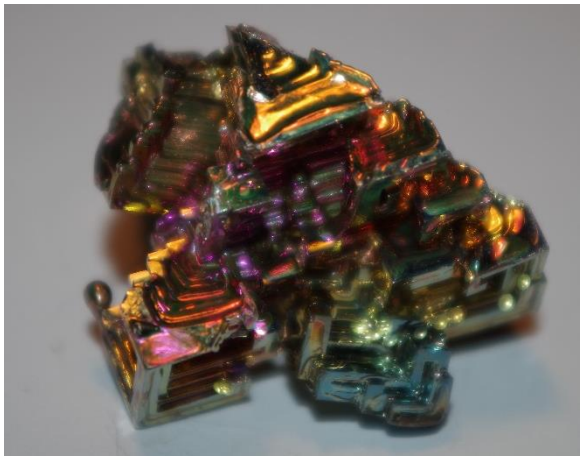
Konzepte zur Synthese eines Tetrazabismutols

Max Thomas

Gliederung

- Einleitung/Motivtion
- Konzept 1: Me_3ECl-Eliminierung ([3+2]-Cycloadditionen)
- Konzept 2: Tetrazenide ([4+1]-Cycloadditionen)
- Zusammenfassung



Einleitung

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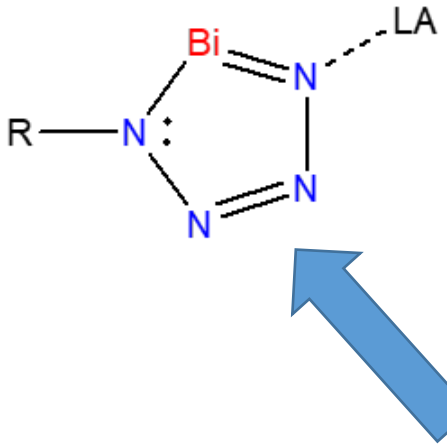
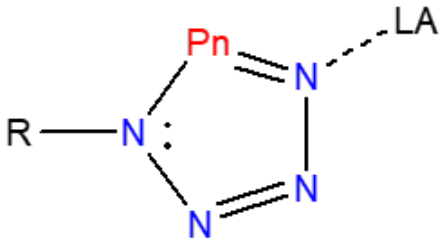
Motivation





Pn = P, As, Sb

Pn = Bi ?

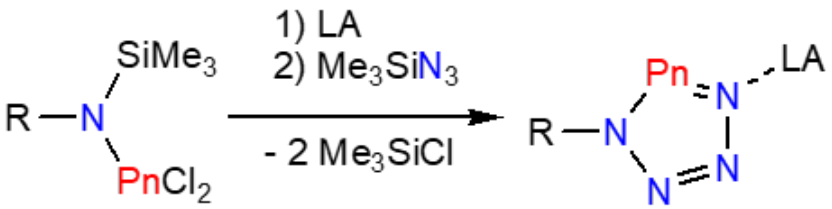
LA = Lewis-Säure

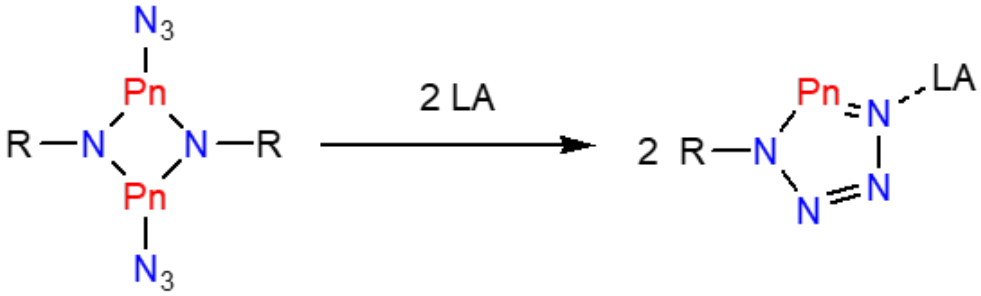
A. Villinger, P. Mayer, A. Schulz, *Chem. Commun.* **2006**, 1236–1238; A. Schulz, A. Villinger, *Angew. Chem., Int. Ed.* **2008**, *47*, 603–606; M. Lehmann, A. Schulz, A. Villinger, *Angew. Chem., Int. Ed.* **2011**, *50*, 5221–5224.

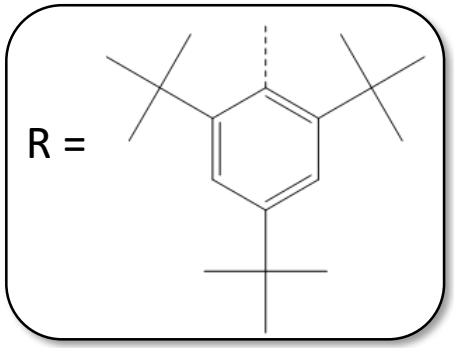
Einleitung

Vorhergehende Arbeiten

Pn = P, As, Sb







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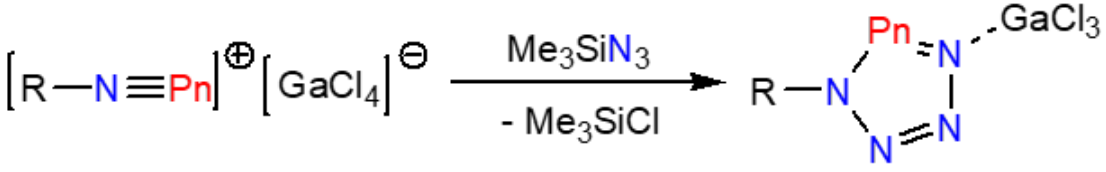
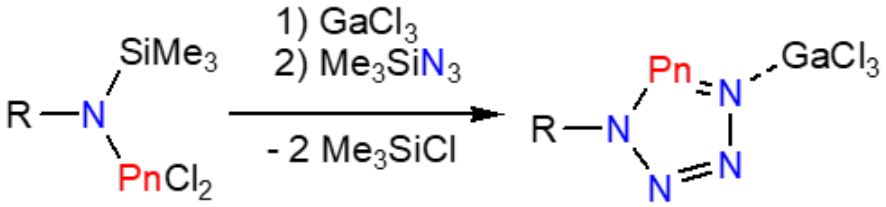
A. Villinger, P. Mayer, A. Schulz, *Chem. Commun.* **2006**, 1236–1238; A. Schulz, A. Villinger, *Angew. Chem., Int. Ed.* **2008**, *47*, 603–606; M. Lehmann, A. Schulz, A. Villinger, *Angew. Chem., Int. Ed.* **2011**, *50*, 5221–5224.

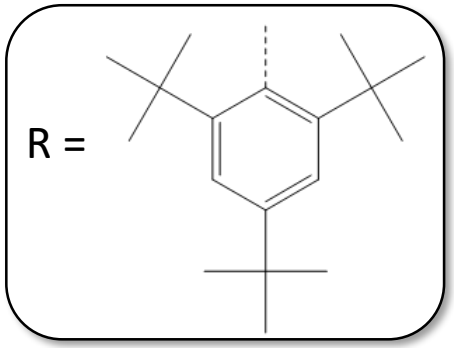
Konzept 1

Eliminierung von Me_3SiCl

Pn = P, As







A. Villinger, P. Mayer, A. Schulz, *Chem. Commun.* **2006**, 1236–1238; A. Schulz, A. Villinger, *Angew. Chem., Int. Ed.* **2008**, *47*, 603–606; M. Kuprat, A. Schulz, A. Villinger, *Angew. Chem., Int. Ed.* **2013**, *52*, 7126–7130.

Konzept 1

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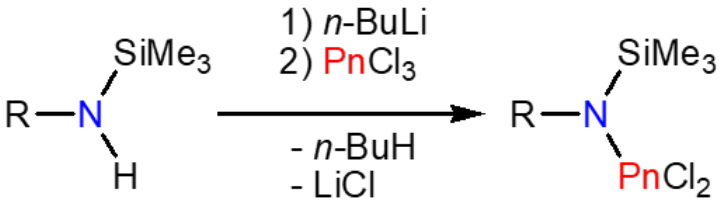
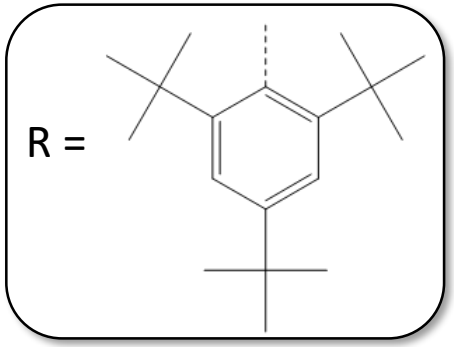
Synthese von Mes*N(SiMe$_3$)BiCl$_2$



Pn = P, As, Sb

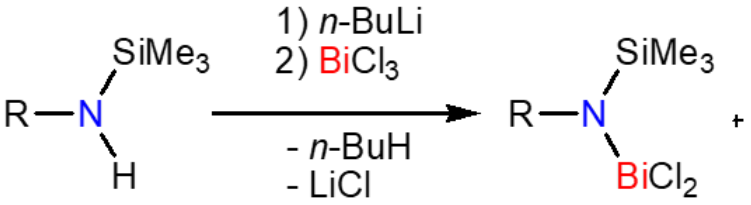
Pn = Bi ?

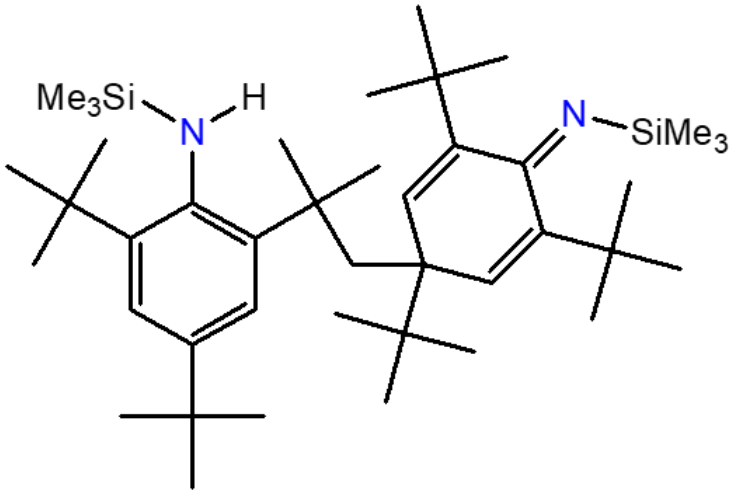


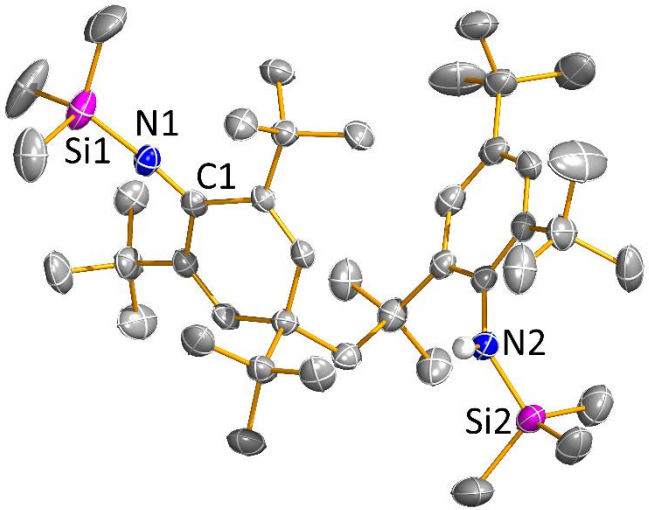
A. Schulz, A. Villinger, A.Westenkirchner, *Inorg. Chem.* **2013**, *52*, 11457–11468; N. Burford, T. S. Cameron, C. L. B. Macdonald, K. N: Robertson, R. Schurko, D. Walsh, *Inorg. Chem.* **2005**, *44*, 8058–8064; M. Lehmann, A. Schulz, A. Villinger, *Eur. J. Inorg. Chem.* **2010**, 5501–5508.

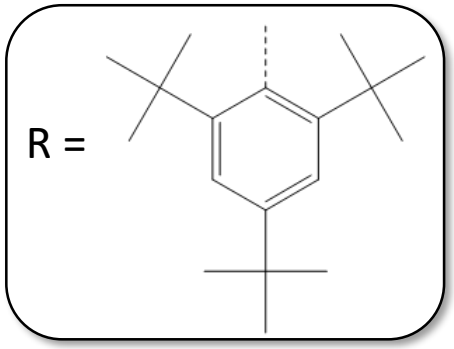
Konzept 1

Synthese von Mes*N(SiMe$_3$)BiCl$_2$









C. Hering-Junghans, A. Schulz, M. Thomas, A. Villinger, *Dalton Trans.* **2016**, *45*, 6053–6059.

Konzept 1

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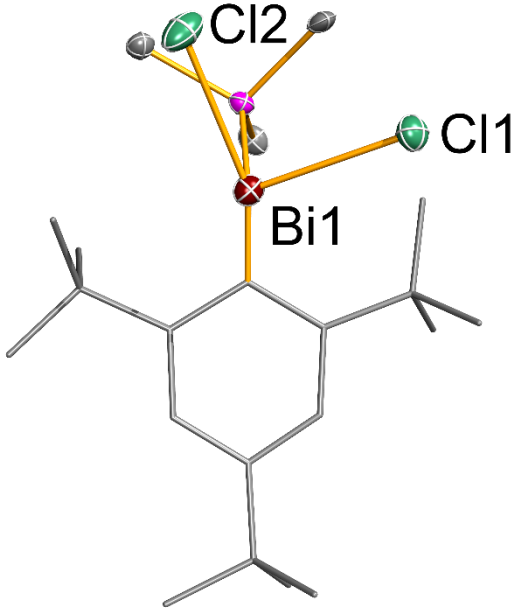
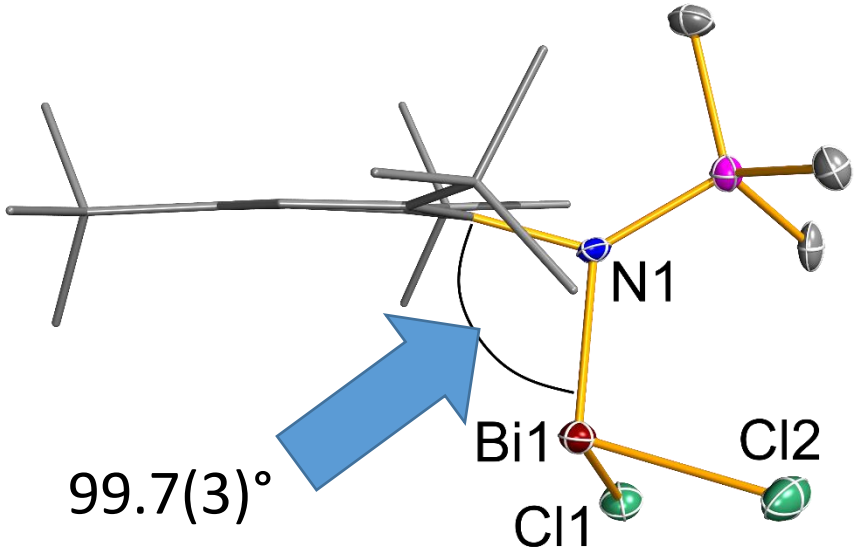
Synthese von $Mes^*N(SiMe_3)BiCl_2$

