

Preparation and Molecular Structures of Stable Bis(germylenes) with Pincer Topology

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Keywords: N-Heterocycles / Germylenes / Pincer ligands

Benzannulated N-heterocyclic bis(germylenes) with pincer ligand topology have been prepared by the reaction of *N,N',N'',N'''*-tetralithiated tetraamines with $\text{GeCl}_2 \cdot 1,4\text{-dioxane}$ or by the transamination reaction between a tetraamine and $\text{Ge}[\text{N}(\text{SiMe}_3)_2]_2$. X-ray diffraction studies have shown,

that the bis(germylenes) exist as monomers in the solid state. Significant intramolecular $\text{Ge} \cdots \text{Ge}$ and $\text{Ge} \cdots \text{N}$ interactions have been observed for the lutidine-bridged bis(germylene). (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2007)

Introduction

Polydentate N-heterocyclic carbene (NHC) ligands^[1] containing two imidazolin-2-ylidene^[2] or benzimidazolin-2-ylidene^[3] donor groups, which are capable of forming chelate complexes including tridentate derivatives with pincer topology,^[4] are known. In addition, some tris(imidazolin-2-ylidenes)^[5] and complexes with cyclic tetrakis(benzimidazolin-2-ylidene)^[6] and [11]ane- $\text{P}_2\text{C}^{\text{NHC}}$ ligands^[7] have been described. Much less is known about polydentate silylenes, germylenes and stannylenes which can act as chelate ligands, although the monodentate derivatives have been prepared.^[8–10]

Previously we described the preparation and coordination chemistry of germanium analogues of benzannulated N-heterocyclic bis(carbenes) in which two benzimidazolin-2-germylene moieties are linked together with an aryl or an alkyl group.^[11] It has been demonstrated that these bis(germylenes) can act as bidentate chelate ligands. Continuing our investigations in this field, we report now on the preparation of the N-heterocyclic benzannulated bis(germylenes) with pincer topology which are potentially tridentate ligands.

Results and Discussion

The N-heterocyclic bis(germylenes) were obtained from the tetraamines **2a** and **2b** which were prepared by reduction of the carbonyl groups in the corresponding tetraamides **1a** and **1b** (Scheme 1). The tetraamides are obtained by acylation of *N*-(*ortho*-aminophenyl)amides with benzene- (**1a**) or lutidine-2,6-bis(carboxylic chlorides) (**1b**)

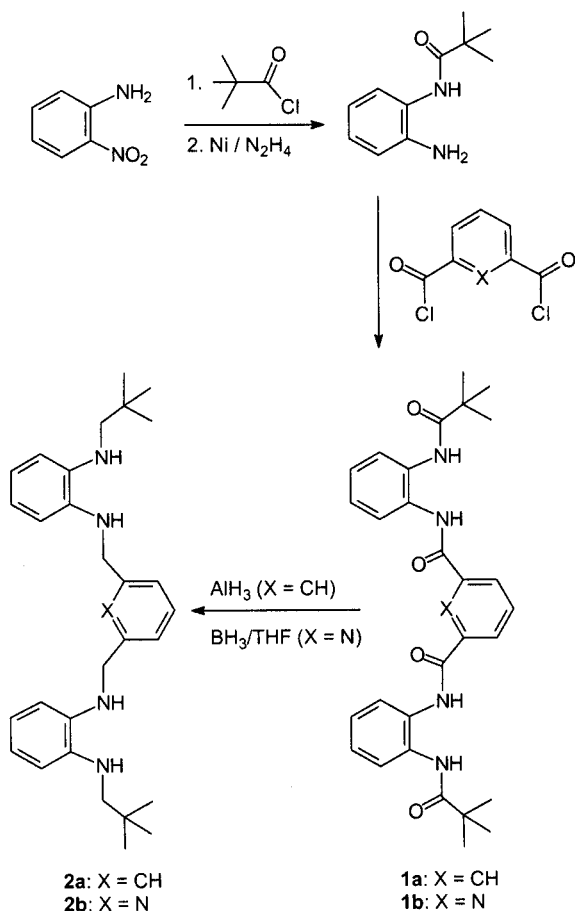
in the presence of Et_3N . The bridging unit present in the tetraamides determined which reducing agent had to be used in the subsequent reaction. Reduction of the carbonyl groups in the phenylene-bridged tetraamide **1a** was achieved with AlH_3 in THF at ambient temperature. The four carbonyl groups in tetraamide **1b** were reduced in good yield (81%) by an excess of freshly prepared BH_3 in THF.

