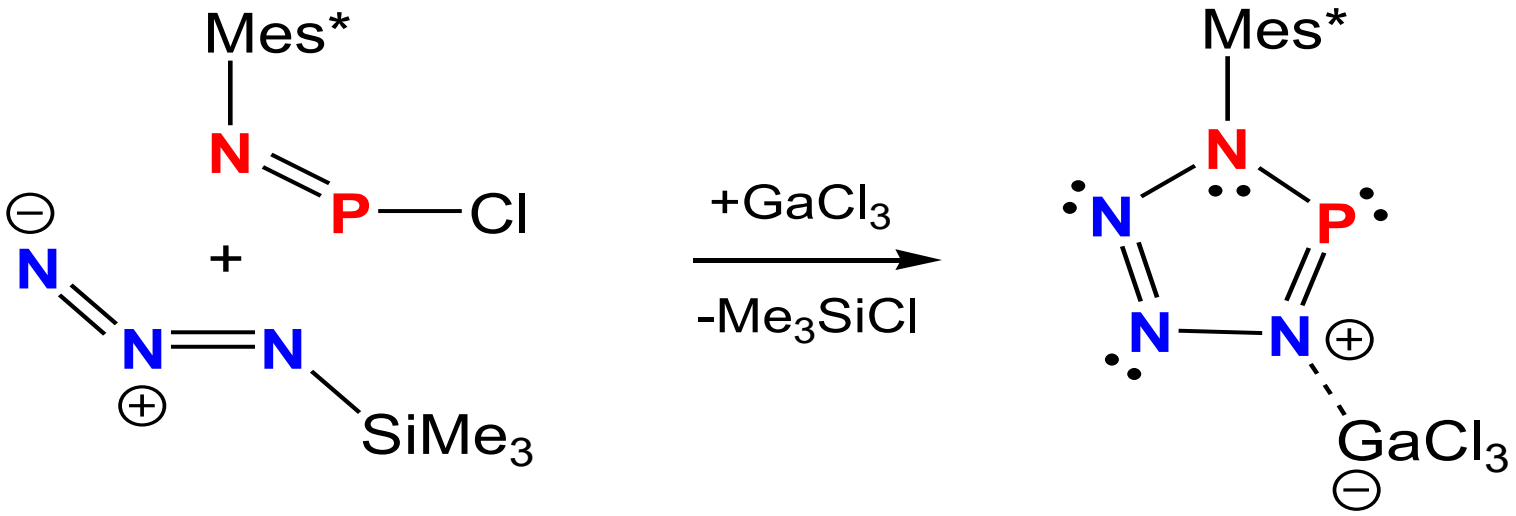
[3+2] zum Dritten

^{31}P-NMR: 228 ppm



Nicht publiziert

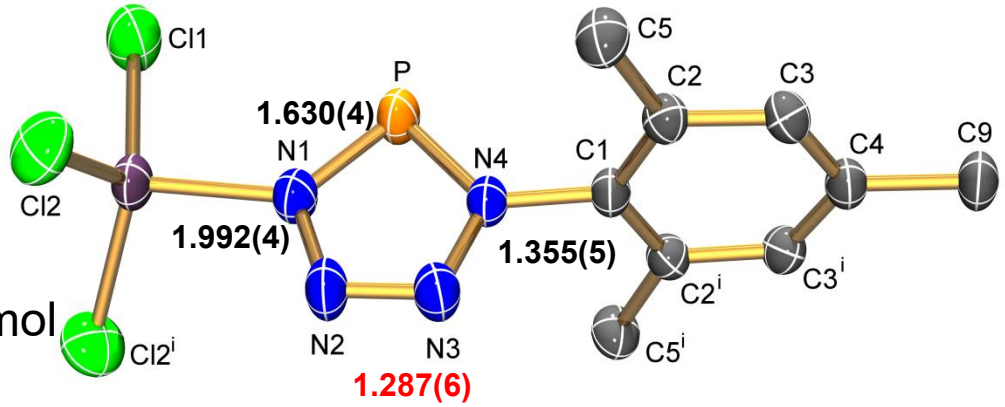
[3+2] zum Vierten

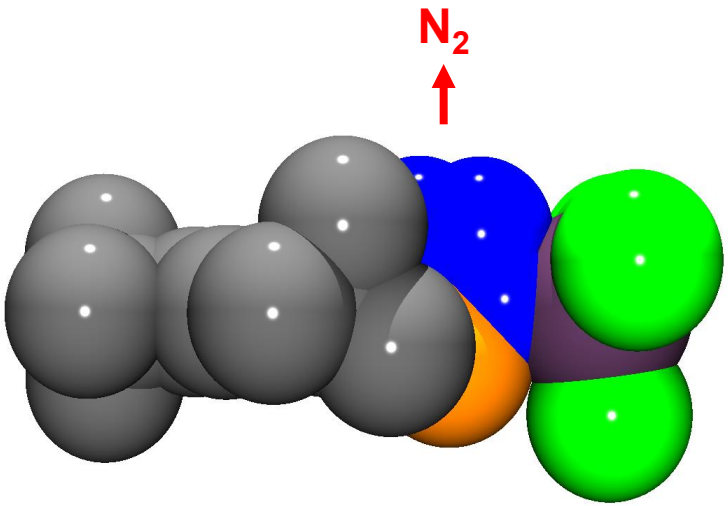


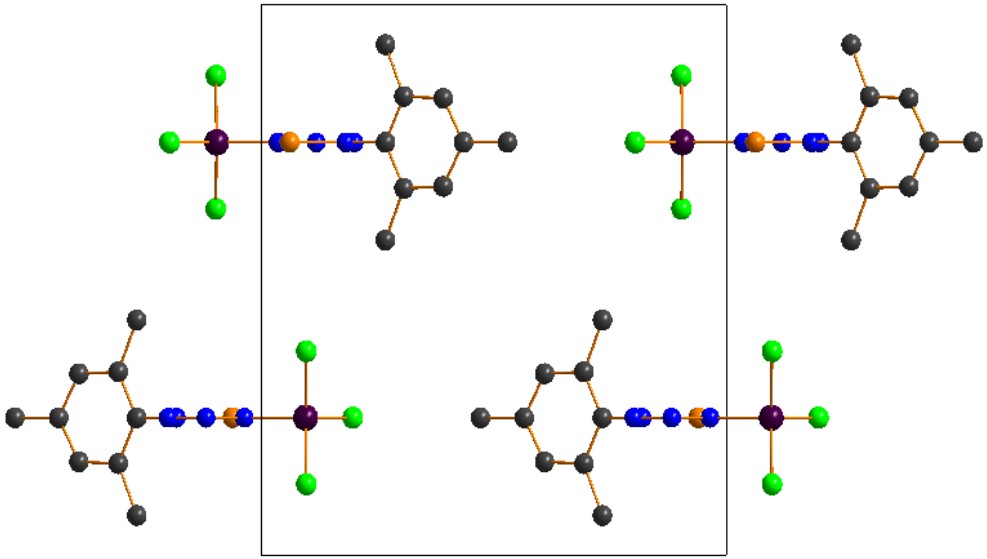
Chem. Commun. **2006**, 1236.

