DOI: 10.1002/ejic.200800866

Mono- and Bidentate Benzannulated N-Heterocyclic Germylenes, Stannylenes and Plumbylenes

Alexander V. Zabula[a] and F. Ekkehardt Hahn*[a]

Keywords: Carbene analogues / Germylenes / Stannylenes / Plumbylenes / Complexes

The current state of the chemistry of mono- and bidentate N-heterocyclic germylenes, stannylenes, plumbylenes, and related compounds is reviewed with special emphasis placed on benzannulated derivatives. The preparation, electronic structure, aggregation behaviour, and the coordination chemistry of the free benzannulated carbene analogues and their adducts with Lewis bases and complexes with transition metals are discussed.

Introduction

The resurge of interest in the organometallic chemistry of the heavier analogues of N-heterocyclic carbenes (NHCs) has been triggered by the isolation of the first stable N-heterocyclic carbene[1] derived from an imidazolium salt by Arduengo III et al. in 1991 and by the subsequent studies on stable carbenes and their complexes.[2] The first reports on the preparation of germanium, tin and lead analogues of NHCs appeared, however, some time before 1991. A great variety of N-heterocyclic silylenes,[3] germylenes[4] and stannylenes derived from different heterocycles and stable at ambient temperature has been prepared up to now. The interest in these compounds is based on their interesting electronic structures and chemical properties and on their capability to act as spectator ligands in catalytically active metal complexes in a manner related to N-heterocyclic carbenes.[5]

In this account we review mono- and polydentate N-heterocyclic germylenes, stannylenes and plumbylenes with the main focus on their aggregation behaviour and coordination chemistry. We focus particularly on the recently emerged benzannulated germylenes, stannylenes and plumbylenes (Scheme 1), which are the heavier group 14 analogues of benzannulated N-heterocyclic carbenes.

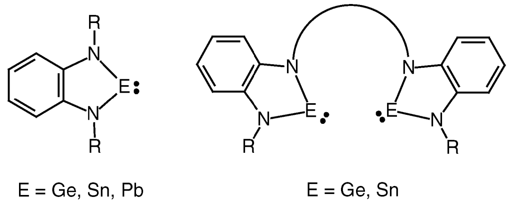
Until very recently our knowledge about bis- or polygermylenes and -stannylenes featuring cyclic or noncyclic germylene or stannylene donor groups was limited to just a few examples, and even fewer of these could act as a chelating ligands. This is in contrast to the situation found for dicarbene ligands,[2a] where bis(carbene) chelate ligands featuring two benzimidazolin-2-ylidene donor groups[6] are

Alexander V. Zabula was born in Batumi, USSR in 1981. He studied chemistry at the Higher Chemical College of the Russian Academy of Sciences, Moscow, where he completed his diploma thesis in 2004 under the supervision of Prof. Dr. L. A. Leites and Dr. S. S. Bukalov (Nesmeyanov Institute of Organoelement Compounds, RAS). He joined the research group of Prof. Hahn in 2004 as a doctoral student funded by a scholarship of the NRW Graduate School of Chemistry, Münster. He prepared and investigated bidentate N-heterocyclic bis(germylenes) and bis(stannylenes) as well as their complexes. In 2007 he graduated with a Dr. rer. nat. degree.

F. Ekkehardt Hahn was born in Jena, Germany in 1955. He was educated at the Technische Universität Berlin and the University of Oklahoma where he earned academic degrees from the Departments of Chemistry in 1982 (MS, University of Oklahoma), 1983 (Dipl.-Chem., Technische Universität Berlin) and 1985 (Dr. rer. nat. with Prof. H. Schumann, Technische Universität Berlin). He continued his education as a postdoc in the laboratory of Prof. K. N. Raymond at the University of California, Berkeley, from 1985 to 1988. In 1988 he returned to the Technische Universität Berlin where he completed his Habilitation in 1990. He became an Associate Professor at the Freie Universität Berlin from 1992 to 1998. In 1998 he accepted the position as chair of Inorganic Chemistry at the University of Münster. Hahn's primary research interests are the organometallic chemistry of multidentate isocyanides, carbenes and their analogues and the coordination chemistry of poly(dithiolato)ligands.