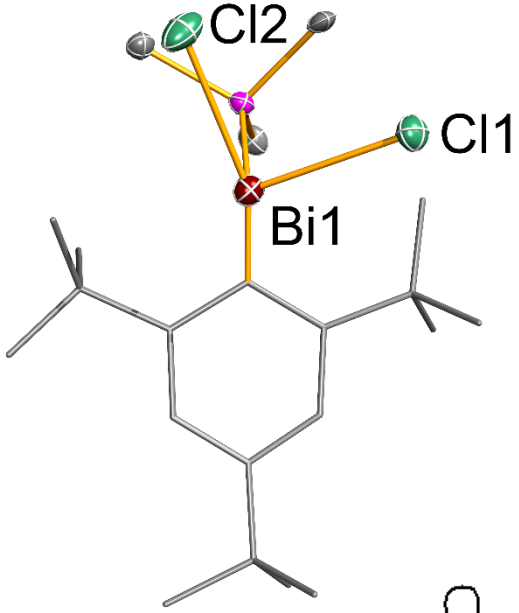


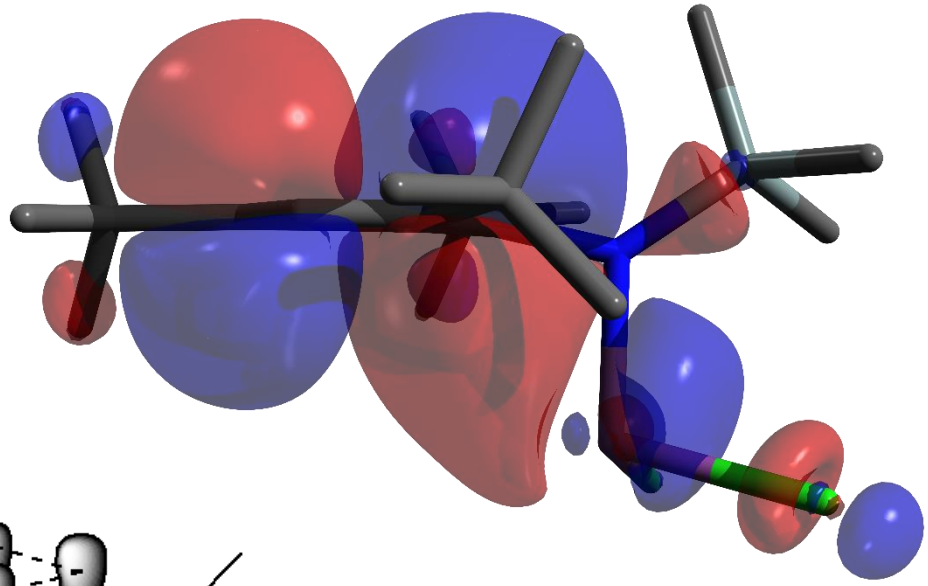


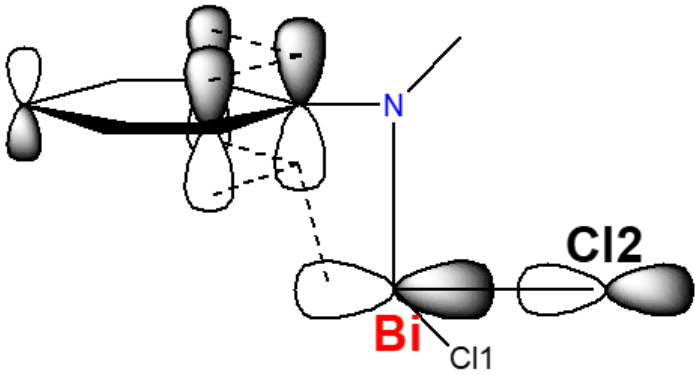
Konzept 1

Universität Rostock Traditio et Innovatio

Synthese von $Mes^*N(SiMe_3)BiCl_2$







Konzept 1

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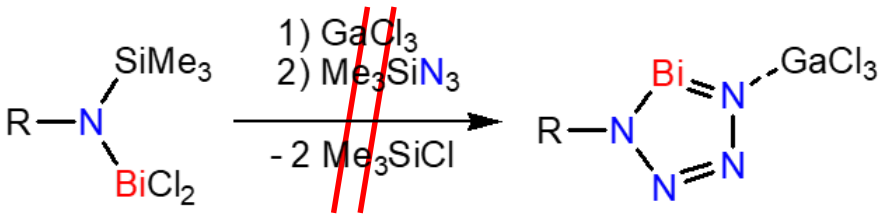
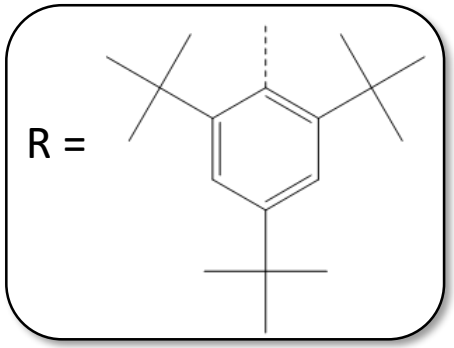
Reaktion von $Mes^*N(SiMe_3)BiCl_2$ mit $GaCl_3$ und Me_3SiN_3

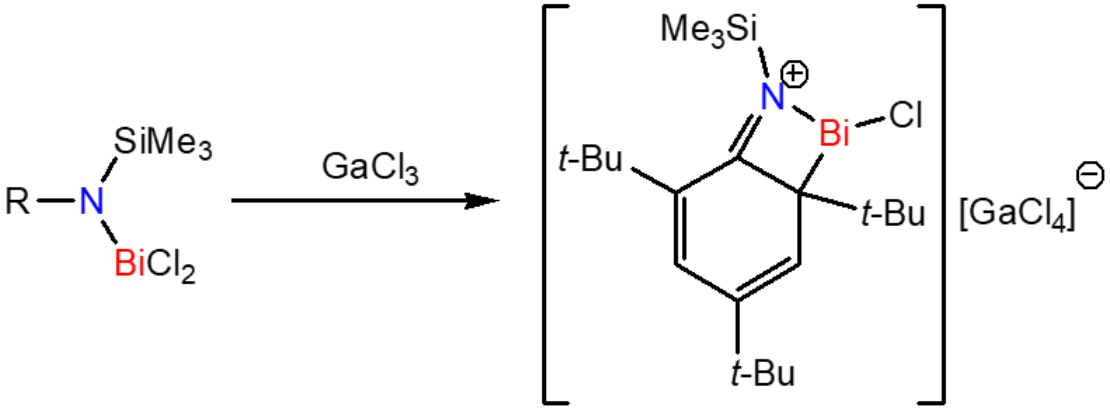


?



Konzept 1

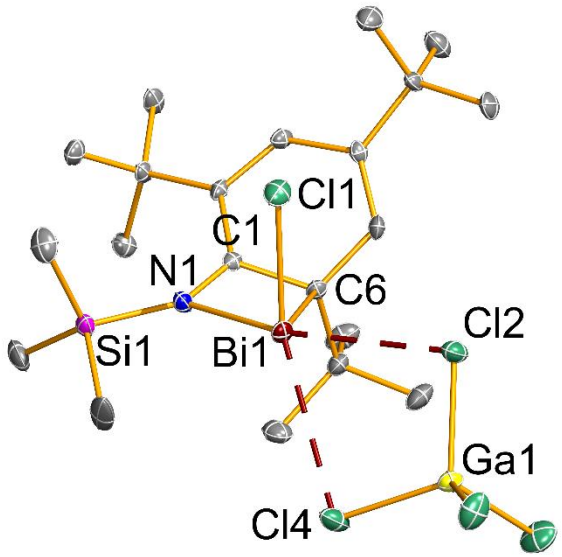
Reaktion von Mes*N(SiMe$_3$)BiCl$_2$ mit GaCl$_3$

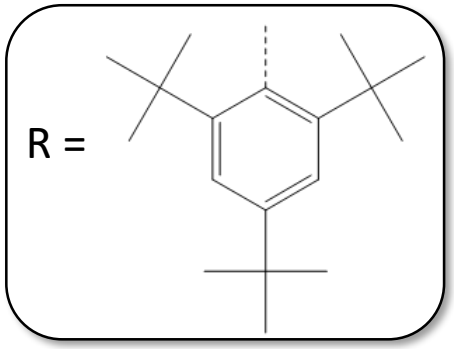


d(N1-Bi1) = 2.315(2) Å

d(C6-Bi1) = 2.348(3) Å

Σr_{kov}(C-Bi) = 2.26 Å



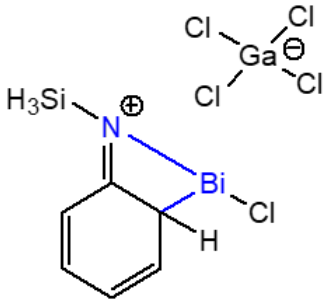


P. Pyykkö, M. Atsumi, *Chem. Eur. J.* **2009**, *15*, 12770–12779.

Konzept 1

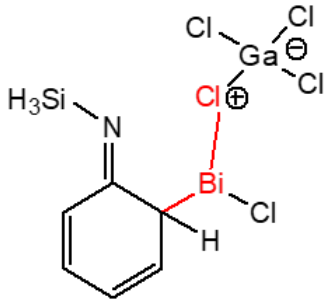
NRT Analyse

1)



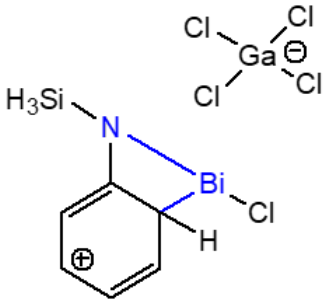
42.19%

2)



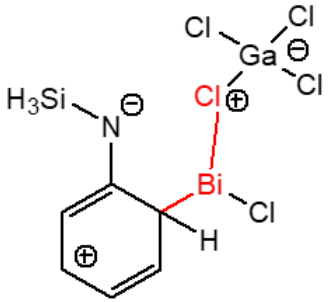
31.34%

3)



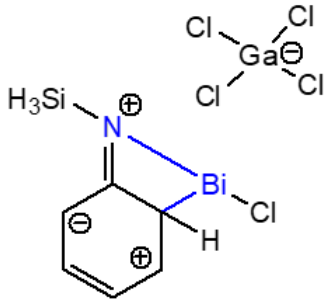
8.81%

4)



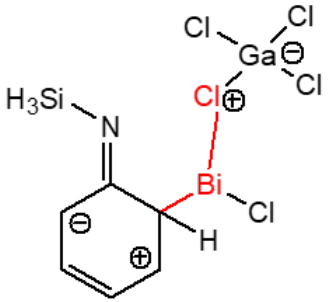
6.95%

5)



5.43%

6)