Das erste Tetrazaphosphol: Struktur, Bindung und Eigenschaften

- Thermisch stabil: **< -5°C**
- **Gibt N_2 ab**
- ^{31}P-NMR: 229 ppm (theo.: 229)
- Ausbeute: > 95%
- Farblose Kristalle
- Adduktbildung: $\Delta_{theo}G_{298}$= –2.1kcal/mol
- Ladungstransfer: Q_{CT} = 0.15 *e*

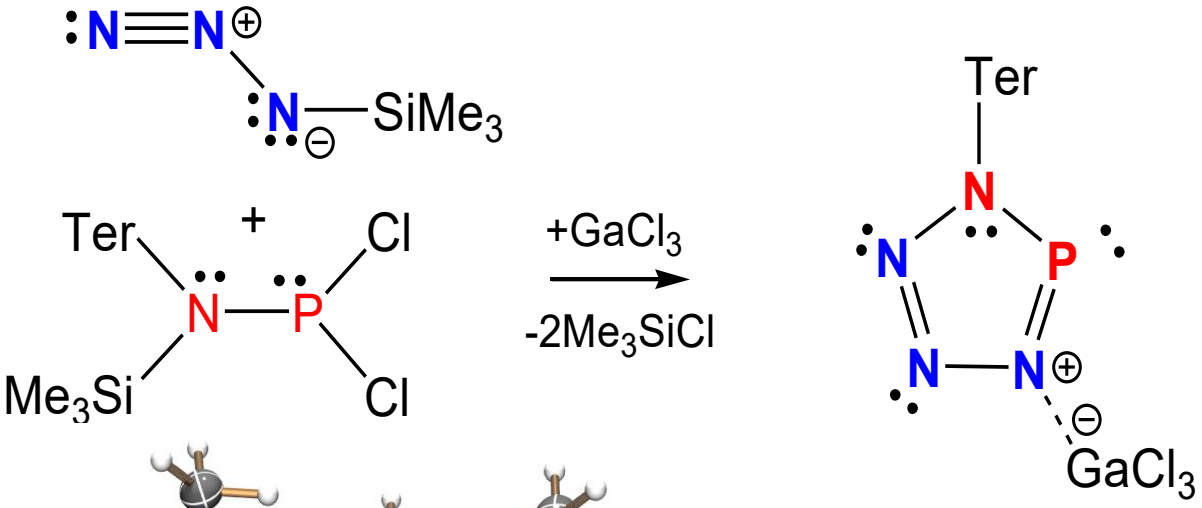


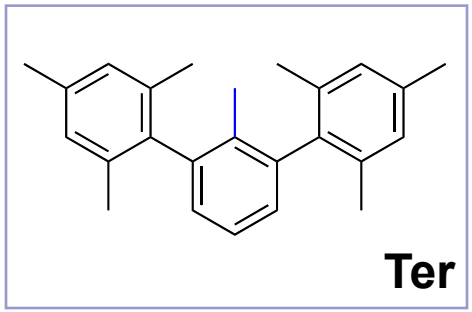


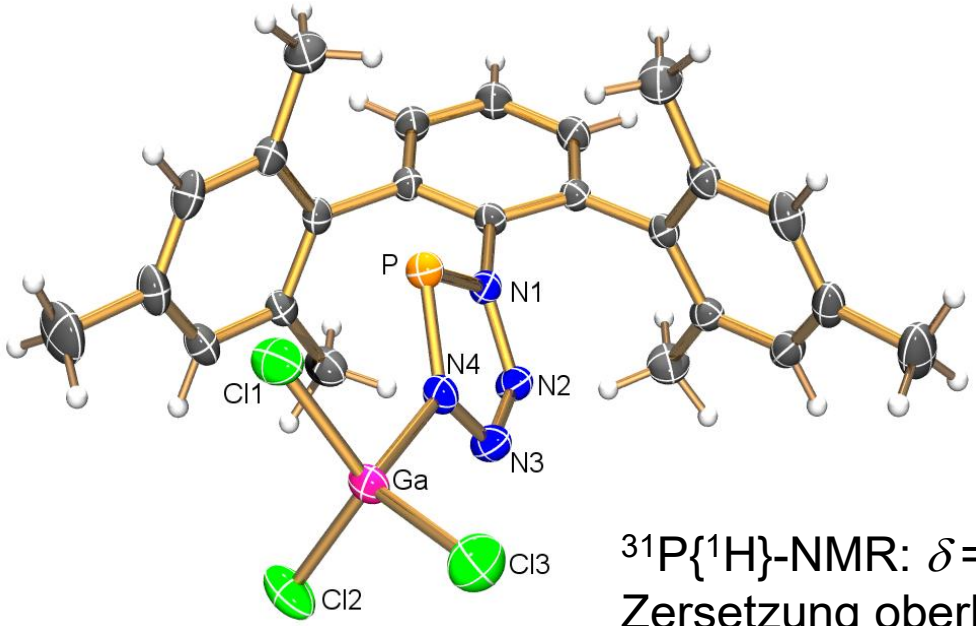


Chem. Commun. **2006**,1236.