---

[a] Institut für Anorganische und Analytische Chemie der Westfälischen Wilhelms-Universität Münster,
Correnssstrasse 36, 48149 Münster, Germany
Fax: +49-251-833-3108
E-mail: fehahn@uni-muenster.de

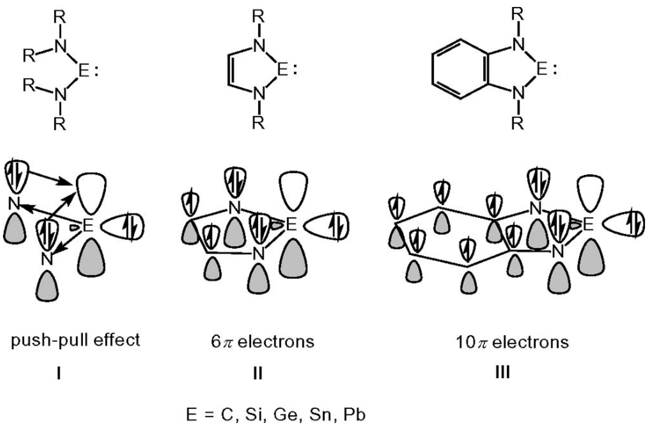


Scheme 1. Mono- and bidentate benzannulated N-heterocyclic germylenes, stannylenes and plumbylenes.

known in addition to complexes with an [11]ane-P_2C^{NHC} ligand[7] or a cyclic tetrakis(benzimidazolin-2-ylidene) ligand.[8] The corresponding knowledge about N-heterocyclic polysilylenes is limited to just one example of a benzannulated bis(silylene) which cannot act as a chelating ligand.[9]

Electronic Structure

Generally, heavier analogues of carbenes are nonlinear, divalent singlet species of type ER_2 (E = Si, Ge, Sn, Pb). The divalent atom E possesses an unshared electron pair and a vacant p-orbital. Different heteroatoms attached to the group 14 atoms (E) significantly stabilize the generally reactive divalent state. The R_2N derivatives of divalent germanium, tin and lead (type **I**, Scheme 2) developed by Lappert et al. exhibit a remarkable stability when compared to the corresponding dialkyl derivatives. They are stable at room temperature under anaerobic conditions, and some derivatives can even be distilled in vacuo.[10]

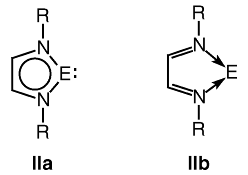


Scheme 2. Electronic structures of R_2N-substituted and N-heterocyclic carbenes and their heavier analogues.

Apart from the steric protection of E by bulky substituents at the nitrogen atoms (e.g. $SiMe_3$), the stabilization of the divalent state of E is caused by a reduction of the σ-electron density at E by the more electronegative nitrogen atoms (inductive effect) and by π-electron donation of the unshared electron pairs at the nitrogen atoms to E (mesomeric effect).[2a,11] The energy gain resulting from this type of stabilization has been calculated by DFT methods to be 36 kcal/mol for $Si(NH_2)_2$ relative to SiH_2.[12] The calculated rotation barriers about Ge–N bonds in diaminogermylene $Ge(NH_2)_2$ are 10.2 and 21.7 kcal/mol, and these values are partially suitable for the description of the energy of the N–Ge π-interaction.[13]

Diaminocarbenes and their analogues can gain additional stability from the effects associated with cyclization. For example, incorporation of the divalent E atom into an unsaturated imidazole or benzimidazole ring systems (Scheme 2, types **II** and **III**, respectively) provides an additional thermodynamic stabilization. Various theoretical[12–14] and experimental[15] studies, carried out for non-annulated rings of type **II** containing a divalent atom E, demonstrated cyclic delocalization of the 6 π-electrons (aromaticity). This effect plays an important but not a crucial role in the stabilization of these heterocycles. This conclusion is also supported by the isolation of the saturated imidazolidin-2-ylidenes.[2a] Replacement of the unsaturated –CH=CH– moiety in **II** with a $–CH_2CH_2–$ group leads to a destabilization of 27.4 kcal/mol for E = Si and 32.1 kcal/mol for E = Ge.[14a]