The bis(germylene) **3** was obtained by lithiation of the corresponding tetraamine **2a** at -78°C in THF followed by the reaction of the generated organolithium compound with $\text{GeCl}_2 \cdot 1,4\text{-dioxane}$ (Scheme 2). An analogous reaction sequence gave also the bis(germylene) **4**, but the product was quite impure and the overall yield was finally less than 30% after multiple recrystallization steps. The yield of bis(germylene) **4** could be improved significantly to 60–65% by reaction of the tetraamine **2b** with $\text{Ge}[\text{N}(\text{SiMe}_3)_2]_2$ in boiling THF.

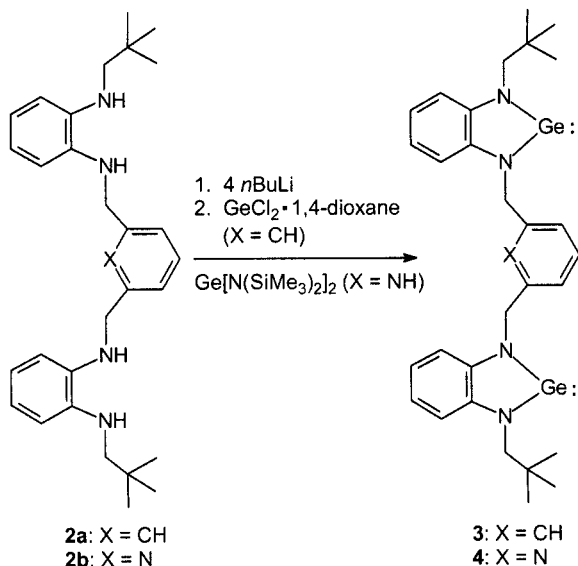
Bis(germylene) **3** was crystallized from hexane. The structure analysis shows monomeric units of the bis(germylene) which exhibit no significant inter- or intramolecular interactions (Figure 1). Bond lengths and angles in **3** are similar to those reported for a monodentate benzannulated germylene^[9e] and other related bis(germylenes).^[11] The nitrogen atoms are planarized as was observed for the analogous benzannulated N-heterocyclic carbenes.^[12] The shortest distance between two germanium atoms is the intermolecular separation between Ge1 and Ge2 [4.226(5) Å] which is too long to be regarded as an interaction. The lack of $\text{Ge} \cdots \text{Ge}$ interactions in **3** is possibly caused by the sterically demanding *N*-substituents. We have observed such $\text{Ge} \cdots \text{Ge}$ interactions in bis(germylenes) with sterically less demanding *N*-substituents.^[11]

The molecular structure of bis(germylene) **4** containing a lutidine bridge between the germylene units is depicted in Figure 2. Its conformation is distinctly different to that of **3**. While no significant intermolecular interactions were noticed, short intramolecular $\text{Ge} \cdots \text{Ge}$ and $\text{Ge} \cdots \text{N}$ contacts

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Scheme 1. Preparation of compounds 1a, 1b and 2a, 2b.



Scheme 2. Preparation of bis(germylenes) 3 and 4.

were found in the molecular structure of 4. The Ge1...Ge2 separation is 3.041(5) Å which is significantly shorter than twice the van der Waals radius of the germanium atom.^[13] It is also shorter than the Ge...Ge separation which we found for alkyl-bridged bis(germylenes) [3.577(2) Å].^[11] The