[3+2] zum Fünften







$^{31}P\{^{1}H\}$-NMR: δ = 217.2
Zersetzung oberhalb 95°

In situ:

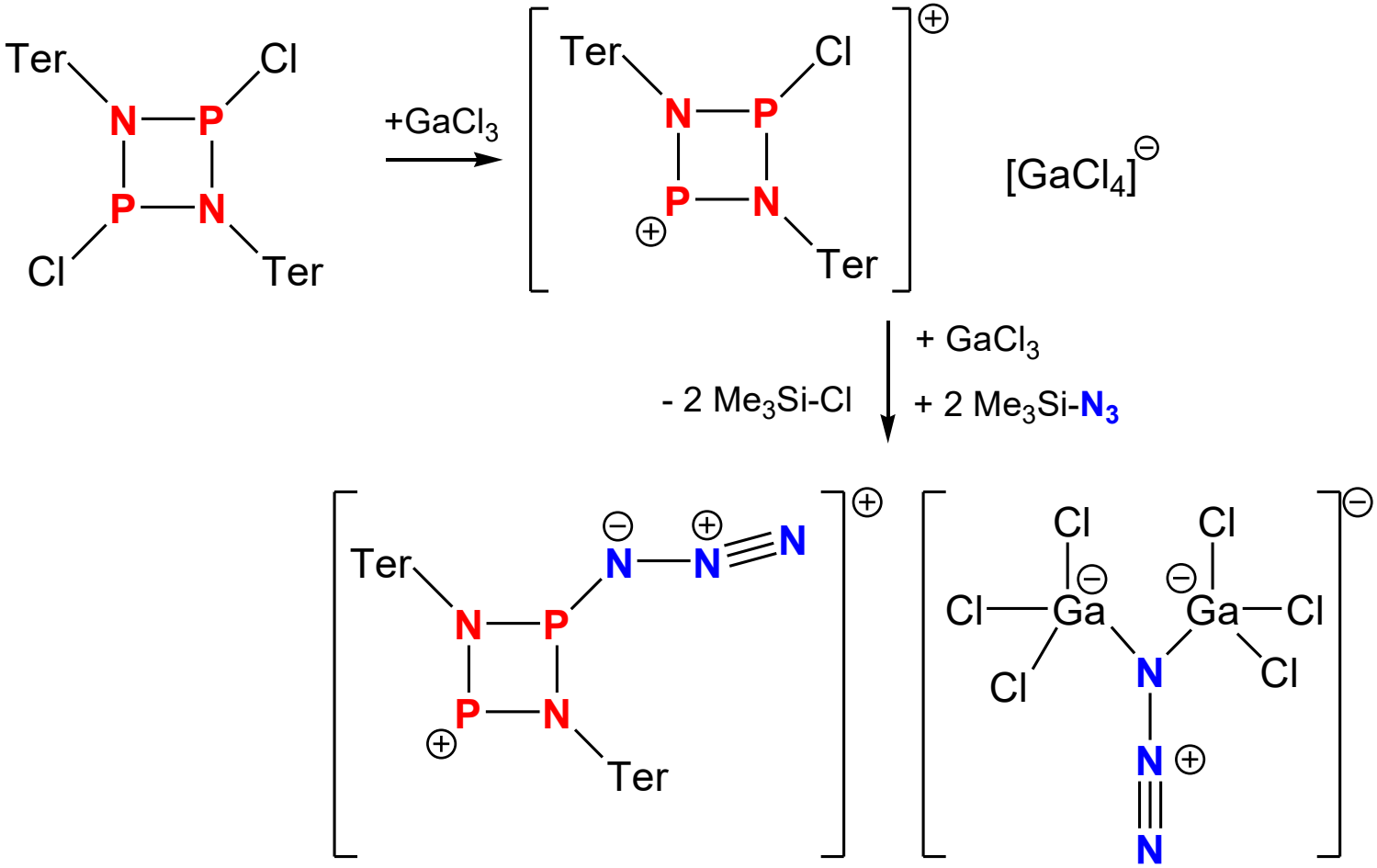
erst

Ter–N=P–Cl

dann

$[Ter–N{\equiv}P]^{+}[GaCl_4]^{-}$

[3+2] zum Sechsten: Pech gehabt, aber!



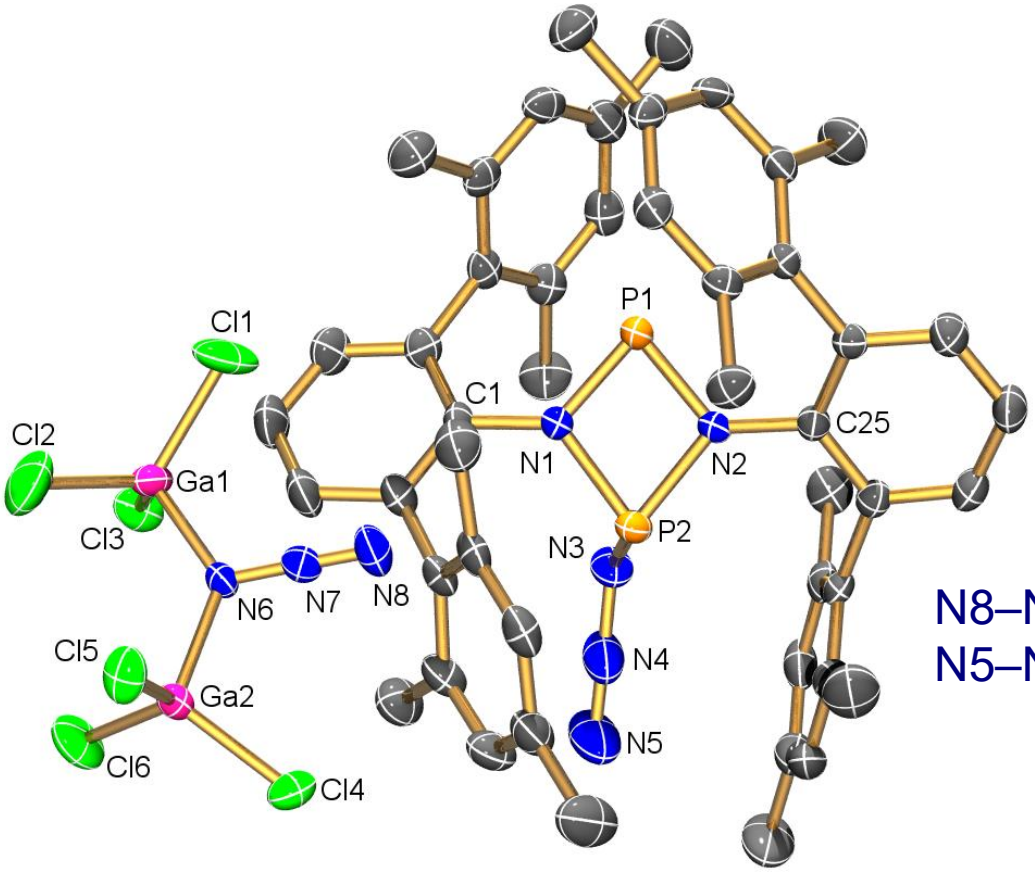
Angew. Chem. **2008**, *120*, 6565.