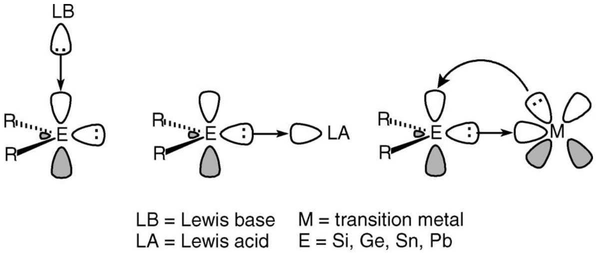
For the ring system **II** an extreme chelate form **IIb** containing a formally zero-valent atom E coordinated by a diimine ligand can be taken into account to describe the bonding in these derivatives (Scheme 3).[14c,15a] The contribution of this resonance form increases from silicon to lead, thereby destabilizing the unsaturated heterocycles of type **II**. In contrast to its lighter analogues, the tin-containing derivatives of Arduengo's carbene decompose at 60 °C[16] to yield diazadienes and Sn^0. Metathesis with exchange of the tin atom has been observed in the reaction of tin-containing heterocycles of type **II** and diazadienes in solution.[16,17] The lead-containing heterocycle of type **II** is still unknown, whereas plumbylenes derived from a saturated N-heterocyclic five-membered ring have recently been prepared (vide infra).



Scheme 3. Aromatic (**IIa**) and E^0-chelating (**IIb**) resonance forms for the heavier analogues of imidazolin-2-ylidenes.

The influence of benzo, naphtho and pyrido annulation on the stability and properties of carbenes and their heavier analogues has been discussed by Heinicke et al.[18,19] It has been concluded that benzo and naphtho annulation have a stabilizing effect. This is in contrast with the situation found for the pyrido-annulated carbenes and their heavier analogues where the unsymmetrical 10 π-electron system leads to a decreased kinetic stability, whereas the thermodynamic stability remains comparable to that of the benzannulated compounds of type **III**.[20] Pyrido[*b*]-annulated analogues of carbenes with a nodal plane through the pyridine nitrogen atom and a rather symmetric π-charge density in the HOMO are less destabilized. No examples of pyrido[*c*]-annulated carbene analogues have been isolated to date due to their kinetic instability. Orbital correlations based on PE spectroscopic data show an inverse order of n- and π-orbitals for the NHCs with respect to their heavier analogues, which has been used to explain the differences in reactivity observed in orbital-controlled reactions of pyrido-annulated N-heterocyclic compounds containing a divalent group 14 atom.[21]

Based on their electronic structure, the heavier analogues of carbene are capable of forming complexes with Lewis acids, Lewis bases and transition metals[22] (Scheme 4). In the latter case the ER_2 ligands are potential σ-donor and π-acceptor ligands. Theoretical investigations carried out for complexes of the analogues of NHC showed that π-back-donation is weak but not negligible.[23] Recent investigations performed on the complexes of benzannulated bis(carbenes), bis(germylenes) and bis(stannylenes) demonstrated that these ligands can also function as π-donors.[24]



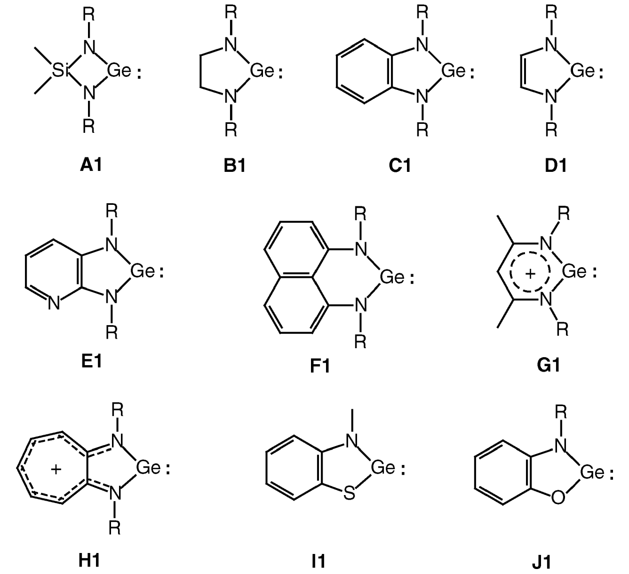
Scheme 4. Potential bonding interactions of carbene analogues with Lewis bases, Lewis acids and transition metals.