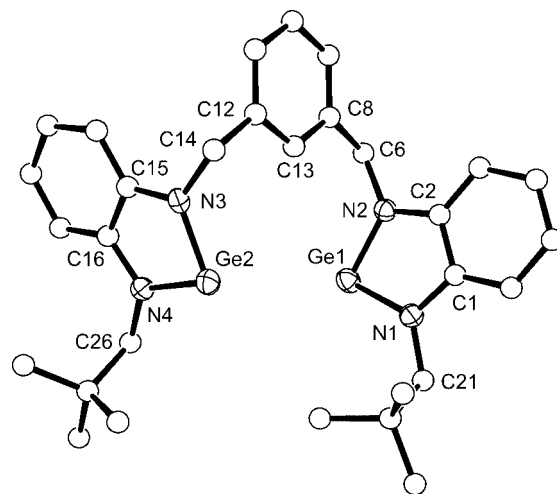


Figure 1. Molecular structure of 3. Selected bond lengths [Å] and angles [°]: Ge1–N1 1.861(2), Ge1–N2 1.852(2), Ge2–N3 1.851(2), Ge2–N4 1.859(2), N1–C1 1.396(3), N1–C21 1.469(4), N2–C2 1.384(3), N2–C7 1.462(3), N3–C15 1.381(3), N3–C14 1.460(3), N4–C16 1.395(3), N4–C26 1.469(3), C1–C2 1.415(4), C15–C16 1.408(4); N1–Ge1–N2 85.05(10), N3–Ge2–N4 85.05(10), Ge1–N1–C1 114.0(2), Ge1–N2–C2 114.5(2), Ge2–N3–C15 114.2(2), Ge2–N4–C16 114.0(2).

geometry of the N₂Ge1...Ge2N₂ moiety is similar to the distorted *trans*-bent arrangement found for E=E double bonds of heavier homologues of alkenes. The intramolecular distances Ge1...N3 [3.386(7) Å] and Ge2...N3 [3.154(7) Å] are again shorter than those found in bimolecular aggregates of bis(germylene) with intermolecular Ge...N separations of about 3.53 Å.^[11]

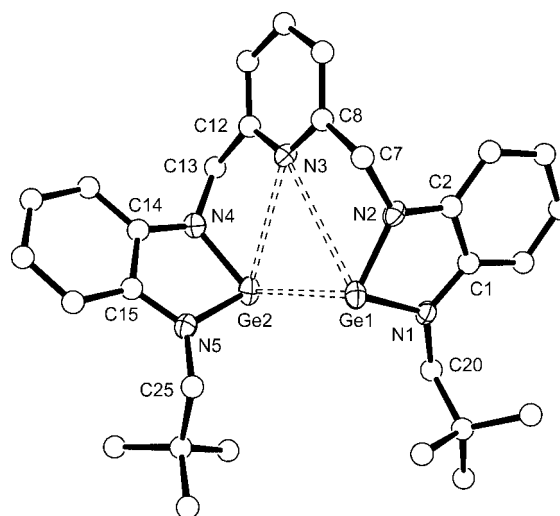


Figure 2. Molecular structure of 4. Selected bond lengths [Å] and angles [°]: Ge1–N1 1.862(3), Ge1–N2 1.847(3), Ge2–N4 1.845(3), Ge2–N5 1.862(3), N1–C1 1.386(5), N1–C20 1.462(5), N2–C2 1.372(5), N2–C7 1.455(5), N4–C14 1.377(5), N4–C13 1.456(5), N5–C15 1.385(5), N5–C25 1.462(5), C1–C2 1.422(5), C14–C15 1.425(5); N1–Ge1–N2 84.88(13), N4–Ge2–N5 85.01(14), Ge1–N1–C1 114.1(2), Ge1–N2–C2 114.9(2), Ge2–N4–C14 115.0(2), Ge2–N5–C15 113.9(3); Ge2...Ge1 3.041(5), Ge1...N3 3.386(7), Ge2...N3 3.154(7).

Conclusions

We have prepared the bis(germylenes) **3** and **4** containing two N-heterocyclic germylene (NHGe) units bridged by a 1,3-phenylene- or 1,3-pyridinediylbis(methylene) group, respectively. These compounds are germanium analogues of N-heterocyclic pincer-type bis(carbene) ligands. Their use in the complex formation with transition metal ions and the properties of such pincer complexes are currently investigated.