Azid im Kation – Azid im Anion

Angew. Chem. **2008**, *120*, 6565 – 6568

Zweimal kurz
P1–N1 1.664(3),
P1–N2 1.681(3),

Zweimal lang
P2–N1 1.773(3),
P2–N2 1.784(2),

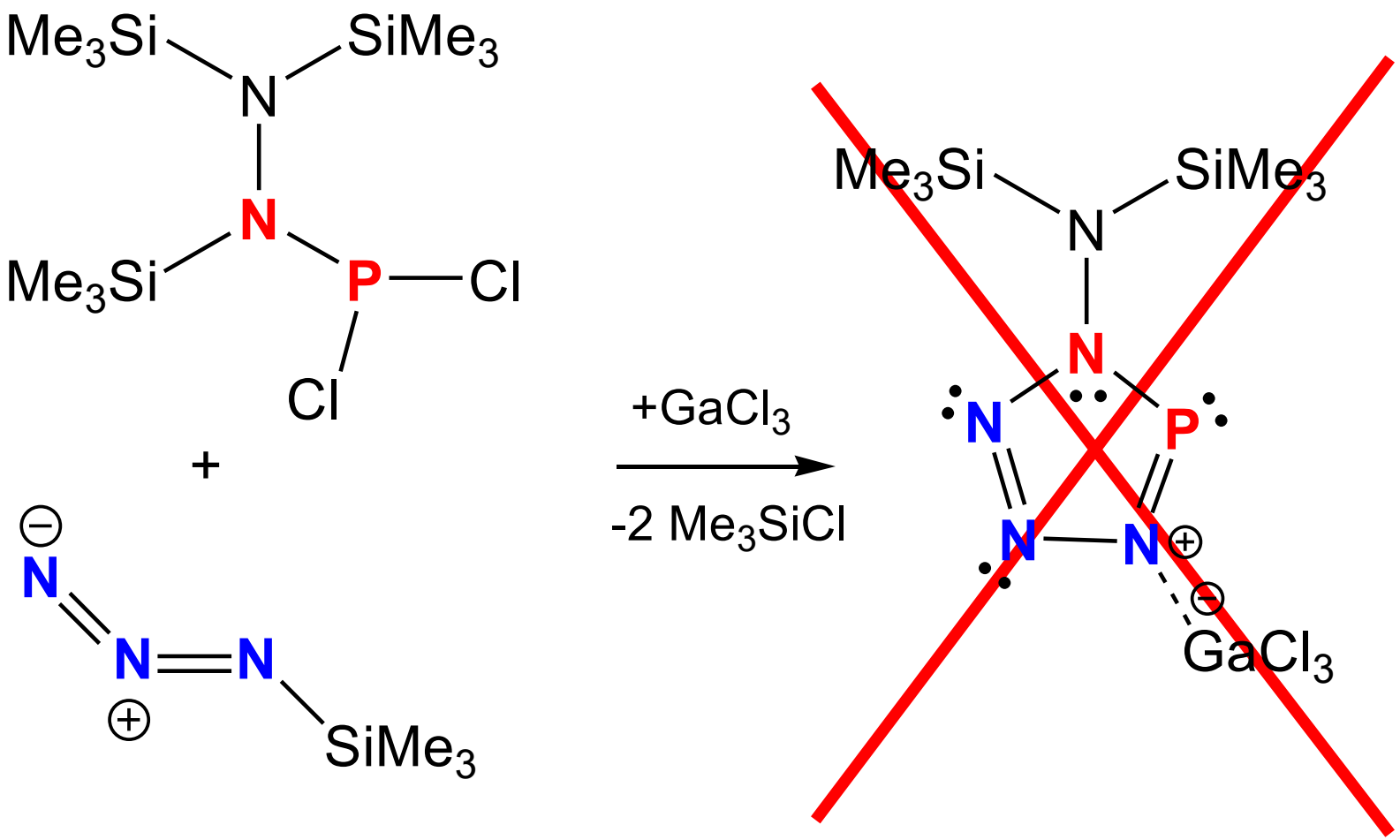


$P2_1/c$

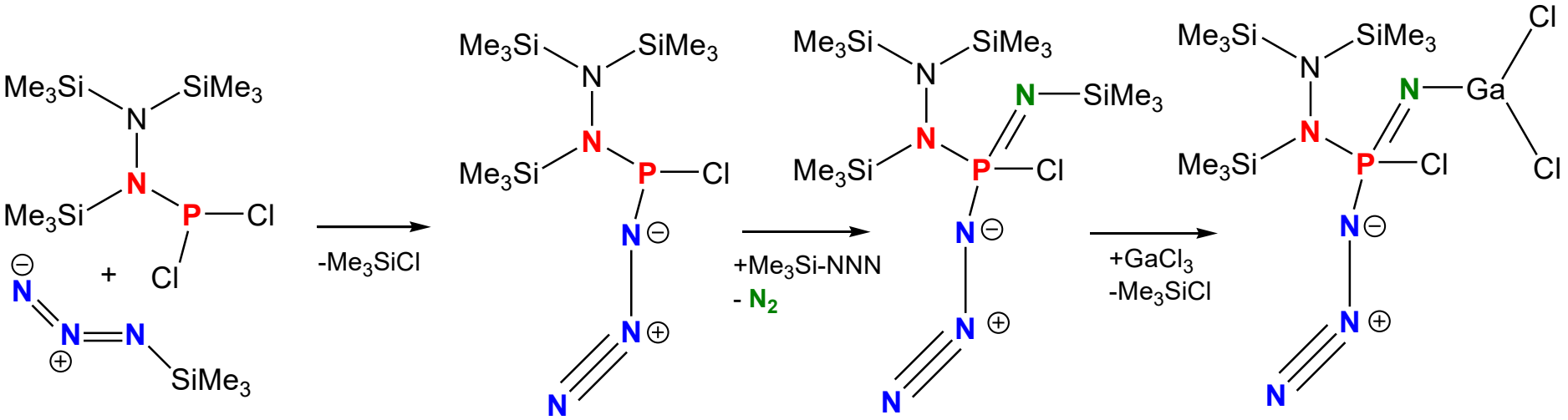
N8–N7–N6 179.3(4),
N5–N4–N3 174.0(5)

1-Azido-*cyclo*-1,3-diphospha-2,4-diazenium-μ-azido-hexachloro-digallat

[3+2] zum Siebten?