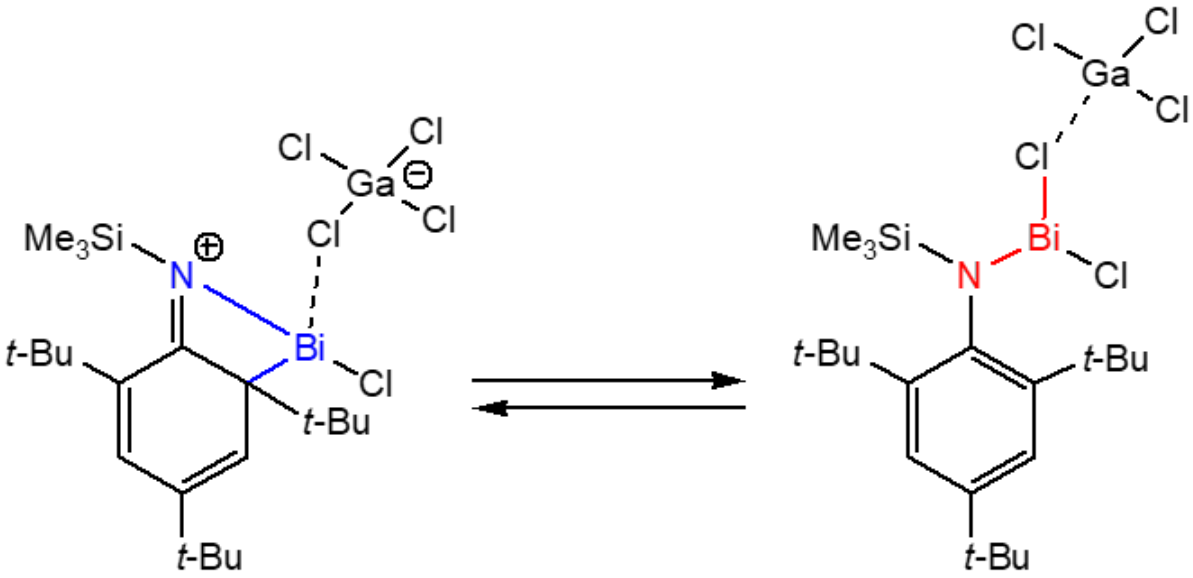


4.29%

E. D. Glendening, C. R. Landis, F. Weinhold, *J. Comp. Chem.* **2013**, *34*, 1429–1437.

Konzept 1

NRT Analyse



E. D. Glendening, C. R. Landis, F. Weinhold, *J. Comp. Chem.* **2013**, *34*, 1429–1437.

Konzept 1

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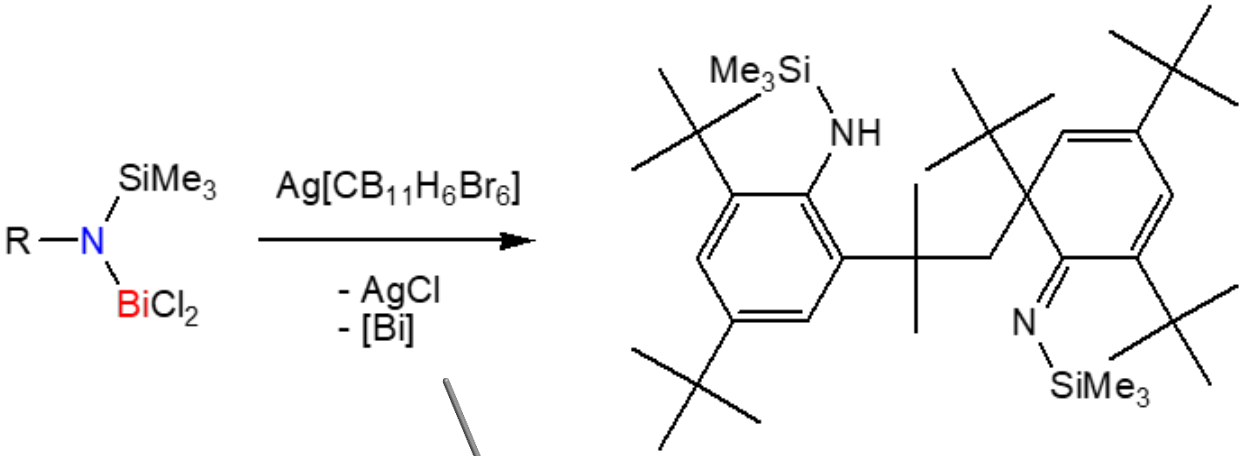
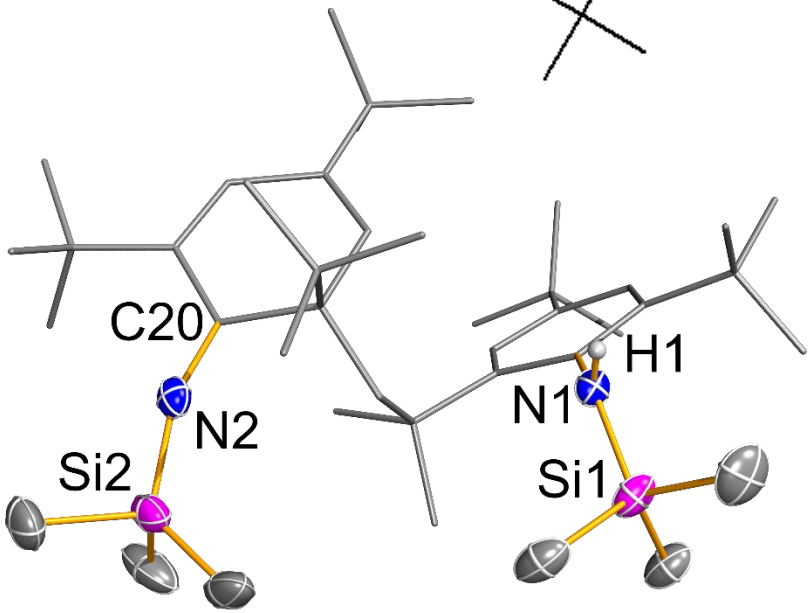
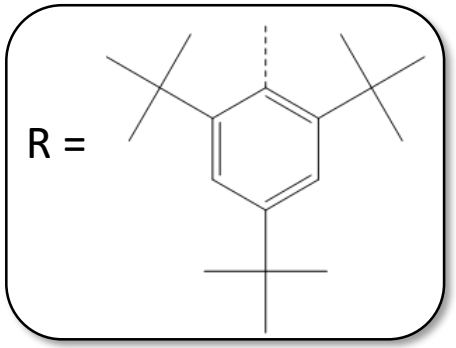
Wirkung eines schwach-koordinierenden Anions (WCA)

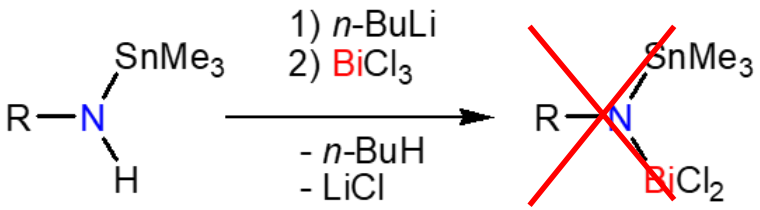


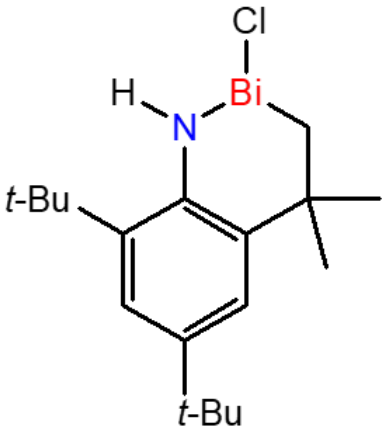


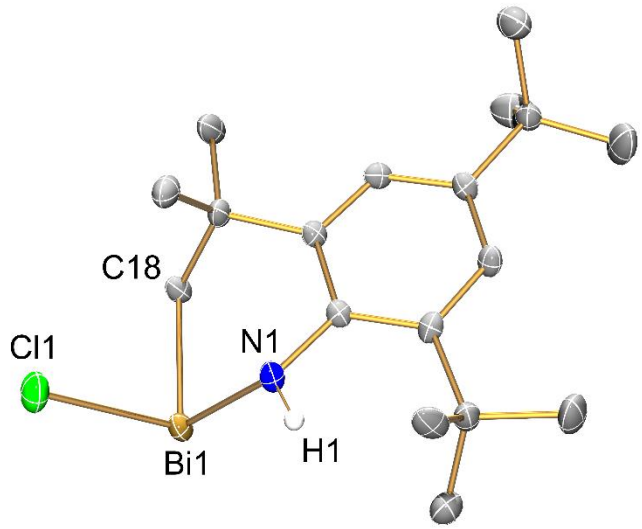


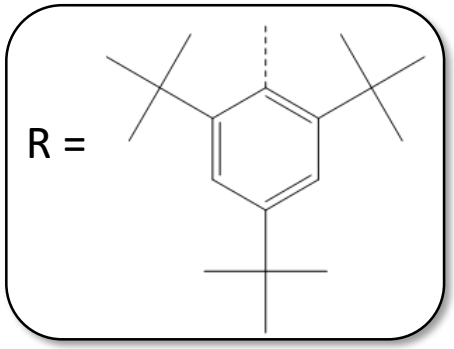
Konzept 1

Reaktion von Mes*N($SnMe_3$)H mit *n*-BuLi und $BiCl_3$





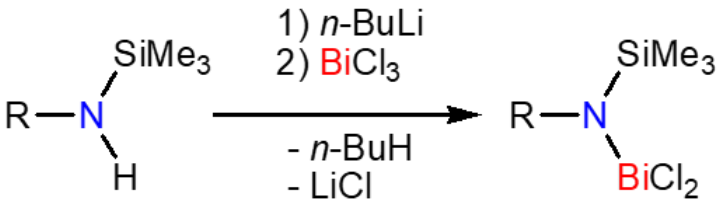


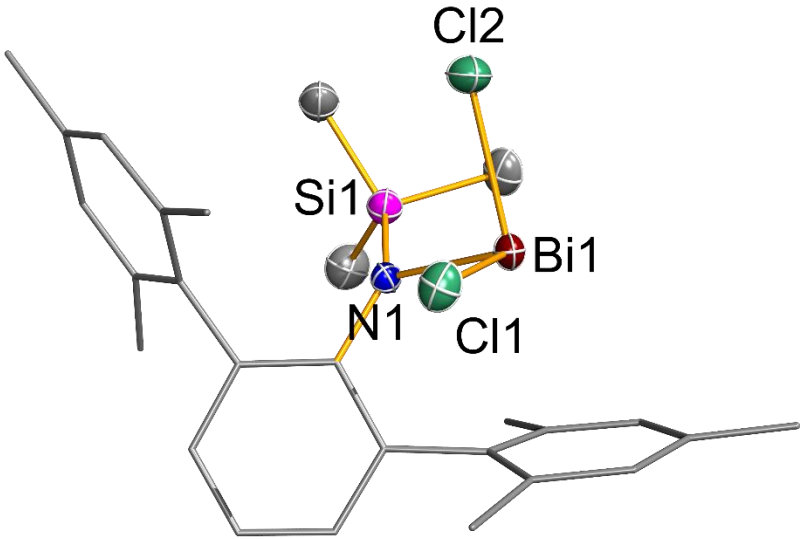


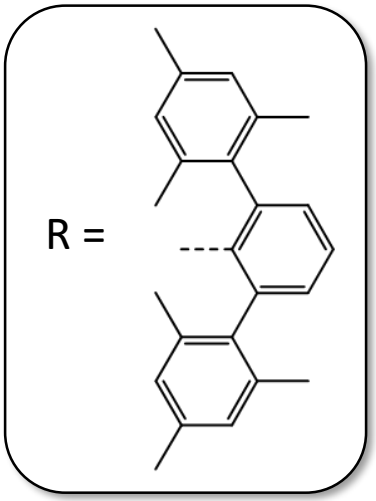
A. Schulz, M. Thomas, A. Villinger, *Z. Anorg. Allg. Chem.* **2017**, *643*, 1406–1414.

Konzept 1

Synthese von TerN(SiMe$_3$)BiCl$_2$



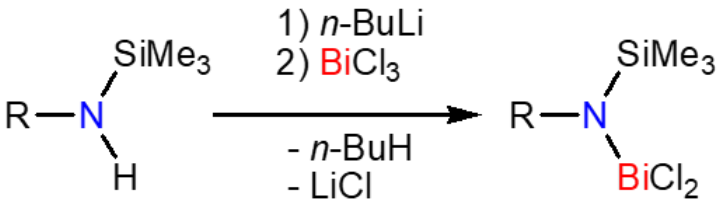


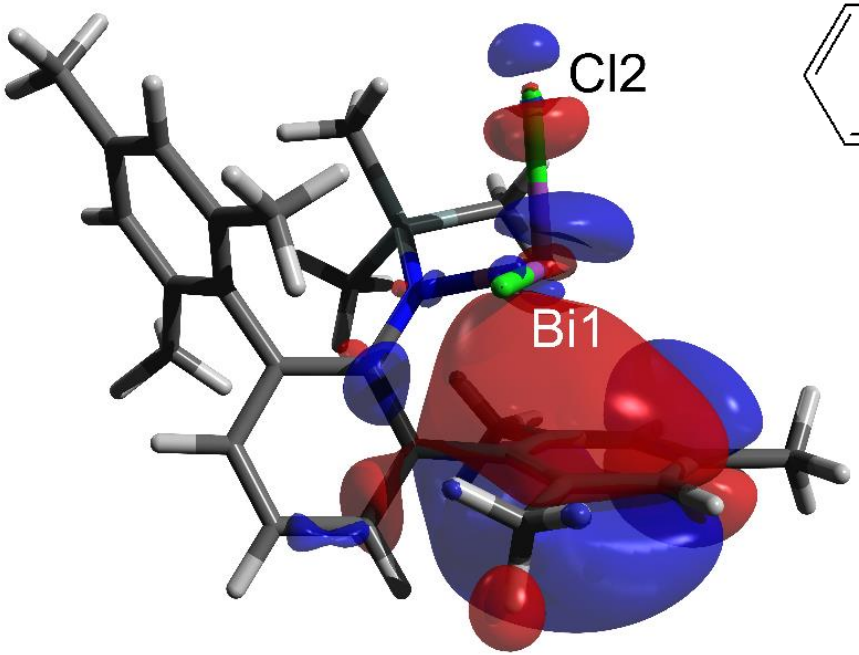


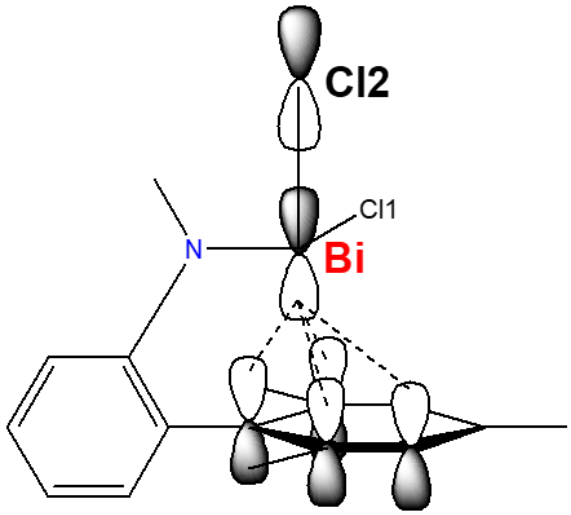
C. Hering-Junghans, A. Schulz, M. Thomas, A. Villinger, *Dalton Trans.* **2016**, *45*, 6053–6059.

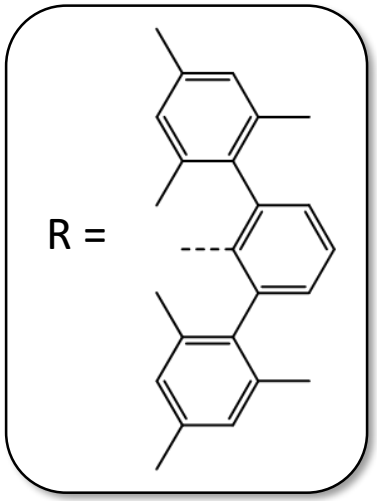
Konzept 1

Synthese von TerN(SiMe$_3$)BiCl$_2$





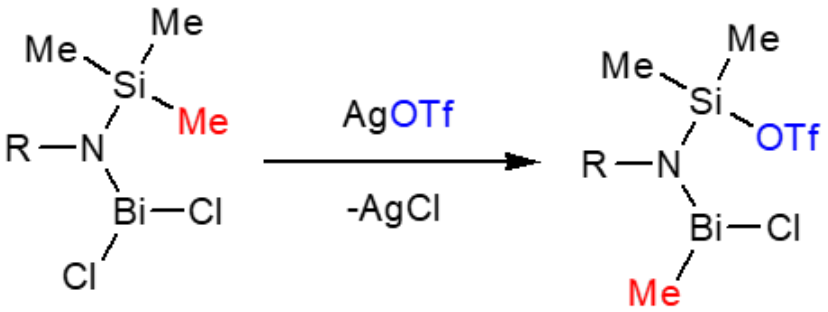


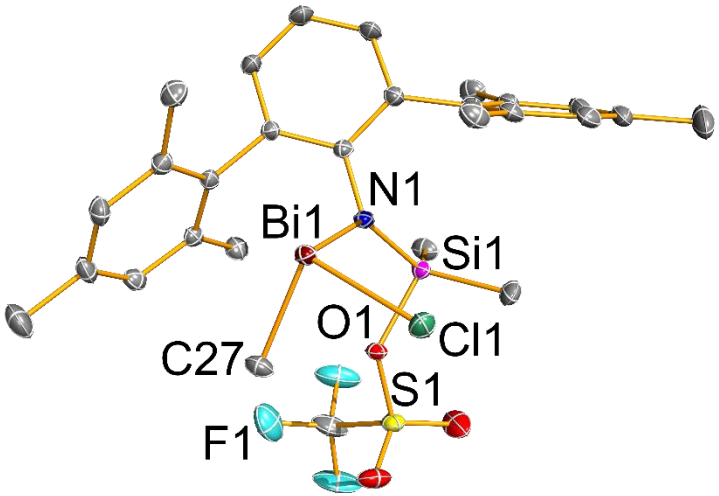


C. Hering-Junghans, A. Schulz, M. Thomas, A. Villinger, *Dalton Trans.* **2016**, *45*, 6053–6059.

Konzept 1

Methyl/Triflat Austausch





D. Michalik, A. Schulz, A. Villinger, *Inorg. Chem.* **2008**, *47*, 11798–11806; C. Hering, M. Lehmann, A. Schulz, A. Villinger, *Inorg. Chem.* **2012**, *51*, 8212–8224.