Annulation of NHGes has been shown to lead to an increased π-acceptor strength of the NHGe ligands.[25] Correlation of the molecular electrostatic potential (MEP) to the values of the Tolman Electronic Parameter (TEP)[26] indicated that the π-acceptor strength of NHGe ligands is similar to that observed for trialkylphosphanes and trialkyl phosphites. The N–E–N π-donor interaction within the heterocycle becomes stronger when the ligand coordinates to a metal center.[15]

Germylenes

Monodentate N-Heterocyclic Germylenes

The first N-heterocyclic germylene **A1** (Scheme 5) was synthesized by Veith et al. in 1982.[27] Saturated germylenes of type **B1** and their chemical properties were investigated by Meller et al.[28] Germylene **B1** reacts with its silicon analogue to give a new germylene where the N-heterocyclic silylene moiety has inserted into one Ge–N bond. The resulting *N*,*Si*-substituted germylene dimerizes with formation of a digermene.[29] The isolation of the first benzannulated germylene of type **C1** and its reactivity towards azides were described in 1989.[30] The preparation of **C1** predated the isolation of a related benzannulated N-heterocyclic carbene in 1999 by 10 years.[31] Later, the preparation of the germanium analogue of Arduengo's carbene – germylene **D1** – as well as the molecular structures of **B1** and the complex [Ni(**B1**)$_2$(CO)$_2$] were reported by Herrmann et al.[32] The molybdenum complex of the unsaturated N-heterocyclic germylene **D1**, *fac*-[Mo(**D1**)$_3$(CO)$_3$], was prepared by the reaction of **D1** with [Mo(CO)$_4$(EtCN)$_2$].[33] Germylenes **B1** and **D1** undergo decomposition with the formation of [Ge]$_\infty$ or [Ge/GeH]$_\infty$ layers upon heating above 900 °C.[32] The thermal decomposition of the N-heterocyclic germylenes **B1** and **D1** makes them interesting substrates for CVD processes.[34]

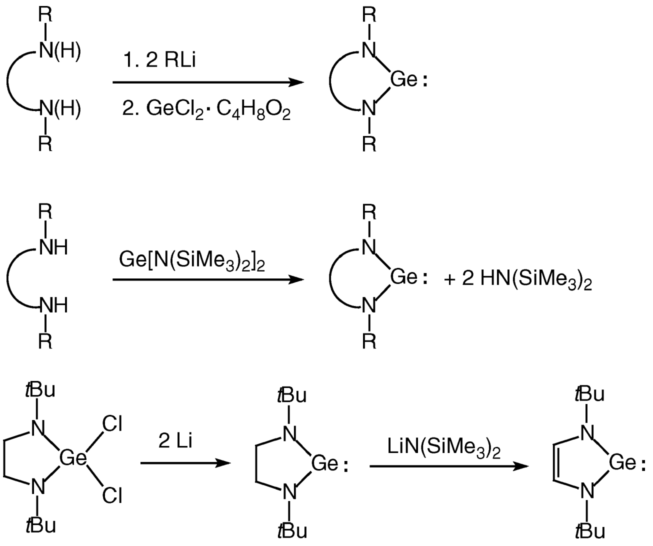


Scheme 5. Monodentate N-heterocyclic germylenes.