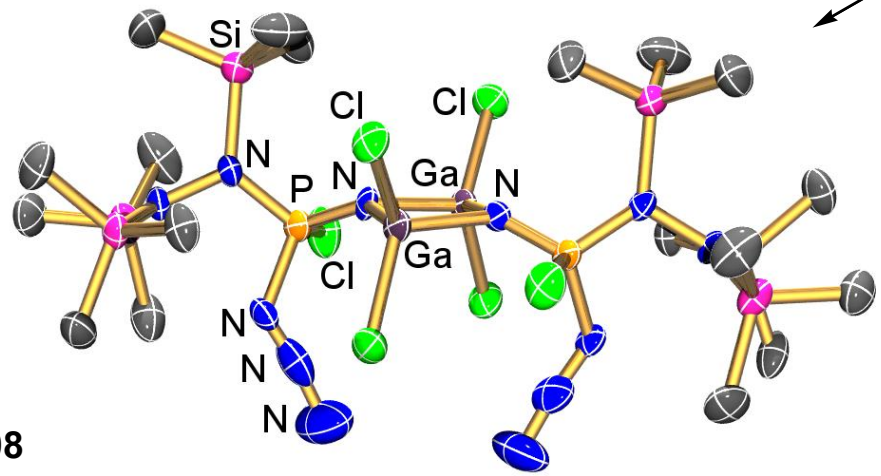


Halogen/Pseudohalogen-Austausch Staudinger-Reaktion



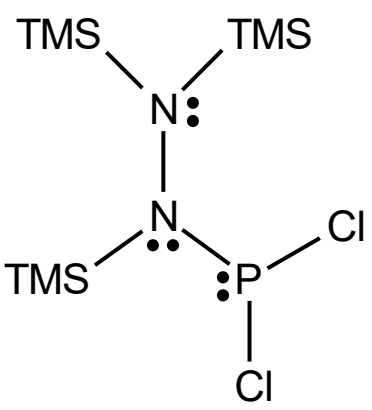
Dimerisation

$P2_1/n$



Eur. J. Inorg. Chem. **2008**

Lewis-Säure Einfluß ?