Konzept 1

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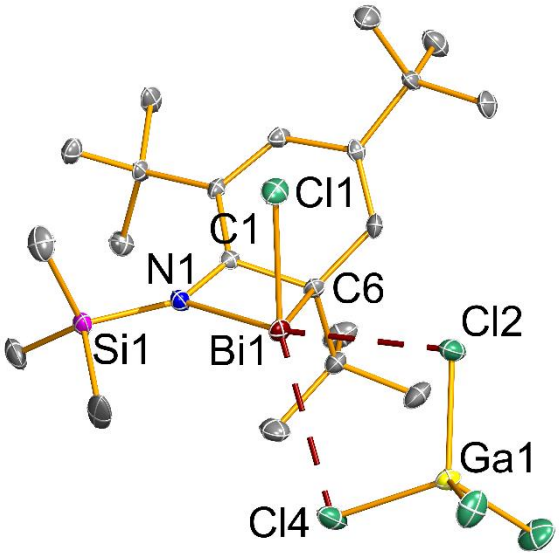
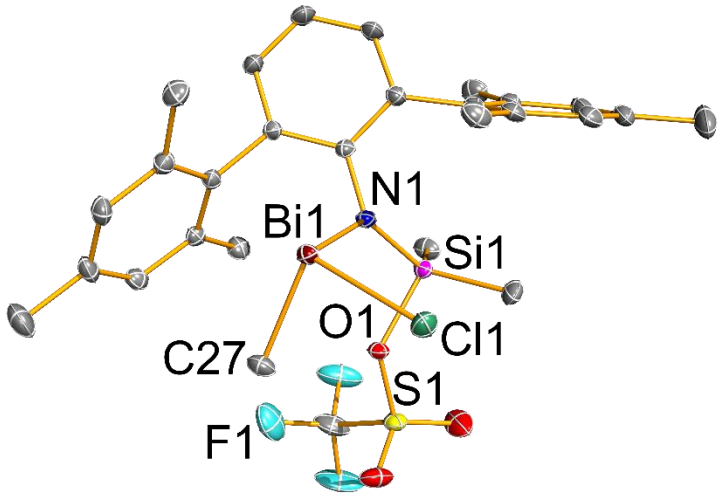
Das Problem:

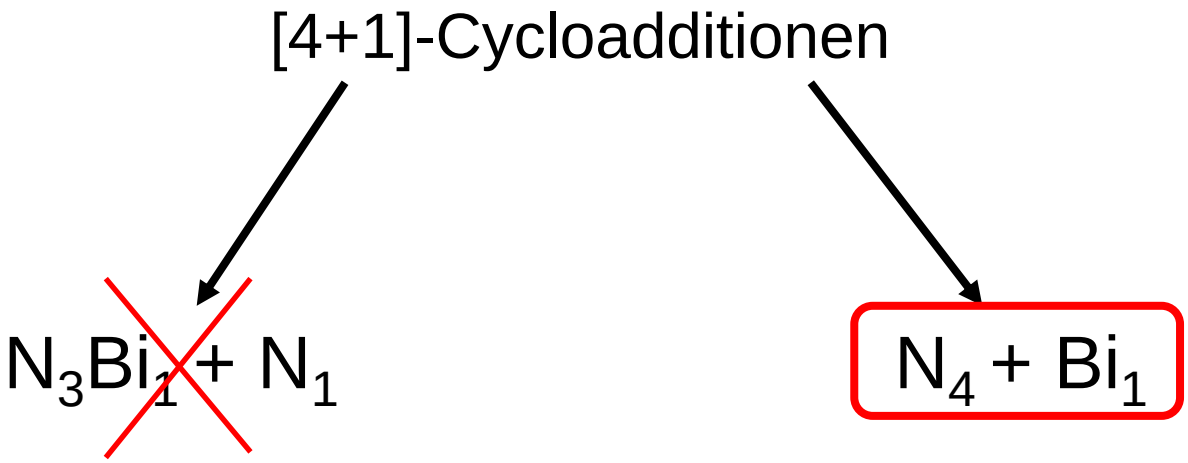




Konzept 2

Universität Rostock Traditio et Innovatio

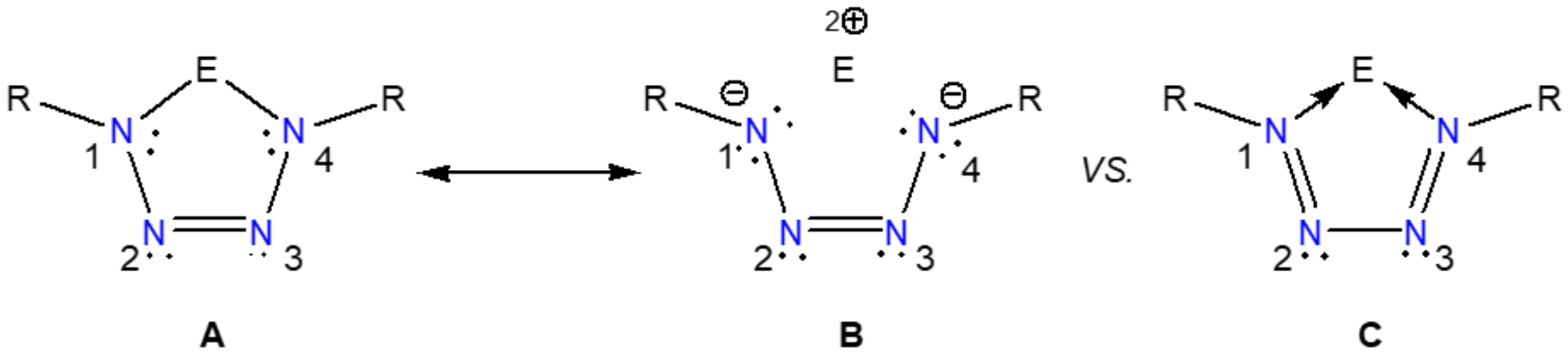
Die mögliche Lösung:



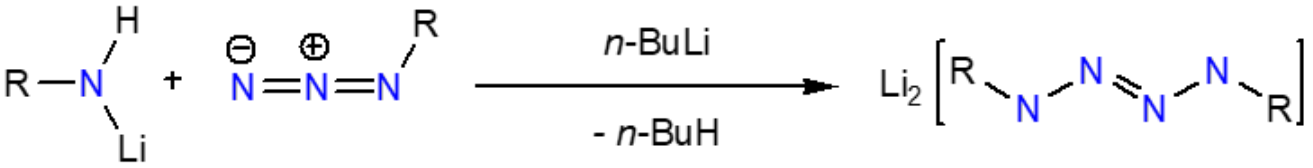
Konzept 2

Universität Rostock Traditio et Innovatio

Tetrazenid *VS.* Tetrazabutadien



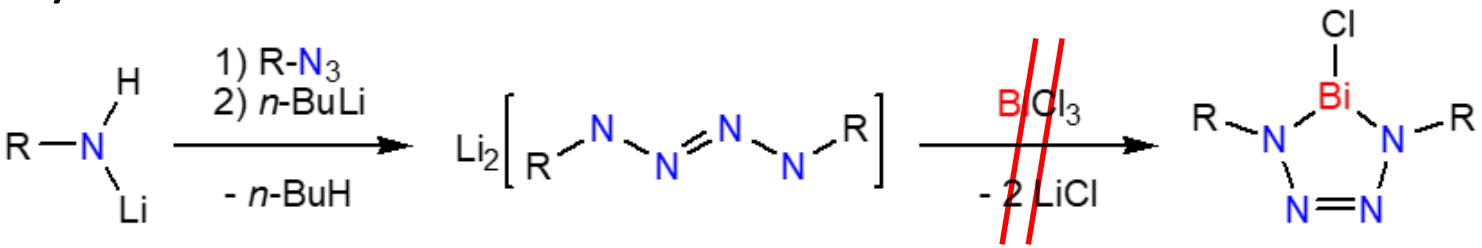
Synthese von Tetrazeniden 1):

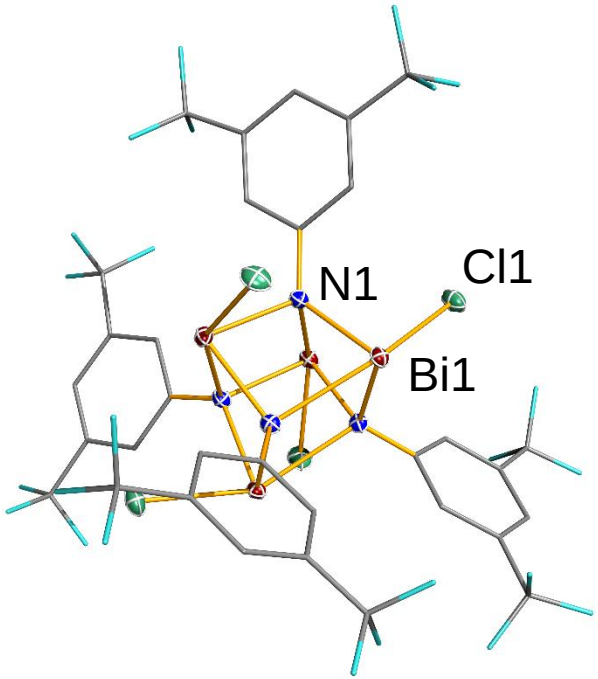


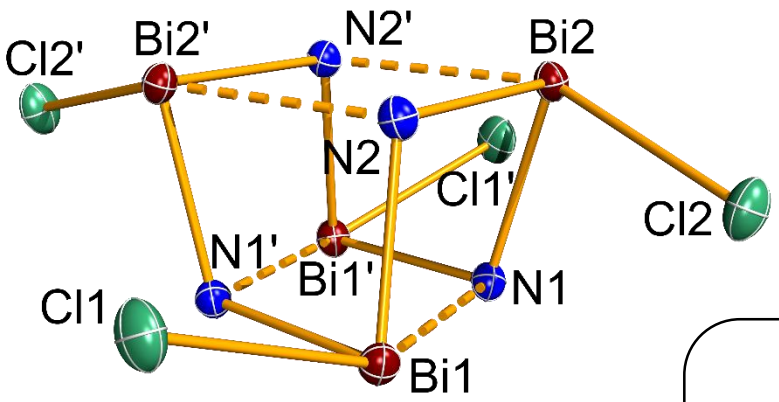
S. W. Lee, G. A. Miller, C. F. Campana, M. L. Maciejewski, W. C. Trogler, *J. Am. Chem. Soc.* **1987**, *109*, 5050–5051.

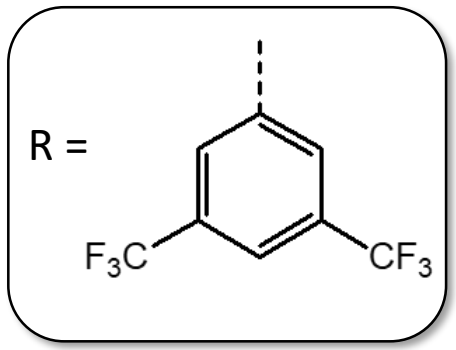
Konzept 2

Synthese von Tetrazeniden





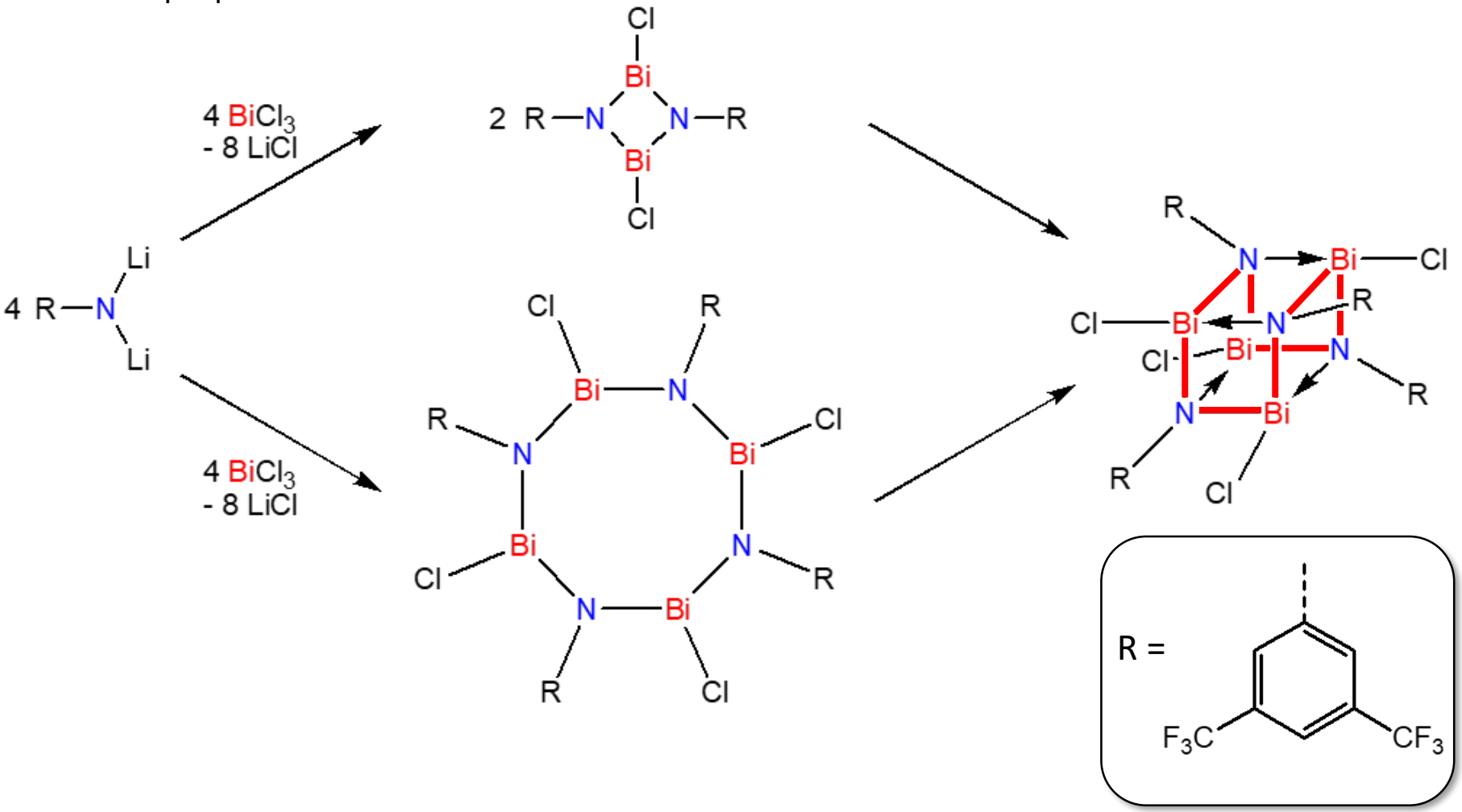




S. W. Lee, G. A. Miller, C. F. Campana, M. L. Maciejewski, W. C. Trogler, *J. Am. Chem. Soc.* **1987**, *109*, 5050–5051.