Experimental Section

Starting Materials, Reaction Conditions and Instrumentation: All manipulation were carried out under argon using Schlenk or glove-box techniques. Toluene and *n*-hexane were dried with sodium/benzophenone and were freshly distilled prior to use. [D₈]Toluene was dried with Na/K alloy. The preparation of the tetraamide **1a** and the tetraamine **2a** have been described.^[11] Compounds **1a** and **1b** were obtained by similar methods. However, **2b** was prepared in analogy to **2a** by using BH₃ instead of AlH₃ as a reducing agent. Ge[N(SiMe₃)₂]₂ was prepared as described in the literature.^[14] ¹H and ¹³C NMR spectra were recorded with a Bruker AC-200 spectrometer.

Tetraamide 1b: Yield 75%, white solid. ¹H NMR (200 MHz, [D₆]-DMSO): δ = 10.91 [s, 2 H, NH-C(O)-C₅H₃N], 9.07 [s, 2 H, NH-C(O)-C(CH₃)₃], 8.45–8.34 (m, 3 H, Ar-H C₅H₃N), 7.73–7.68 (m, 2 H, Ar-H C₆H₄), 7.52–7.47 (m, 2 H, Ar-H C₆H₄), 7.31–7.26 (m, 4 H, Ar-H C₆H₄), 1.01 [s, 18 H, C(CH₃)₃] ppm. ¹³C NMR (50.3 MHz, [D₆]-DMSO): δ = 176.9 [C(O)-C₅H₃N], 161.4 (C α -C₅H₃N), 148.2 [C(O)-C(CH₃)₃], 140.5 (C γ -C₅H₃N), 131.4, 130.6 (Ar-C_{ipso} C₆H₄), 126.2 (C β -C₅H₃N), 125.7, 125.5, 125.1, 125.0 (Ar-C_{meta} and Ar-C_{ortho} C₆H₄), 38.7 [C(CH₃)₃], 26.9 [C(CH₃)₃] ppm. MS (MALDI): *m/z* (%) = 516 [M + H]⁺, 538 [M + Na]⁺.

Tetraamine 2b: A 1 M solution of BH₃ in THF (40 mmol, 40 mL) was added to the solid tetraamide **1b** (500 mg, 0.97 mmol) at 0 °C. The mixture was stirred at room temperature for 3 h, then heated under reflux for 4 h. Excess BH₃ was hydrolyzed with CH₃OH at 0 °C. The resulting boron compound was transformed into the tetraamine by hydrolysis in a THF/H₂O mixture with NaOH. **2b** was extracted from the reaction mixture 3 times with CH₂Cl₂ (20 mL each). The combined organic phases were dried with Na₂SO₄. Removal of the solvent gave an oil, which was dissolved in hexane and filtered. Evaporation of the hexane gave **2b** as a colorless or yellowish air-sensitive oil. Yield 360 mg (81%). ¹H NMR (200 MHz, CDCl₃): δ = 7.52 (t, 1 H, H γ -C₅H₃N), 7.11 (d, 2 H, H β -C₅H₃N), 6.75–6.52 (m, 8 H, Ar-H C₆H₄), 4.37 (s, 4 H, NCH₂-C₅H₃N), 3.81 (s br, 4 H, NH), 2.79 [s, 4 H, NCH₂-C(CH₃)₃], 0.96 [s, 18 H, C(CH₃)₃] ppm. ¹³C NMR (50.3 MHz, CDCl₃): δ = 158.2 (C α -C₅H₃N), 138.0, 137.2, 137.0 [Ar-C_{ipso} for (NH)₂C₆H₄ and C γ -C₅H₃N], 119.7 (C β -C₅H₃N), 119.4, 118.9 [Ar-C_{meta} for (NH)₂C₆H₄], 112.1, 111.8 [Ar-C_{ortho} for (NH)₂C₆H₄], 56.1 (NCH₂-C₅H₃N), 49.7 [NCH₂-C(CH₃)₃], 31.4 [C(CH₃)₃], 27.8 [C(CH₃)₃] ppm. MS (EI, 70 eV): *m/z* (%) = 459 (100) [M]⁺.

Bis(germylenes) 3 and 4: The bis(germylenes) were prepared from GeCl₂·1,4-dioxane or Ge[N(SiMe₃)₂]₂ as described by us for related derivatives.^[11] Crystals for the X-ray analyses were grown by slow diffusion of hexane into a saturated solution of **4** in toluene or directly from an *n*-hexane solution of **3**.