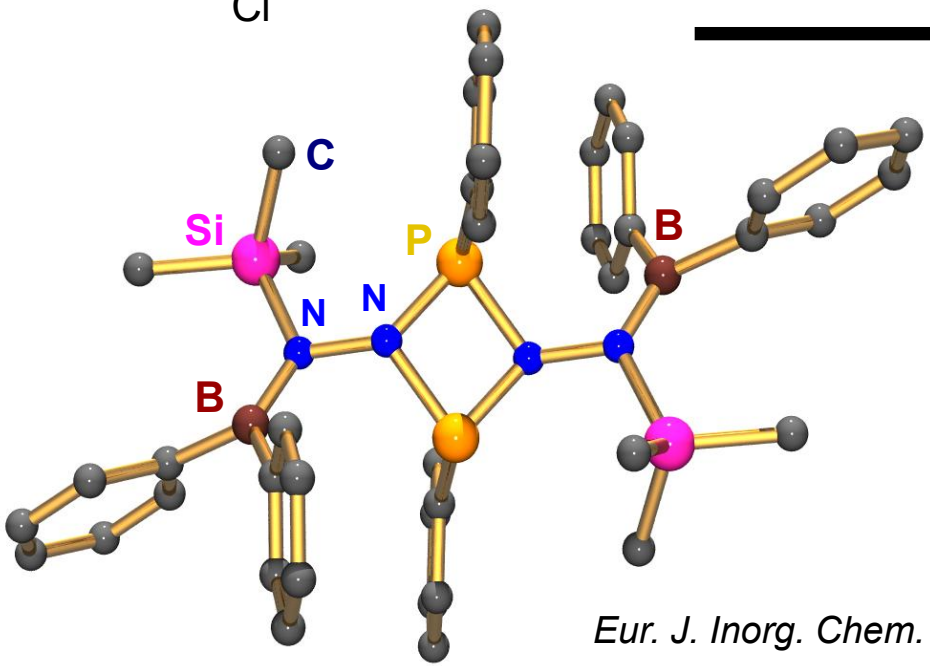


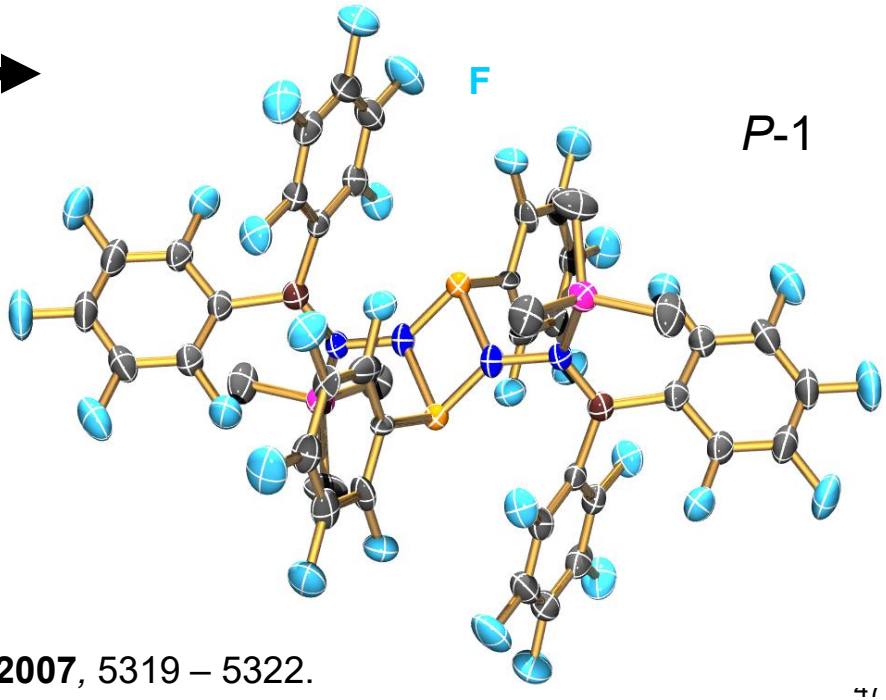
+

BF_3 → -100° Keine Reaktion

$Et_2O{\cdot}BF_3$ → +25° Zersetzung

$B(C_6F_5)_3$ →

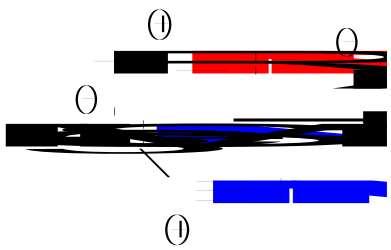




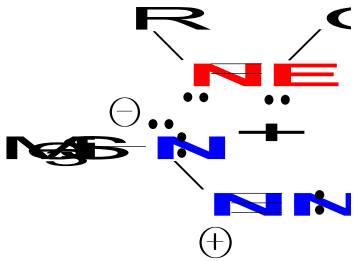
P-1

Eur. J. Inorg. Chem. **2007**, 5319 – 5322.

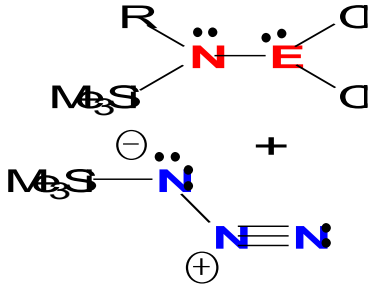
Tetrazapnictoles
Synthetic Routes



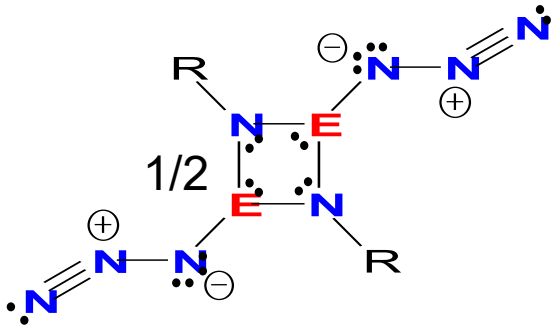
A



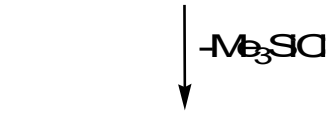
B

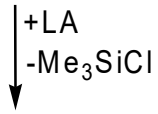


C

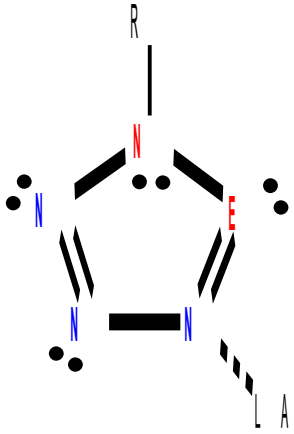


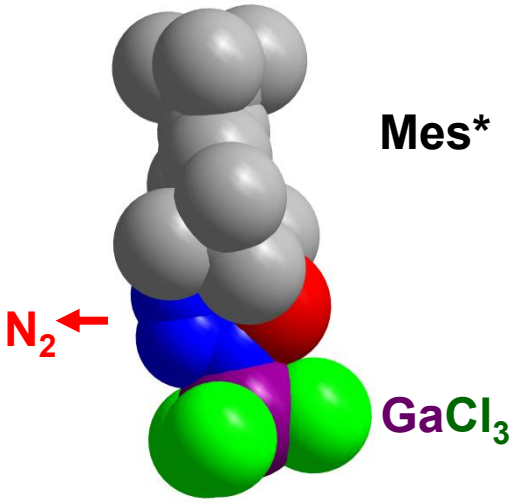
D





A [3+2] cycloaddition (E = N, P, As)
B [3+2] cycloaddition (E = P, As)
C [3+2] cycloaddition (E = P, As)
(disguised dipolarophile)
D isomerization (E = Sb)