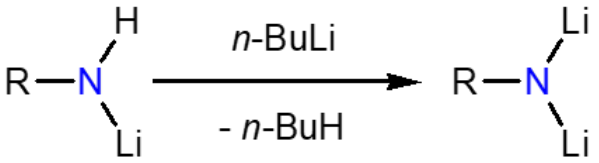
Konzept 2

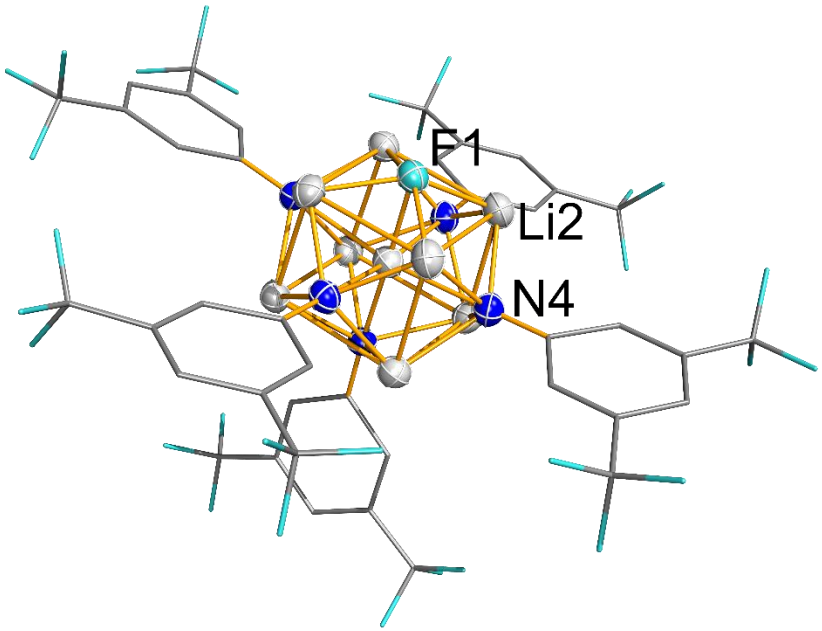
Ein Bi_4N_4 - Heterokuban

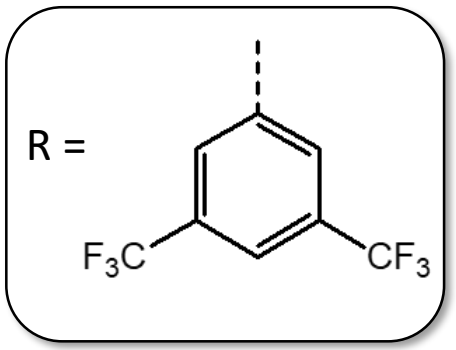


Konzept 2

Ein Dilithium-Salz

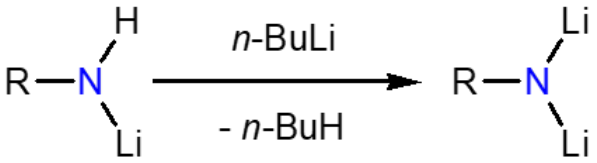


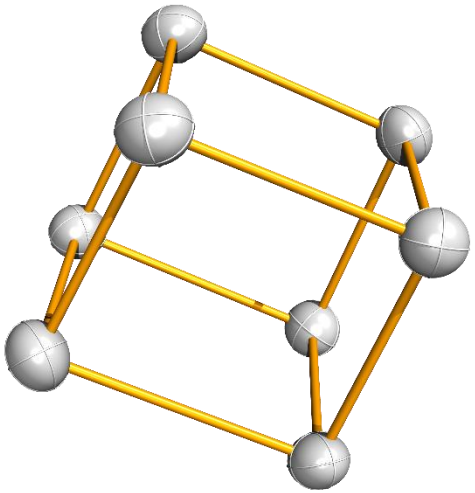


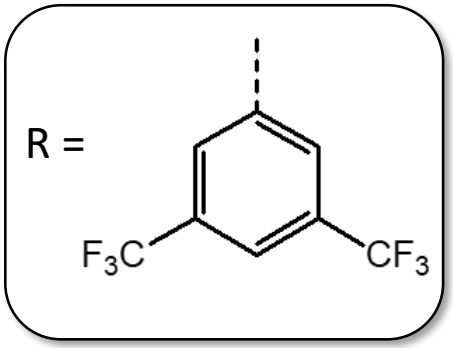


Konzept 2

Ein Dilithium-Salz

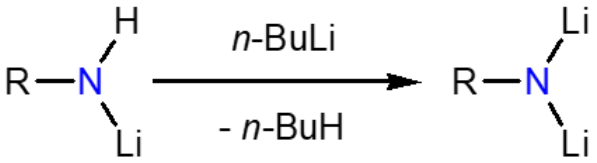


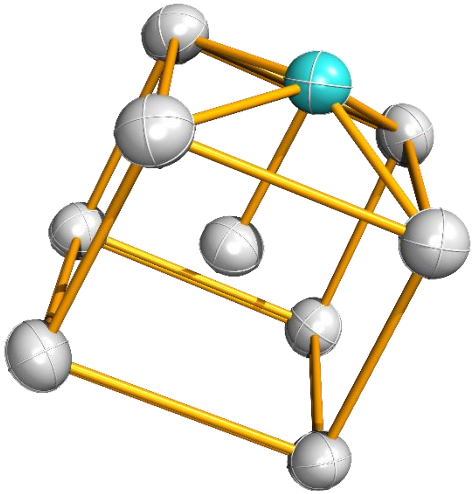


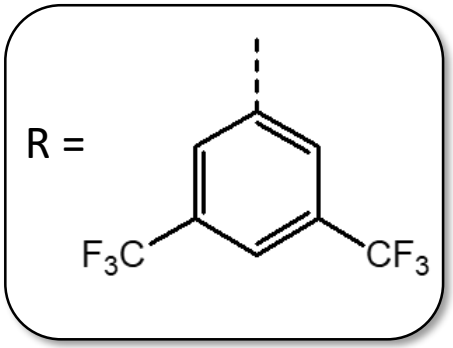


Konzept 2

Ein Dilithium-Salz







Konzept 2

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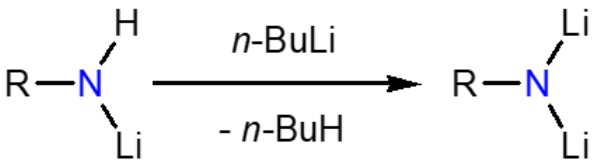
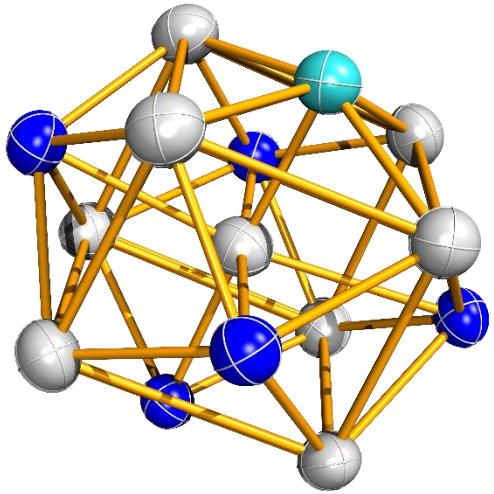
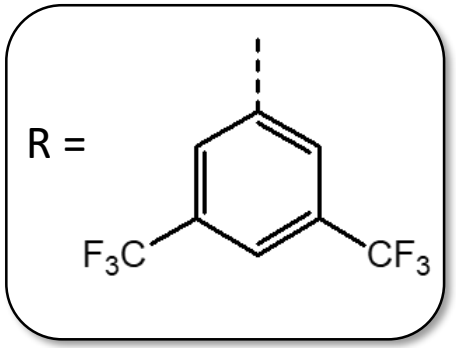
Ein Dilithium-Salz



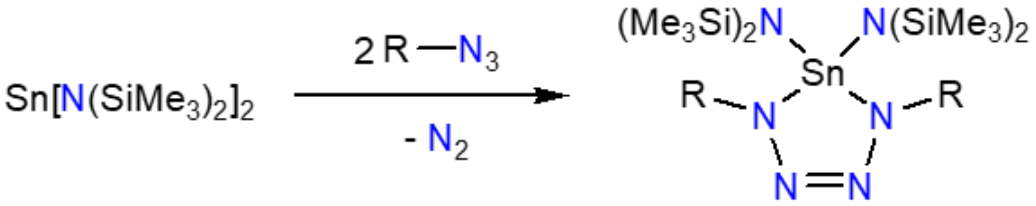


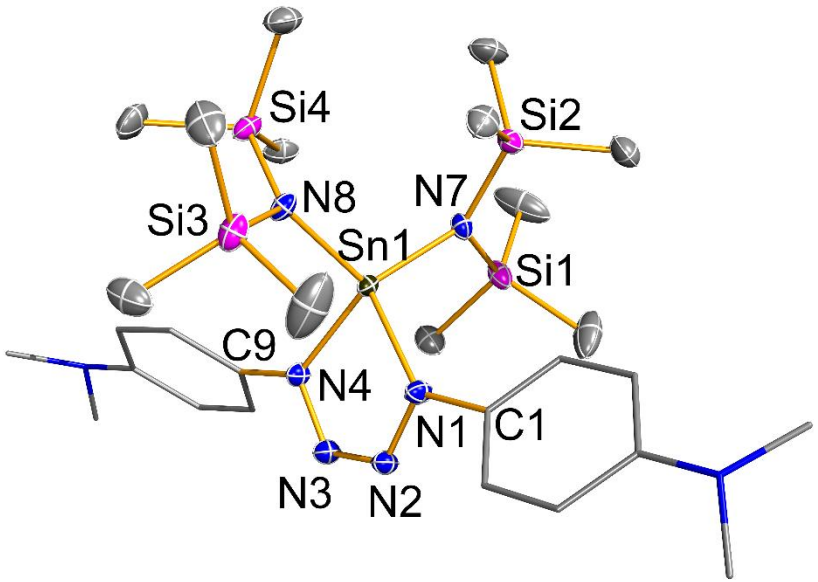


Konzept 2

Universität Rostock Traditio et Innovatio

Synthese von Tetrazeniden 2):

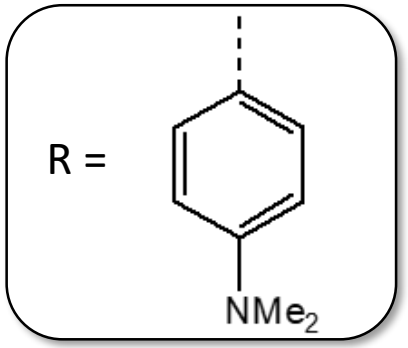




N1-N2 = 1.375(3) Å

N2-N3 = 1.272(3) Å

N3-N4 = 1.384(3) Å

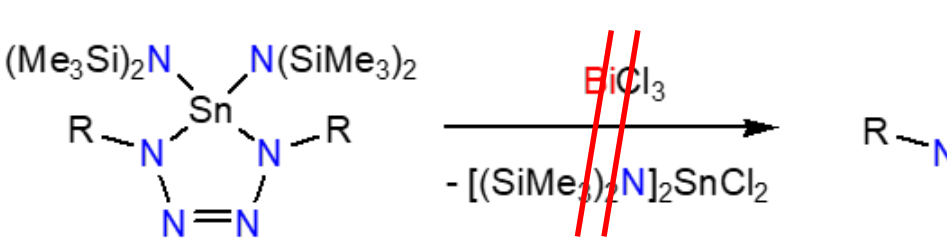


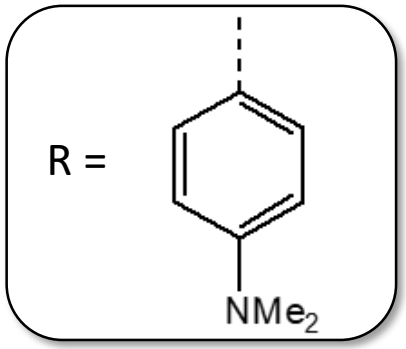
G. Ossig, A. Meller, S. Freitag, R. Herbst-Irmer, *Chem. Commun.* **1993**, 497–499.