Selected Spectroscopic Data for 3: Yield 80%. ¹H NMR (200 MHz, [D₈]toluene): δ = 7.14–7.00 (m, 12 H, Ar-H), 4.82 (s, 4 H, NCH₂-

C₆H₄), 3.85 [s, 4 H, NCH₂-C(CH₃)₃], 0.86 [s, 18 H, C(CH₃)₃] ppm. ¹³C NMR (50.3 MHz, [D₈]toluene): δ = 144.2, 142.2 (Ar-C_{ipso} GeN₂-C₆H₄), 140.6 (Ar-C_{ipso} NCH₂-C₆H₄), 129.2, 128.3, 127.3 (NCH₂-C₆H₄), 118.7, 118.1 (Ar-C_{meta} GeN₂-C₆H₄), 110.5, 110.3 (Ar-C_{ortho} GeN₂-C₆H₄), 56.8 (NCH₂-C₆H₄), 50.5 [NCH₂-C(CH₃)₃], 33.0 [C(CH₃)₃], 28.6 [C(CH₃)₃] ppm. MS (EI, 70 eV): *m/z* (%) = 600 (68) [M]⁺, 543 (91) [M - *t*Bu]⁺.

Selected Spectroscopic Data for 4: Yield 240 mg (64%). ¹H NMR (200 MHz, [D₈]toluene): δ = 7.02–6.59 (m, 11 H, Ar-H), 5.18 (s, 4 H, NCH₂-C₅H₃N), 3.77 [s, 4 H, NCH₂-C(CH₃)₃], 0.90 [s, 18 H, C(CH₃)₃] ppm. ¹³C NMR (50.3 MHz, [D₈]toluene): δ = 159.3 (C α -C₅H₃N), 144.0, 142.1 (Ar-C_{ipso} C₆H₄), 137.2 (C γ -C₅H₃N), 119.8 (C β -C₅H₃N), 118.6, 118.1 (Ar-C_{meta} C₆H₄), 110.4, 110.3 (Ar-C_{ortho} C₆H₄), 56.8 (NCH₂-C₅H₃N), 51.9 [NCH₂-C(CH₃)₃], 33.0 [C(CH₃)₃], 28.6 [C(CH₃)₃] ppm. MS (EI, 70 eV): *m/z* (%) = 601 (46) [M]⁺, 544 (100) [M - *t*Bu]⁺.

X-ray Diffraction Studies: Diffraction data for **3** and **4** were collected with a Bruker AXS APEX CCD diffractometer equipped with a rotation anode at 153(2) K using graphite-monochromated Mo-K α radiation (λ = 0.71073 Å). Diffraction data were collected over the full sphere and were corrected for absorption. The data reduction was performed with the Bruker SMART^[15] program package. The structures were solved with the SHELXS-97^[16] package using the heavy-atom method and were refined with SHELXL-97^[17] against $|F^2|$ using first isotropic and then anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added to the structure models in calculated positions. CCDC-641062 (**3**) and -641063 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data/request/cif.

Crystal Data for Bis(germylene) 3: C₃₀H₃₈Ge₂N₄, *M* = 599.82, triclinic, *P* $\bar{1}$, *Z* = 2, *a* = 9.4855(12), *b* = 9.8055(12), *c* = 15.744(2) Å, α = 85.590(3), β = 89.526(2), γ = 77.424(2)°, *V* = 1427.7(3) Å³, 14127 measured reflections, 6544 unique reflections (*R*_{int} = 0.0371), *R* = 0.0414, *wR* = 0.0905 for 4947 contributing reflections [*I* ≥ 2σ(*I*)], refinement against $|F^2|$ with anisotropic thermal parameters for all non-hydrogen atoms and hydrogen atoms in calculated positions.