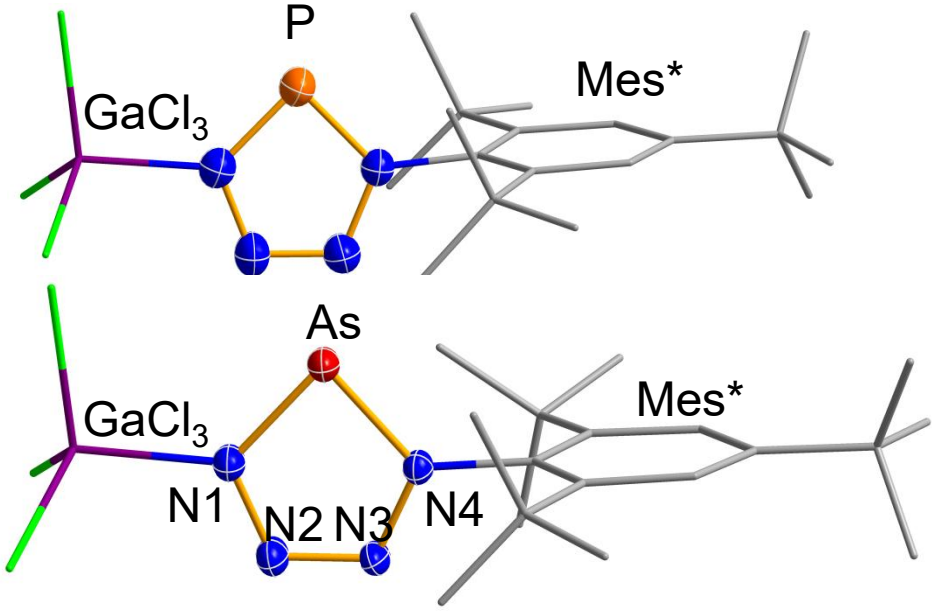


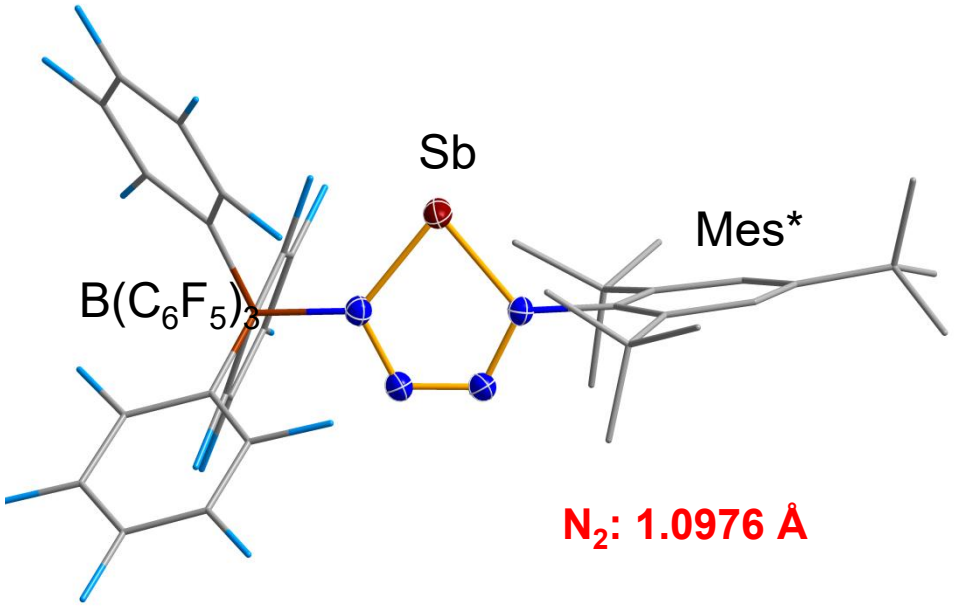


Angew. Chem., Int. Ed. **2011**, *50*, 5221;
Angew. Chem., Int. Ed. **2008**, *47*, 603;
Chem. Commun. **2006**, 1236.

Tetrazapnictoles

Structure



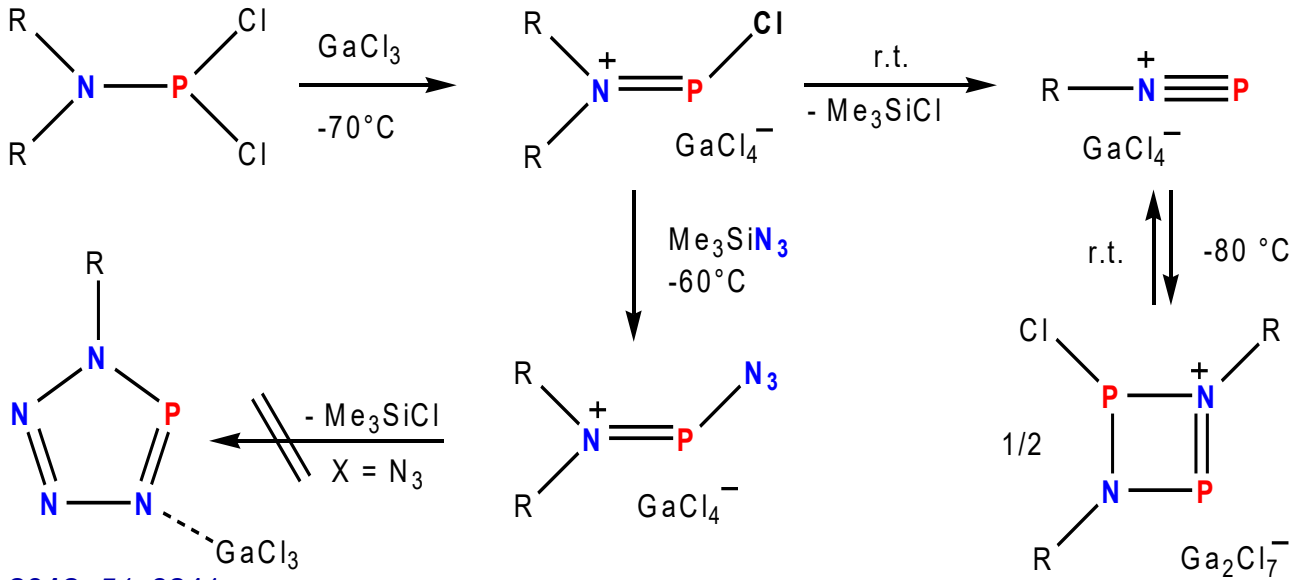


N_2: 1.0976 Å

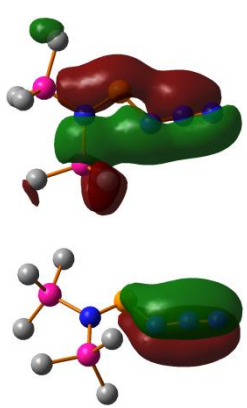
N_4E	E = N	E = P	E = As	E = Sb
E–N1	1.322(2)	1.631(4)	1.805(2)	2.000(2)
N1–N2	1.322(2)	1.355(5)	1.349(2)	1.352(2)
N2–N3	**1.307(2)**	**1.286(5)**	**1.286(3)**	**1.272(3)**
N3–N4	1.338(2)	1.374(5)	1.366(3)	1.357(3)
N4–E	1.307(2)	1.664(3)	1.784(2)	1.975(2)
N1–E–N4/°	105.4(1)	88.2(2)	82.8(1)	77.01(7)
T_{dec}/°C	-5	145	190	160