Pyrido[*b*]- (**E1**) and naphtho-annulated N-heterocyclic germylenes were prepared by Heinicke et al.[18,19] Germylene **F1**, derived from 1,8-naphthalene and its homoleptic tetrahedral Ni^0 complex [Ni(**F1**)$_4$] have also been described.[35] The cationic germylene **G1**[36] was prepared by the addition of B(C$_6$F$_5$)$_3$ to Ge(Cl)(dipp$_2$nacnac) in water. The C4-methylene group of **G1** can be deprotonated to give the germylene derivative with a betaine structure and reactivity.[37] The chemical properties of the cationic aminotroponiminate derivatives of germanium(II) **H1** and of its chloro[38] and azido derivatives[39a,39b] have been investigated in addition to complexes of this germylene with silver(I).[39b–39d] The benzannulated mixed N,S-heterocyclic germylene **I1** is thermally stable as its S,S-heterocyclic analogue.[30b] The N,O-stabilized germylenes of type **J1** have been prepared recently.[40] Germanium(II) bis(amidinates)[41] and Ge^{II} complexes of tetradentate dianionic N$_4$ macrocycles[42] represent more unusual examples of N-heterocyclic germylenes. The germanium atoms in these derivatives exhibit a pyramidal tetracoordination by four nitrogen atoms.

A general route for the preparation of N-heterocyclic germylenes comprises the dilithiation of an appropriate diamine or diimine followed by the reaction or the organolithium compound with GeCl$_2$·1,4-dioxane (Scheme 6). Alternatively, N-heterocyclic germylenes have been obtained by the transamination reaction between a diamine and Ge[N(SiMe$_3$)$_2$]$_2$. Finally, the reductive dehalogenation of

Ge^{IV} compounds has been applied for the preparation of the saturated germylene **B1**, which can be transformed into the unsaturated germylene **D1** by dehydrogenation of the heterocycle.[32]



Scheme 6. Methods for the preparation of monodentate N-heterocyclic germylenes.

The benzannulated germylene of type **C1** with N,N'-$(SiMe_3)_2$ substituents was found to be monomeric in the solid state.[30a] Other benzannulated germylenes like **1** (R = CH_2tBu) or the pyrido-annulated germylene **2** were described as monomers in the solid state.[18] A close inspection of the interatomic distances between the germanium atom and the carbon atoms of the benzene rings of a parallel oriented adjacent molecule suggests the presence of weak intermolecular $[\eta^4\text{-}(C_6H_4)\cdots Ge]_\infty$ and $[\eta^2\text{-}(C_5H_3N)\cdots Ge]_\infty$ interactions (Figure 1). The intermolecular Ge···C separations fall in the range of 3.281–3.647 Å for **1** and 3.308 and 3.335 Å for **2**.

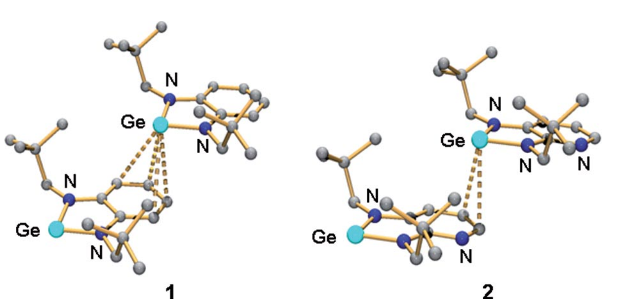
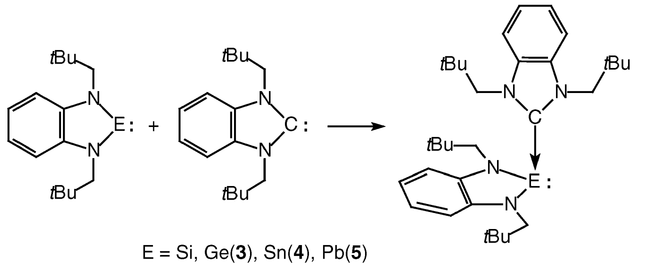


Figure 1. Molecular structures and packing in the lattice of the benzannulated germylene **1** and the pyrido-annulated germylene **2**.

Germylene **1** reacts with its carbon NHC analogue with formation of carbene–germylene adduct **3**, thereby acting as a Lewis acid (Scheme 7).[43] Formation of similar adducts between the benzannulated N-heterocyclic carbene and the benzannulated silylene, stannylene (**4**) and plumbylene (**5**) has also been reported,[43] demonstrating the facile formation of coordinative E–C bonds (Scheme 7).



Scheme 7. Adducts of a benzannulated carbene with its heavier analogues.