Crystal Data for Bis(germylene) 4: C₂₉H₃₇Ge₂N₅, *M* = 600.82, triclinic, *P* $\bar{1}$, *Z* = 2, *a* = 9.690(2), *b* = 9.807(2), *c* = 14.792(3) Å, α = 91.743(4), β = 96.699(4), γ = 96.715(4)°, *V* = 1385.1(4) Å³, 11194 measured reflections, 4890 unique reflections (*R*_{int} = 0.0392), *R* = 0.0449, *wR* = 0.1143 for 3839 contributing reflections [*I* ≥ 2σ(*I*)], refinement against $|F^2|$ with anisotropic thermal parameters for all non-hydrogen atoms and hydrogen atoms in calculated positions.

Acknowledgments

The authors thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support. A. V. Z. thanks the NRW Graduate School of Chemistry, Münster for a predoctoral grant.

- [1] a) Recent short review on NHC ligands: F. E. Hahn, *Angew. Chem.* **2006**, *118*, 1374–1378; *Angew. Chem. Int. Ed.* **2006**, *45*, 1348–1352; b) W. A. Herrmann, *Angew. Chem.* **2002**, *114*, 1342–1363; *Angew. Chem. Int. Ed.* **2002**, *41*, 1290–1309; c) B. Bourissou, O. Guerret, F. P. Gabbaï, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39–91.
- [2] a) W. A. Herrmann, M. Elison, J. Fischer, C. Köcher, G. R. J. Artus, *Angew. Chem.* **1995**, *107*, 2602–2605; *Angew. Chem. Int.*