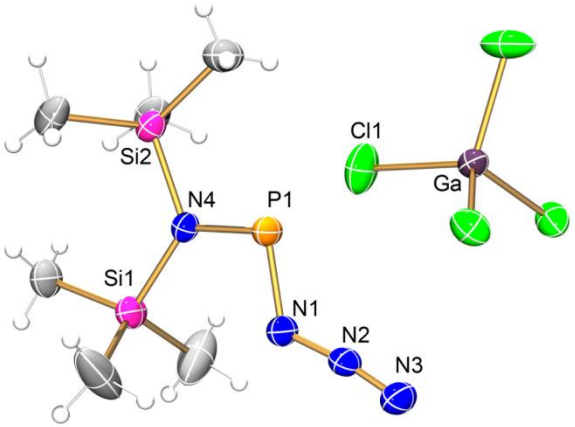
Tetrazapnictole
Mechanism of Formation

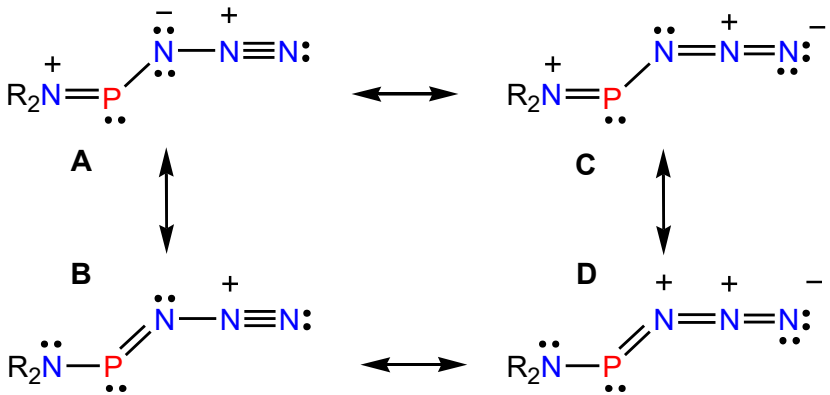
R = SiMe$_3$



Angew. Chem., Int. Ed. **2012**, *51*, 6241.

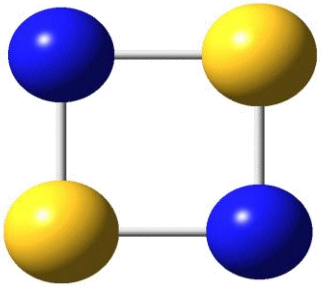




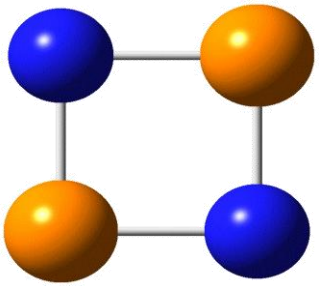


Binäre planare PN-Species

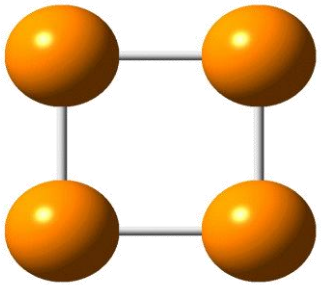
S_2N_2



$P_2N_2^{2-}$



P_4^{2-}

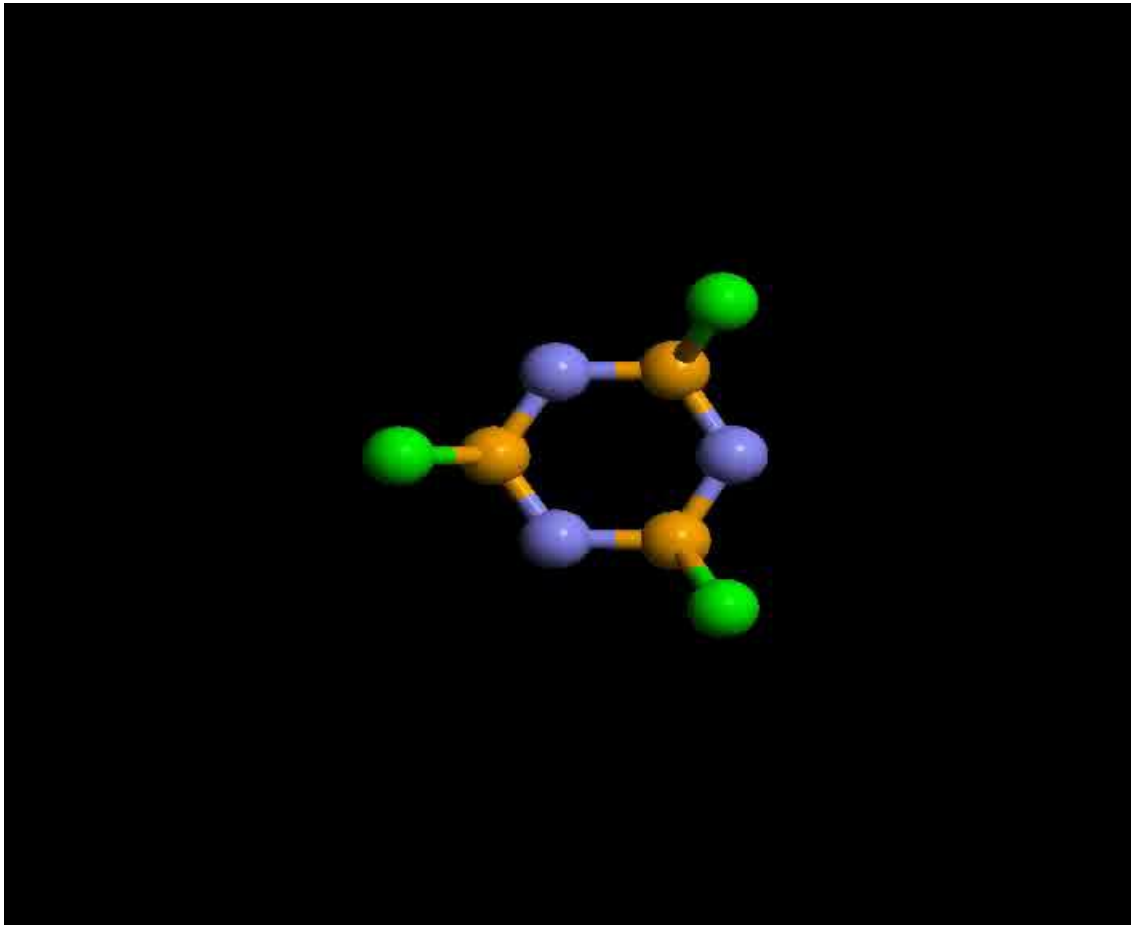


6π Elektronensysteme

R.D. Harcourt, A. Schulz
J. Chem. Phys. **1998**, 1850.

F. Kraus, J. C. Aschenbrenner, N. Korber
Angew. Chem. **2003**, *115*, 4162

Vom Molekül zum Polymer: Zum Informationsträger ?



Internet Electronic Journal of Molecular Design **2003**, *2*, 653.