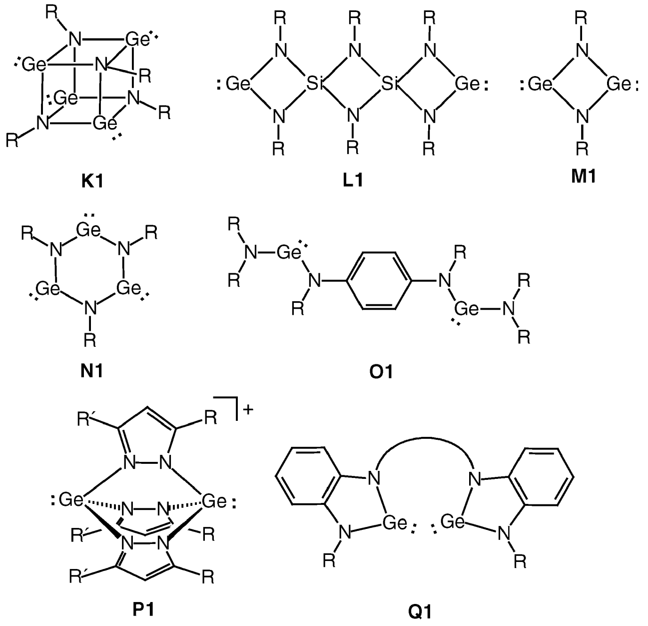
Benzannulated N-heterocyclic germylenes and acyclic diaminogermylenes react with *p*-benzoquinones in a 2:1 ratio to give periodic copolymers with $(O\text{–}Ge\text{–}Ge\text{–}O)_n$ or $(O\text{–}Ge\text{–}O)_n$ cores in high yield.[44] Germylene **C1** (R = $SiMe_3$) was also used for the polymerization of cyclic α,β-unsaturated ketones to give the germanium-containing poly(germanium enolate).[45]

Bis- and Polydentate Germylenes

Some polydentate *N*-substituted bis- or polygermylenes are known (Scheme 8). The cubane-type tetrakis(germylene) **K1** and some cage compounds containing Ge^{II} were prepared by the oligomerization of Ge=N–R species.[27,46] Bis(germylene) **L1** with two spiro-silicon atoms was the first bis(germylene) with two NHGe moieties.[47] The cyclic tris(germylene) **M1**[48] and the germanazene **N1**[49] contain planar Ge_2N_2 or Ge_3N_3 cores in the solid state. The acyclic bis(germylene) **O1** was prepared by the reaction of R_2NGeCl with an organolithium compound by Kobayashi et al.[50] and independently by Braunschweig et al.[51] Cage compounds of type **P1** with three or four pyrazolyl ligands have been described.[52]

Bis(germylenes) of type **Q1**, in which two benzimidazolin-2-germylene moieties are linked by different bridging groups through the ring nitrogen atoms, have recently been prepared.[53,54] Compared to the polygermylenes **K1**–**P1** only the compounds of type **Q1** possess a backbone flexible enough to allow the bis(germylene) to act in a chelating fashion. Bis(germylenes) with sterically demanding substituents at the nitrogen atoms (R = CH_2tBu) have been obtained by the reaction between N,N',N'',N'''-tetralithiated tetraamines and $GeCl_2$·1,4-dioxane in yields of up to 86%. $Ge[N(SiMe_3)_2]_2$ was used as a germanium(II) starting material for the preparation of bis(germylenes) with the sterically non-demanding *N*-substituents (R = Et) or a lutidine bridging unit.

Bis(germylenes) of type **Q1** exhibit various aggregation modes in the solid state depending on the N,N'-substituents. Compound **6** with a $–(CH_2)_4–$ linking unit crystallizes as monomers (Figure 2).[53a] The bis(germylene) **7** with a longer $–(CH_2)_5–$ bridge exhibits a weak intermolecular



Scheme 8. Bis- and polydentate *N*-substituted germylenes.