- Ed. Engl.* **1995**, *34*, 2371–2374; b) K. Öfele, W. A. Herrmann, D. Mihailios, M. Elison, E. Herdtweck, T. Priermeier, P. Kiprof, *J. Organomet. Chem.* **1995**, *498*, 1–14; c) R. E. Douthwaite, D. Haüssinger, M. L. H. Green, P. J. Silcock, P. D. Gomes, A. M. Martins, A. A. Danopoulos, *Organometallics* **1999**, *18*, 4584–4590; d) J. Schwarz, V. P. W. Böhm, M. J. Gardiner, M. Grosche, W. A. Herrmann, W. Hieringer, G. Raudaschl-Sieber, *Chem. Eur. J.* **2000**, *6*, 1773–1780; e) M. V. Baker, B. W. Skelton, A. H. White, C. C. Williams, *J. Chem. Soc., Dalton Trans.* **2001**, 111–120; f) M. Muehlhofer, T. Strassner, W. A. Herrmann, *Angew. Chem.* **2002**, *114*, 1817–1819; *Angew. Chem. Int. Ed.* **2002**, *41*, 1745–1747; g) M. Albrecht, R. H. Crabtree, J. Mata, E. Peris, *Chem. Commun.* **2002**, 32–33; h) L. G. Bonnet, R. E. Douthwaite, R. Hodgson, *Organometallics* **2003**, *22*, 4384–4386; i) J. A. Mata, A. R. Chianese, J. R. Miecznikowski, M. Poyatos, E. Peris, J. W. Faller, R. H. Crabtree, *Organometallics* **2004**, *23*, 1253–1263.
- [3] a) F. E. Hahn, M. Foth, *J. Organomet. Chem.* **1999**, *585*, 241–245; b) F. E. Hahn, L. Wittenbecher, D. Le Van, W. Fröhlich, *Angew. Chem.* **2000**, *112*, 551–554; *Angew. Chem. Int. Ed.* **2000**, *39*, 541–544; c) F. E. Hahn, T. von Fehren, T. Lügger, *Inorg. Chim. Acta* **2005**, *358*, 4137–4144; d) D. M. Khamarov, A. J. Boydston, C. W. Bielawski, *Angew. Chem.* **2006**, *118*, 6332–6335; *Angew. Chem. Int. Ed.* **2006**, *45*, 6186–6189.
- [4] a) Review: D. Pugh, A. A. Danopoulos, *Coord. Chem. Rev.* **2007**, *251*, 610–641; b) F. E. Hahn, M. C. Jahnke, T. Pape, *Organometallics* **2006**, *25*, 5927–5936; c) F. E. Hahn, M. C. Jahnke, T. Pape, *Organometallics* **2007**, *26*, 150–154.
- [5] a) U. Kernbach, M. Ramm, P. Luger, W. P. Fehlhammer, *Angew. Chem.* **1996**, *108*, 333–335; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 310–312; b) review: X. Hu, K. Meyer, *J. Organomet. Chem.* **2005**, *690*, 5474–5484.
- [6] F. E. Hahn, V. Langenhahn, T. Lügger, T. Pape, D. Le Van, *Angew. Chem.* **2005**, *117*, 3825–3829; *Angew. Chem. Int. Ed.* **2005**, *44*, 3759–3763.
- [7] O. Kaufhold, A. Stasch, P. G. Edwards, F. E. Hahn, *Chem. Commun.*, DOI: 10.1039/b617033a.
- [8] a) B. Gehrhus, M. F. Lappert, J. Heinicke, R. Boese, D. Bläser, *J. Chem. Soc., Chem. Commun.* **1995**, 1931–1932; b) B. Gehrhus, P. B. Hitchcock, M. F. Lappert, J. Heinicke, R. Boese, D. Bläser, *J. Organomet. Chem.* **1996**, *521*, 211–220; c) B. Gehrhus, P. B. Hitchcock, M. F. Lappert, *J. Chem. Soc., Dalton Trans.* **2000**, 3094–3099; d) B. Gehrhus, P. B. Hitchcock, M. F. Lappert, *Z. Anorg. Allg. Chem.* **2005**, *631*, 1383–1386; e) B. Gehrhus, M. F. Lappert, *J. Organomet. Chem.* **2001**, *617*–618, 209–223; f) M. Haaf, T. A. Schmedake, R. West, *Acc. Chem. Res.* **2000**, *33*, 704–714; g) N. J. Hill, R. West, *J. Organomet. Chem.* **2004**, *689*, 4165–4183.
- [9] a) J. Pfeiffer, W. Maringgele, M. Noltemeyer, A. Meller, *Chem. Ber.* **1989**, *122*, 245–252; b) W. A. Herrmann, M. Denk, J. Behm, W. Scherer, F.-R. Klingan, H. Bock, B. Solouki, M. Wagner, *Angew. Chem.* **1992**, *104*, 1489–1492; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1485–1488; c) J. Heinicke, A. Oprea, M. K. Kindermann, T. Karpati, L. Nyulászi, T. Veszprémi, *Chem. Eur. J.* **1998**, *4*, 541–545; d) P. Bazinet, G. P. A. Yap, D. S. Richeson, *J. Am. Chem. Soc.* **2001**, *123*, 11162–11167; e) O. Kühl, P. Lönnecke, J. Heinicke, *Polyhedron* **2001**, *20*, 2215–2222.
- [10] a) H. Braunschweig, B. Gehrhus, P. B. Hitchcock, M. F. Lappert, *Z. Anorg. Allg. Chem.* **1995**, *621*, 1922–1928; b) F. E. Hahn, L. Wittenbecher, M. Kühn, T. Lügger, R. Fröhlich, *J. Organomet. Chem.* **2001**, *617*–618, 629–634.
- [11] A. V. Zabula, F. E. Hahn, T. Pape, A. Hepp, *Organometallics* **2007**, *26*, 1972–1980.
- [12] a) F. E. Hahn, L. Wittenbecher, R. Boese, D. Bläser, *Chem. Eur. J.* **1999**, *5*, 1931–1935; b) F. E. Hahn, L. Wittenbecher, D. Le Van, R. Fröhlich, *Angew. Chem.* **2000**, *112*, 551–554; *Angew. Chem. Int. Ed.* **2000**, *39*, 1541–1544.
- [13] L. A. Leites, A. V. Zabula, S. S. Bukalov, A. A. Korlyukov, P. S. Koroteev, O. S. Maslennikova, M. P. Egorov, O. M. Nefedov, *J. Mol. Struct.* **2005**, *750*, 116–122.
- [14] D. H. Harris, M. F. Lappert, *J. Chem. Soc., Chem. Commun.* **1974**, 895–896.
- [15] SMART: Bruker AXS, **2000**.
- [16] SHELXS-97: G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467.
- [17] SHELXL-97: G. M. Sheldrick, University of Göttingen, **1997**.

Received: March 15, 2007
Published Online: May 3, 2007