Konzept 2

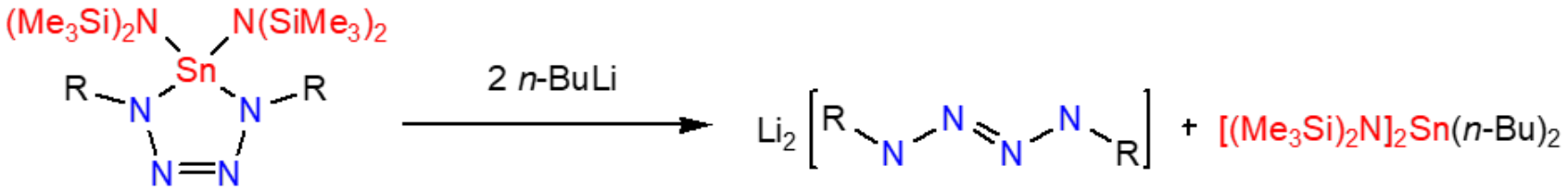
Universität Rostock Traditio et Innovatio

Reaktivität von Tetrazeniden 2):





a)



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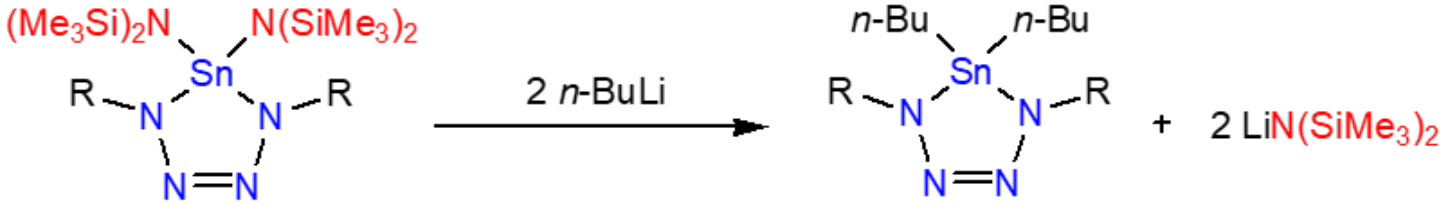
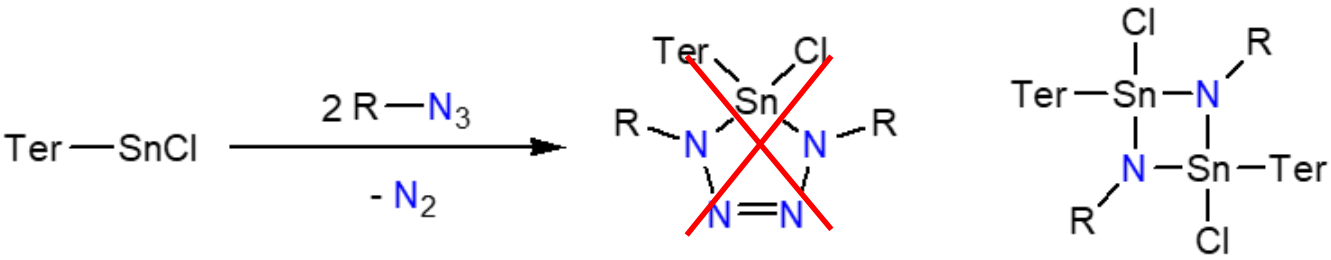
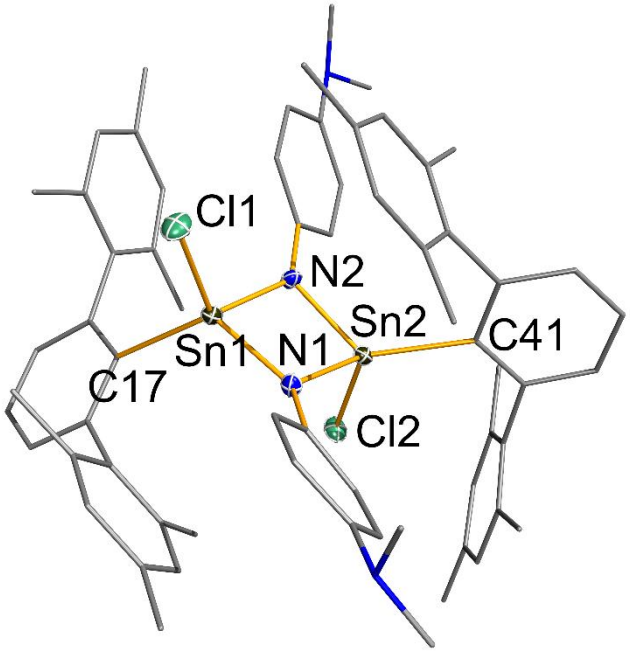


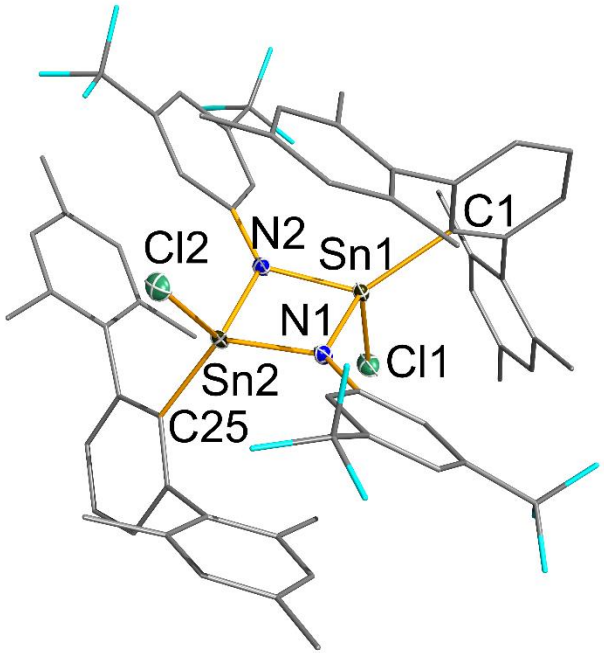
Konzept 2

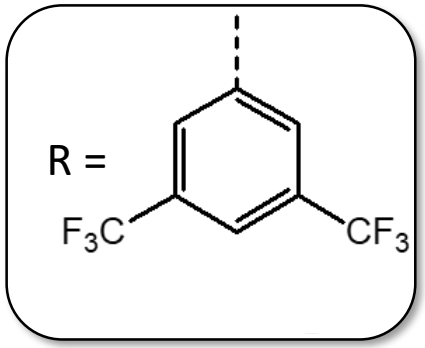
Universität Rostock Traditio et Innovatio

Organo-Zinn Tetrazenide:

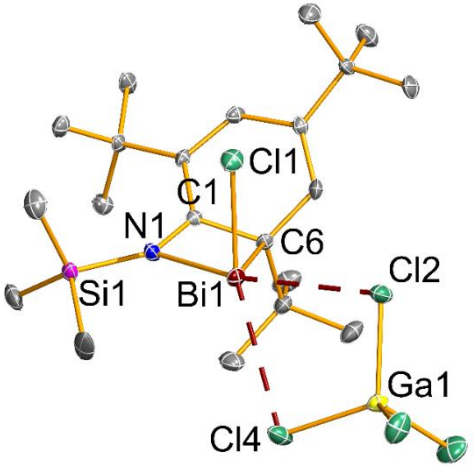


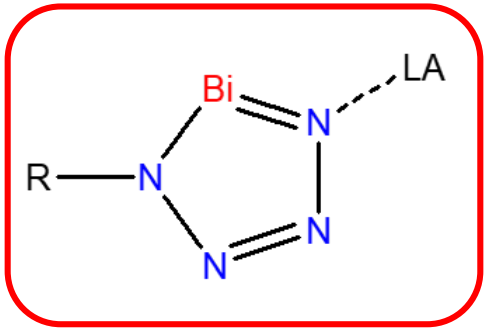


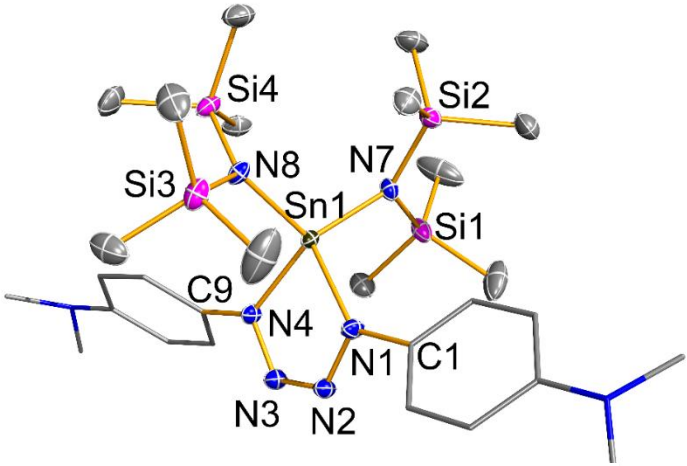


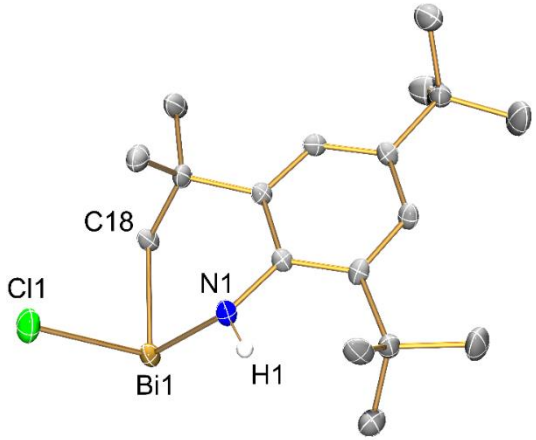


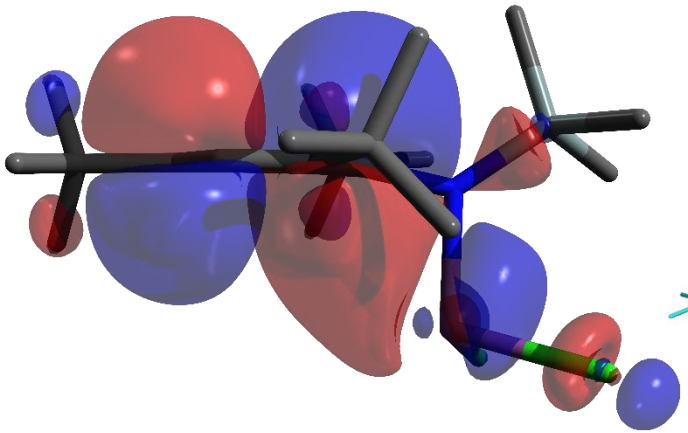
Zusammenfassung

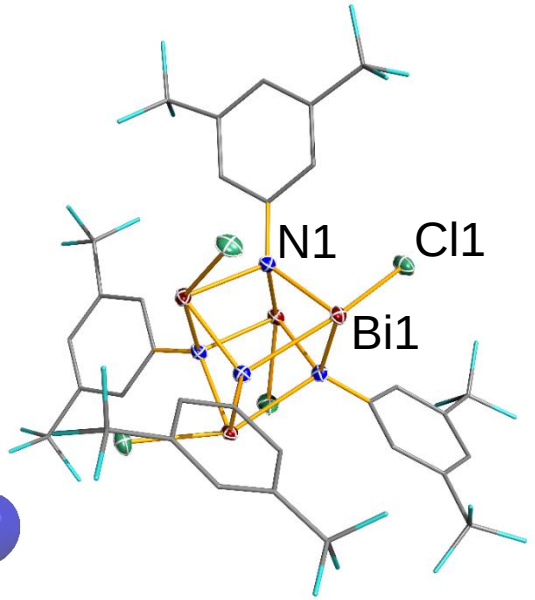












Danksagung:

Prof. Dr. Axel Schulz

Dr. Jonas Bresien

Dr. Alexander Villinger

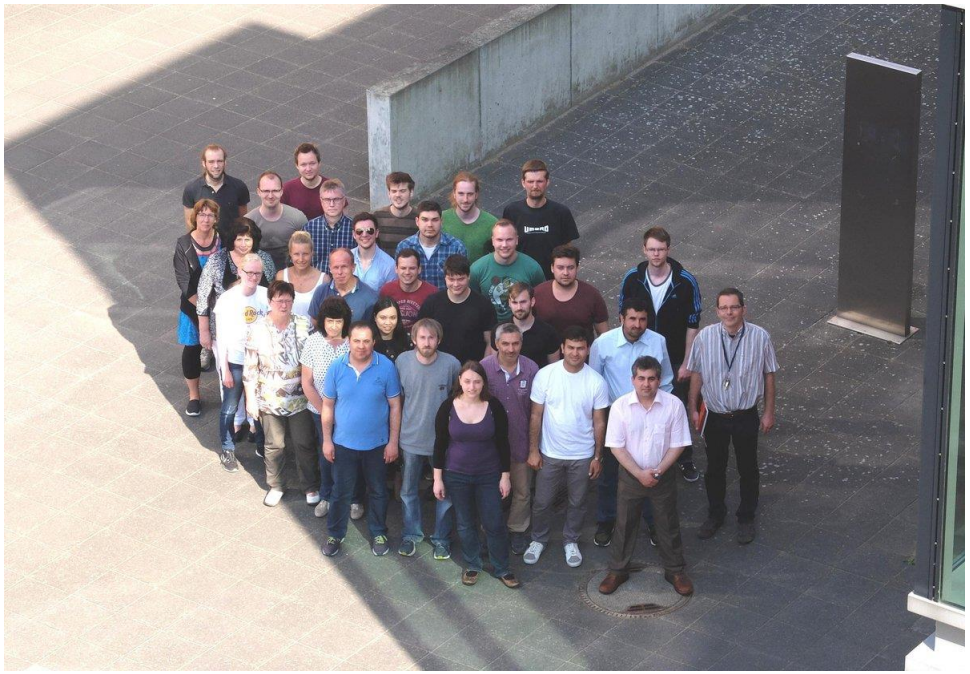
Isabel Schicht

AK Mitgliedern

Dr. Christian Hering-Junghans

NMR-Abteilung

Freunden und Familie



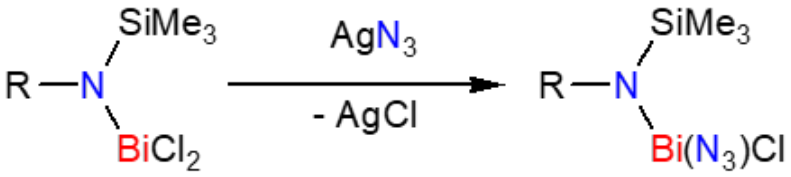
Danke für die Aufmerksamkeit!