Ge···Ge [3.577(2) Å] interaction leading to a polymeric arrangement of bis(germylene) molecules in the solid state (Figure 2).[53a]

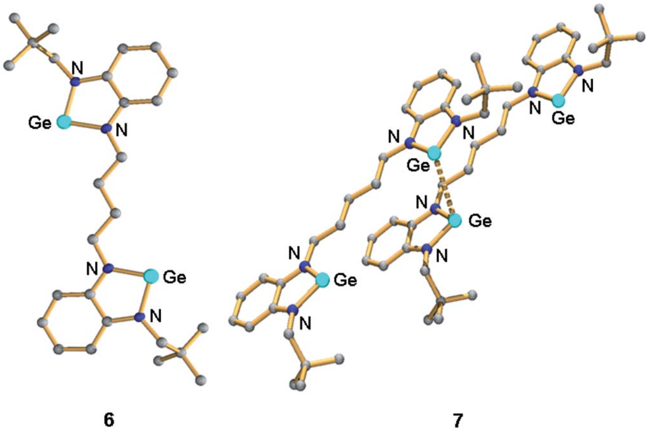


Figure 2. Molecular structures of the bis(germylenes) **6** and **7**.

An intermolecular interaction between the vacant p-orbital at the Ge^{II} atom and the aromatic benzene π-system of a parallel oriented adjacent molecule was observed for the bis(germylene) **8** with a 1,2-$(CH_2)_2C_6H_4$ linking unit (Figure 3).[53a] The interatomic distances Ge···C_6 fall in the range 3.199(3)–4.036(2) Å. This interaction resembles the one found for germylene **1** (Figure 1) and leads to a polymeric arrangement of the molecules **8** in the solid state. In contrast to the situation found for **8** the bis(germylene) **9** with a 1,3-$(CH_2)_2C_6H_4$ linker exists as a monomer in the solid state (Figure 3).[53b]

A different mode of aggregation was observed for bis(germylenes) with sterically non-demanding *N*-CH_2CH_3 substituents. They crystallize as dimers[53a] or polymers[54] with formation of weak intermolecular Ge···N contacts. The intermolecular Ge···N separations measure 3.533(2) and 3.532(2) Å in the bimolecular aggregate of bis(germylene) **10** (Figure 4). These values are indicative of weak donor–acceptor interactions caused by the donation of free electron pairs at the nitrogen atoms to the vacant p-orbitals at the germanium atoms.

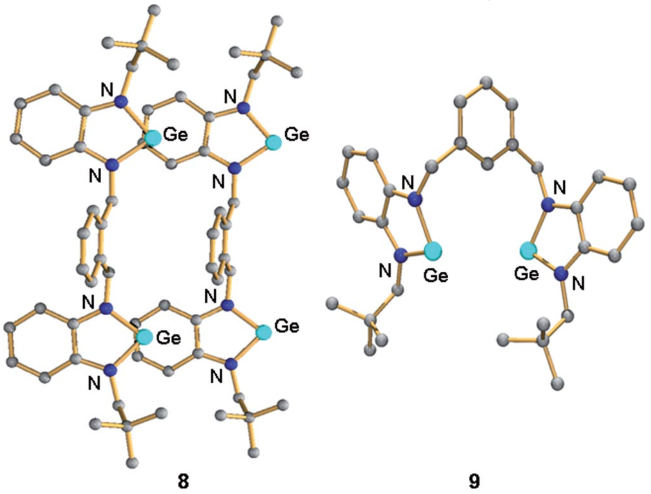


Figure 3. Molecular structures of bis(germylenes) **8** and **9**.

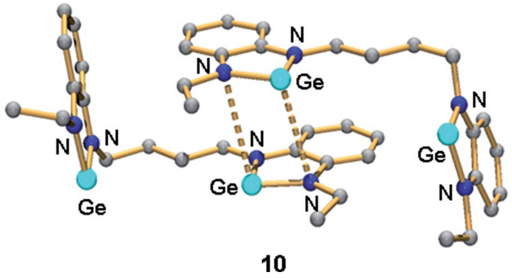
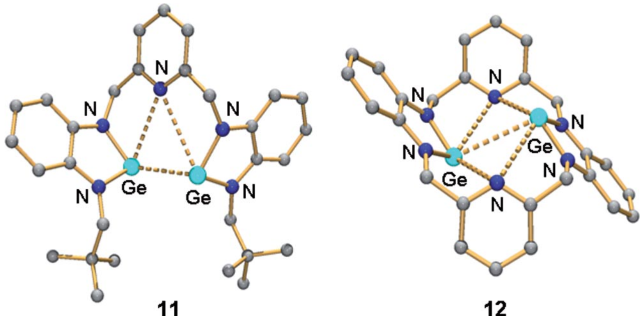


Figure 4. Molecular structure of the bis(germylene) **10**.