Nachsitzung: Aufenthaltsraum der AC

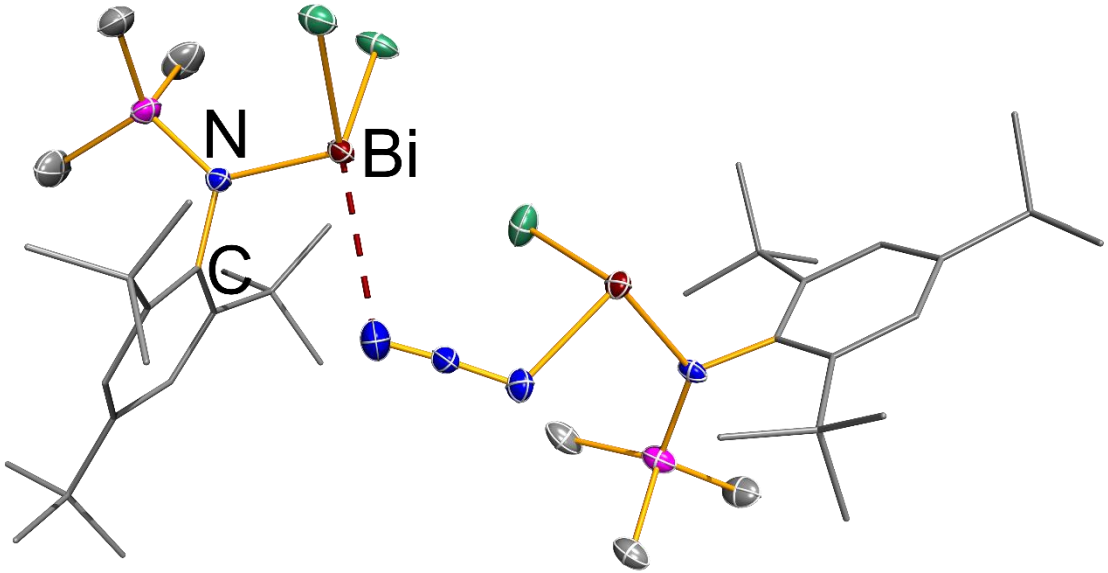
Konzept 1

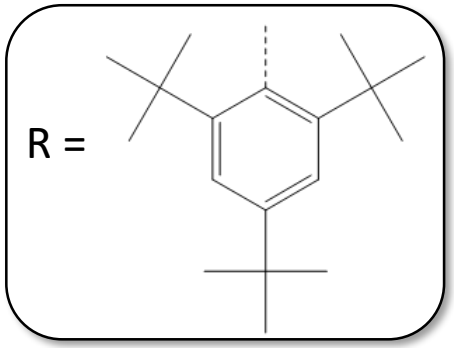
Universität Rostock Traditio et Innovatio

Synthese von Mes*N(SiMe$_3$)Bi(N$_3$)Cl



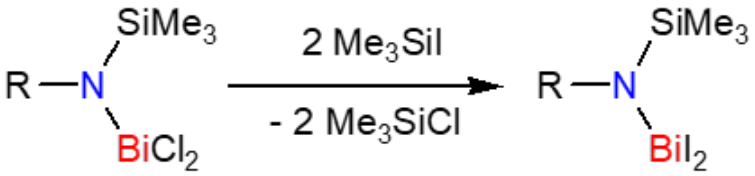
∢(C-N-Bi) = 114.6(3)°

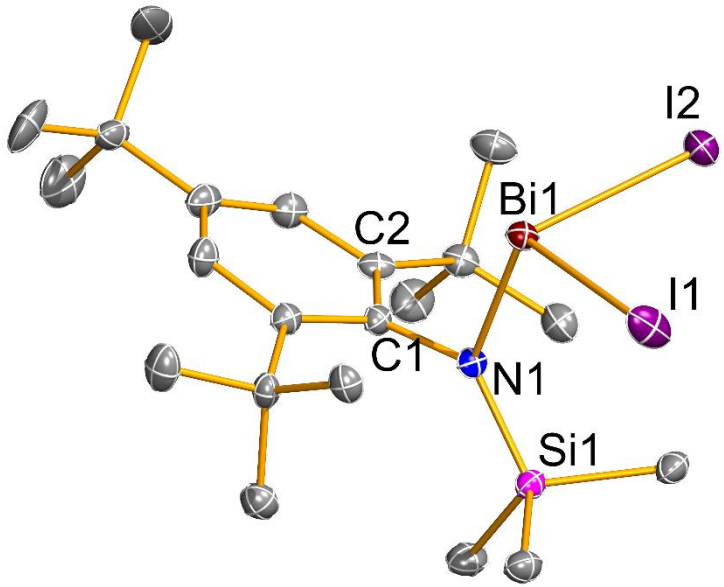


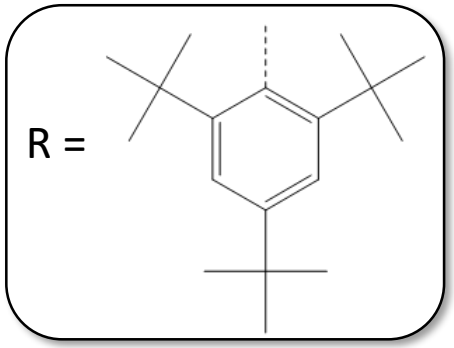


Konzept 1

Synthese von Mes*N(SiMe$_3$)BiI$_2$

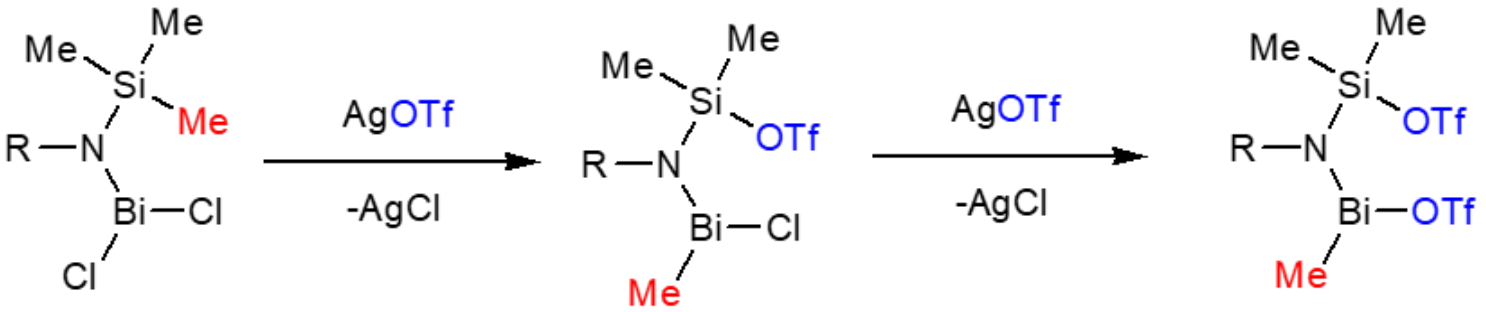


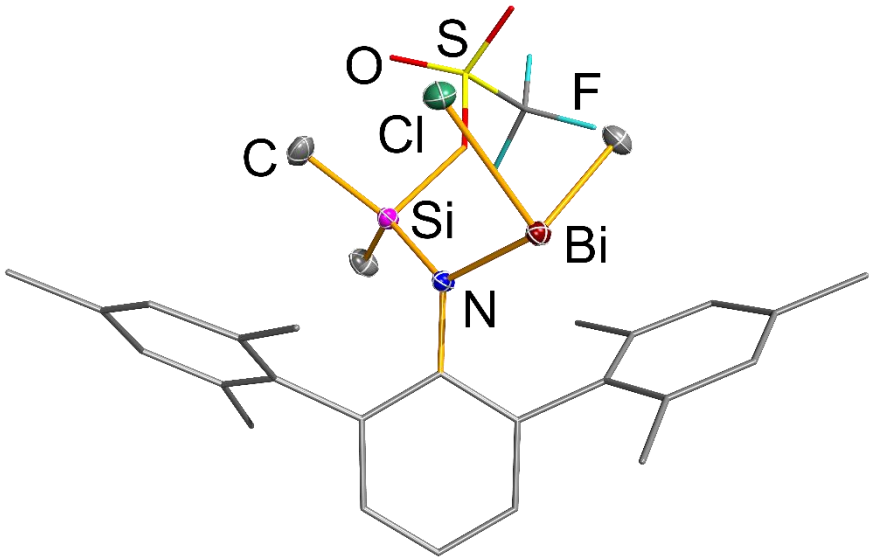


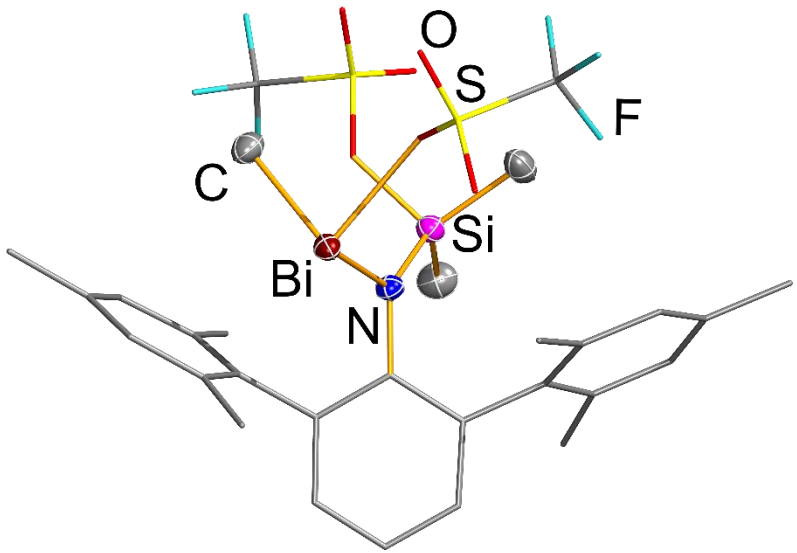


Konzept 1

Methyl/Triflat Austausch



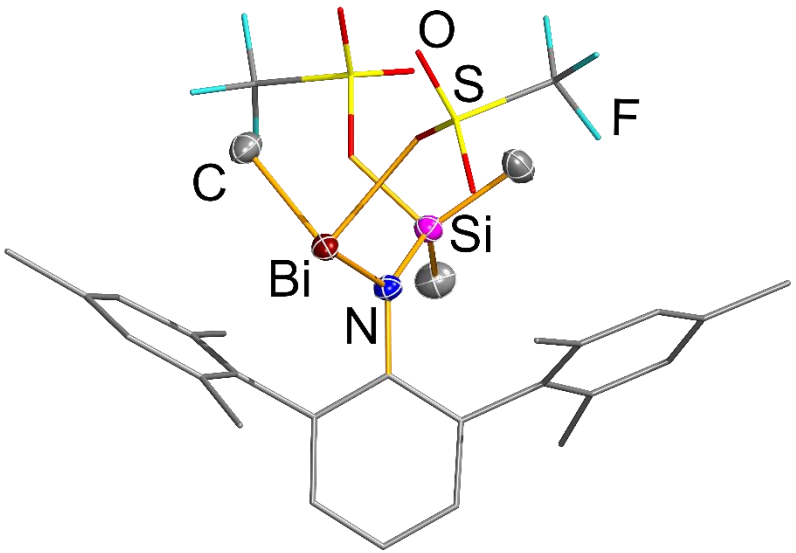




D. Michalik, A. Schulz, A. Villinger, *Inorg. Chem.* **2008**, *47*, 11798–11806; C. Hering, M. Lehmann, A. Schulz, A. Villinger, *Inorg. Chem.* **2012**, *51*, 8212–8224.

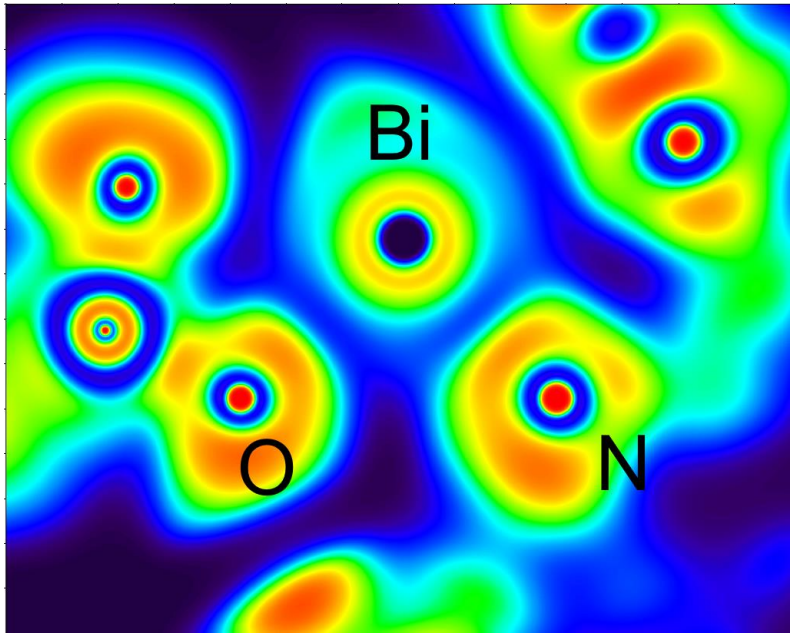
Konzept 1

Methyl/Triflat Austausch



d(O-Bi) = 2.375(2) Å

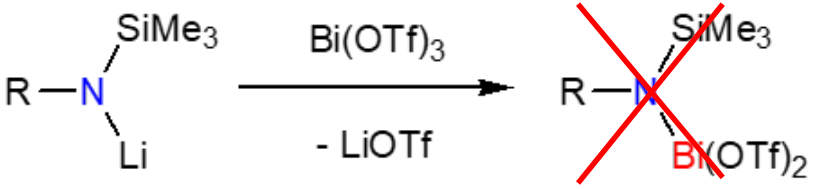
Σr_{kov}(O-Bi) = 2.14 Å

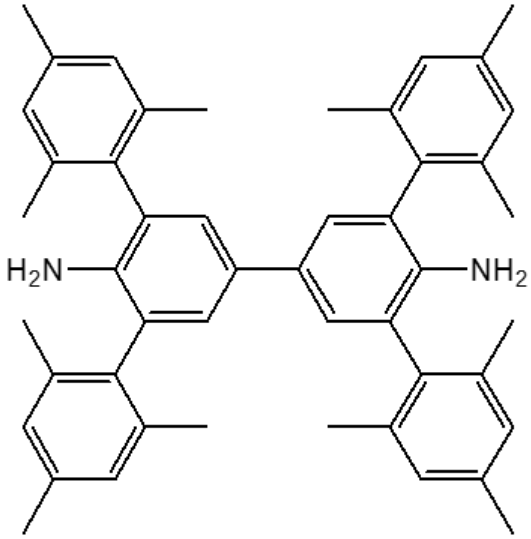


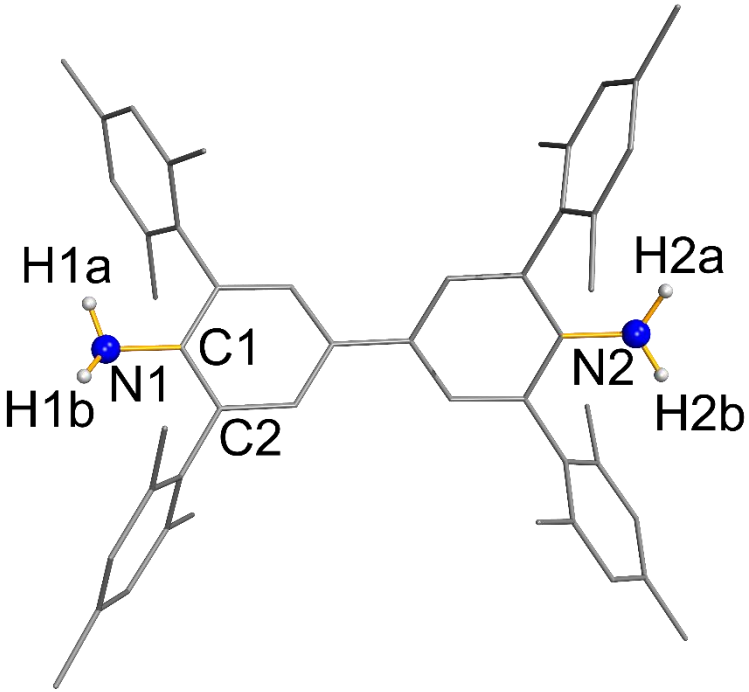
P. Pyykkö, M. Atsumi, *Chem. Eur. J.* **2009**, *15*, 12770–12779.

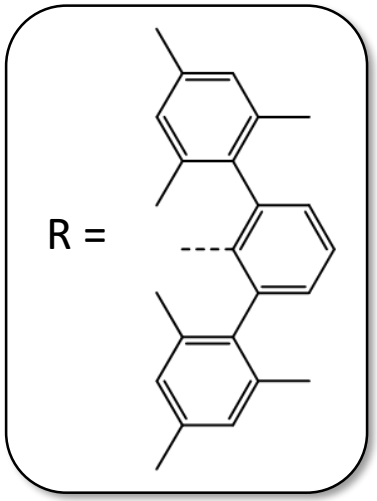
Konzept 1

Methyl/Triflat Austausch





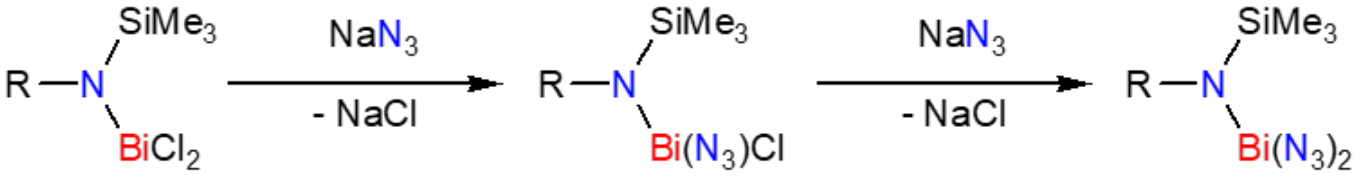


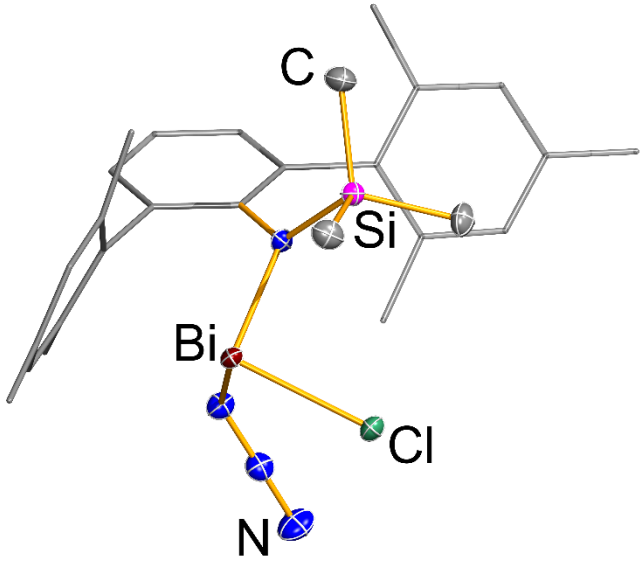


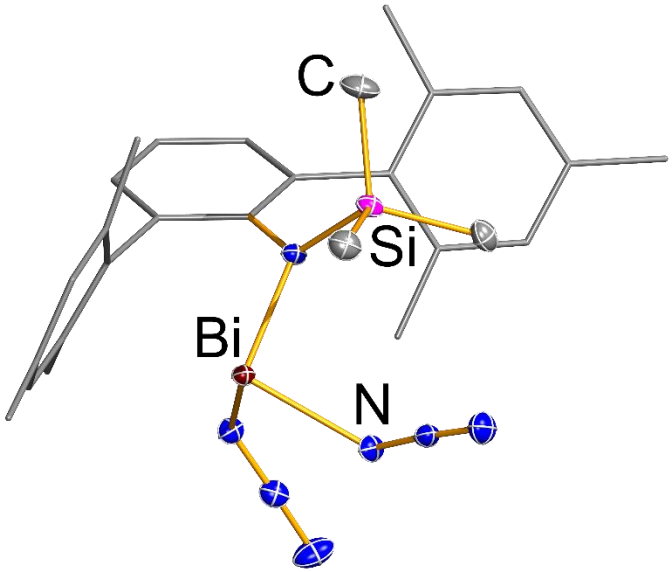
Konzept 1

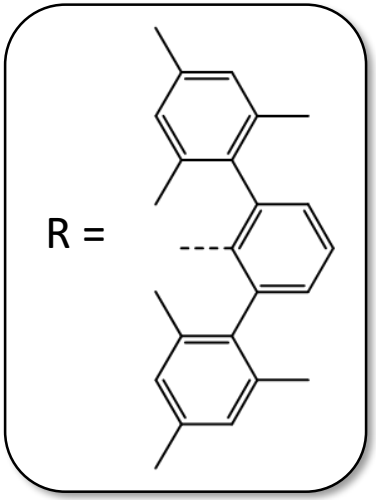
Universität Rostock Traditio et Innovatio

Synthese von TerN(SiMe$_3$)Bi(N$_3$)Cl und TerN(SiMe$_3$)Bi(N$_3$)$_2$



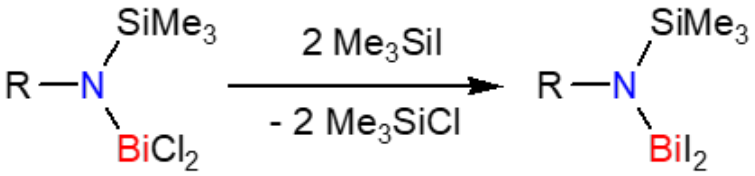


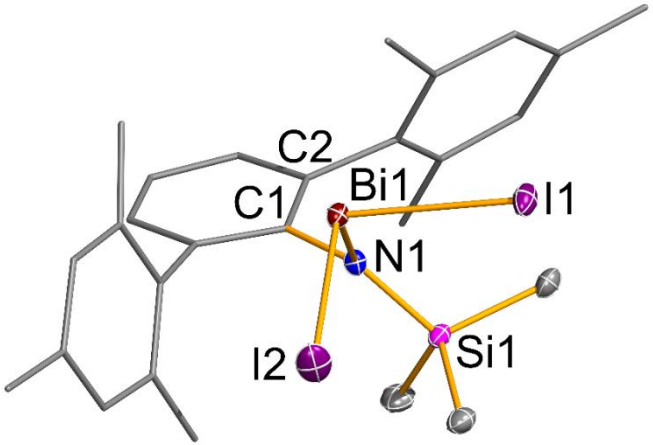


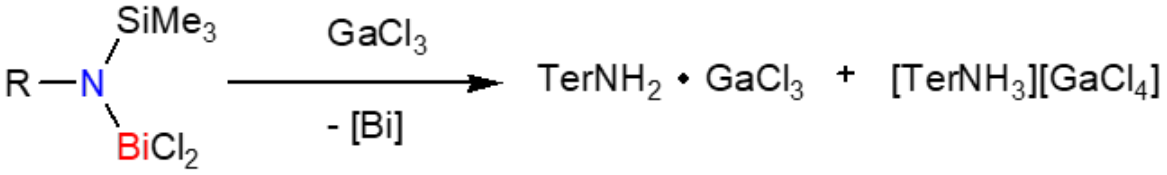


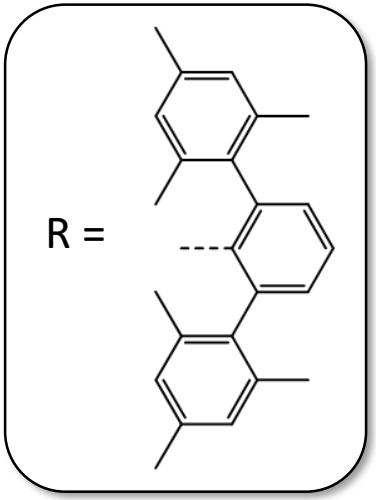
Konzept 1

Weitere Reaktionen von $TerN(SiMe_3)BiCl_2$









Konzept 2

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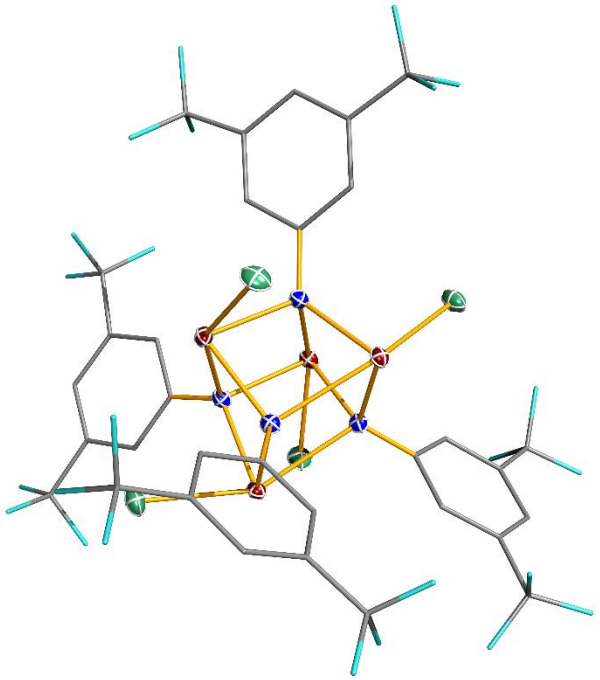
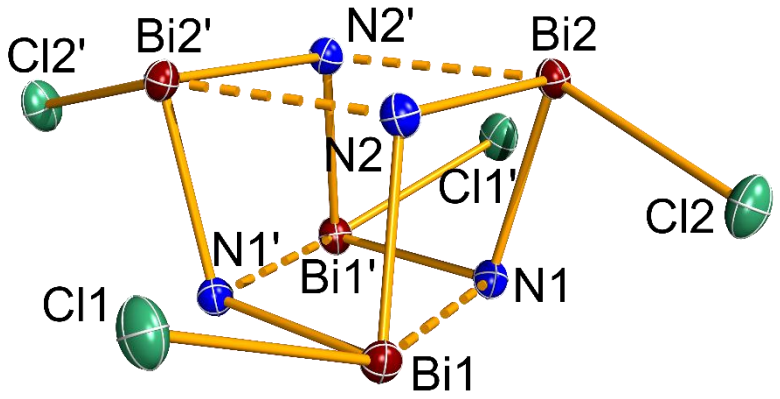
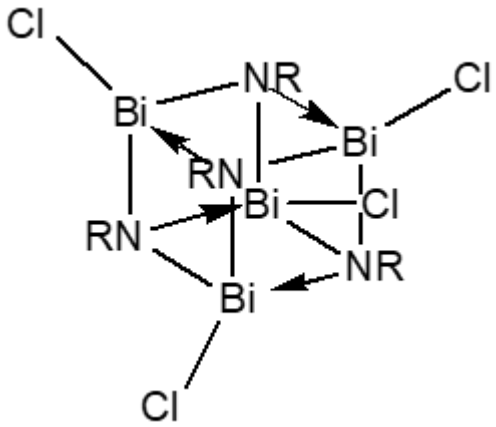
Ein Bi_4N_4 - Heterokuban







Konzept 2

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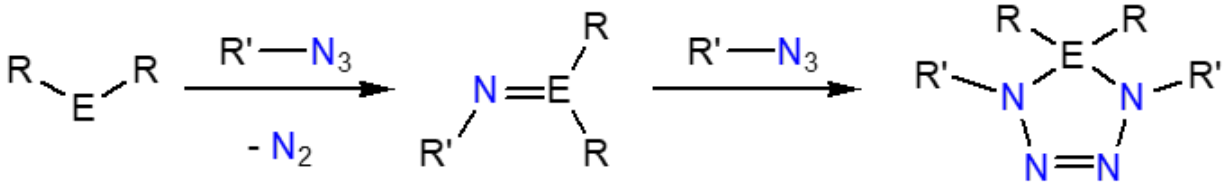
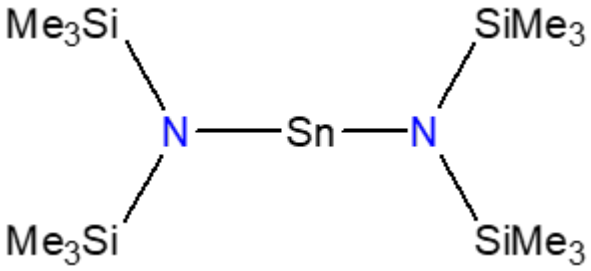
Synthese von Tetrazeniden 2):





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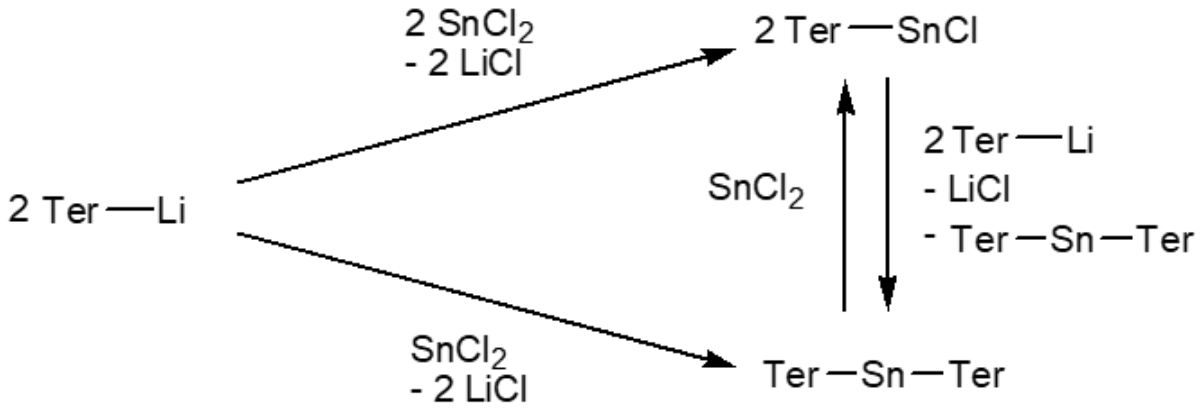
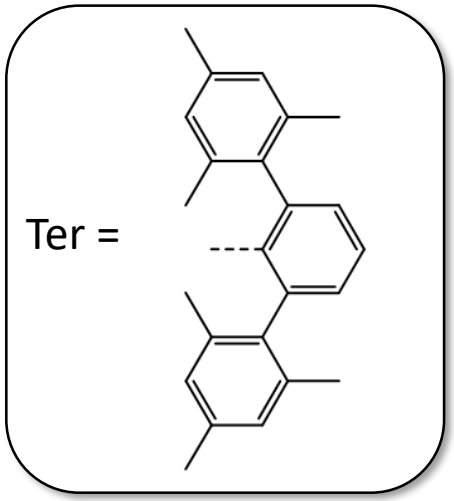
Konzept 2

Organo-Zinn Tetrazenide:





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