Bis(germylenes) **11**[53b] and **12**[55] exhibiting a Ge–N–Ge pincer topology have been prepared. X-ray diffraction analysis for bis(germylene) **11** with the lutidine linker and *N*-CH_2*t*Bu substituents revealed an unprecedented intramolecular Ge···Ge interaction [3.041(5) Å] and Ge···$N_{lutidine}$ interactions [3.386(7) and 3.154(7) Å]. Macrocyclic bis(germylene) **12** with two lutidine bridging units exhibits similar Ge···Ge [3.337(3) Å] and Ge···N [3.223(1) and 3.250(1) Å] interactions (Figure 5). Although the Ge···Ge interactions are not particularly strong in both **11** and **12** it should be noted that the geometry of N_2Ge···GeN_2 fragments is typical for the *trans*-bent arrangement, previously described for the heavy alkene analogues of type $R_2E{=}ER_2$.[56]

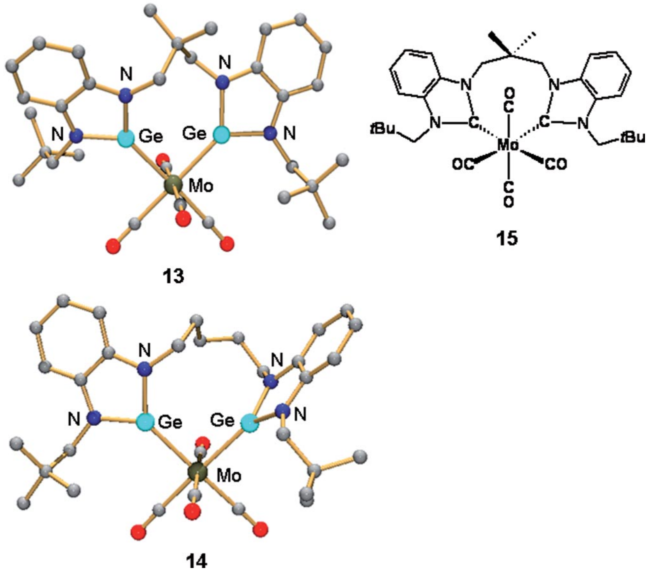
It has been demonstrated that the benzannulated bis(germylenes) of type **Q1** are capable to coordinate to metal centers in a chelating fashion. The complexes **13**[53a] and **14**[54] with the tetracarbonylmolybdenum fragment have been isolated and characterized by X-ray diffraction. The complexes were obtained by the reaction of the bis(germylenes) with $[Mo(CO)_4(nbd)]$ (nbd = norbornadiene). The molecular structure of complex **13** (Figure 6) resembles that of the related bis(carbene) complex **15**.[6b] The Ge–Mo bonds in **13**



11 **12**

Figure 5. Molecular structures of the bis(germylenes) **11** and **12**.

[2.5204(6) and 2.5189(6) Å] are longer than the $C_{carbene}$–Mo bonds in **15** [2.324(3) Å]. This expansion of about 0.2 Å is, however, much smaller than the lengthening of the intracyclic N–E bond lengths of about 0.4 Å for the transition E = C → E = Ge. The ^1H NMR spectrum at low temperature shows that the methylene protons of **13** become diastereotopic upon complex formation due to a restricted rotation about the N–CH_2 bonds.[53a] Vibration spectroscopy and X-ray diffraction analysis showed the presence of two conformers of **14** in the solid state. These conformers significantly differ from each other by the orientation of the germylene moieties.[54] The geometry of the bridging –$(CH_2)_5$– unit in **14** is strongly distorted compared to the all-*trans* arrangement found for the free bis(germylene) **7** (Figure 2).



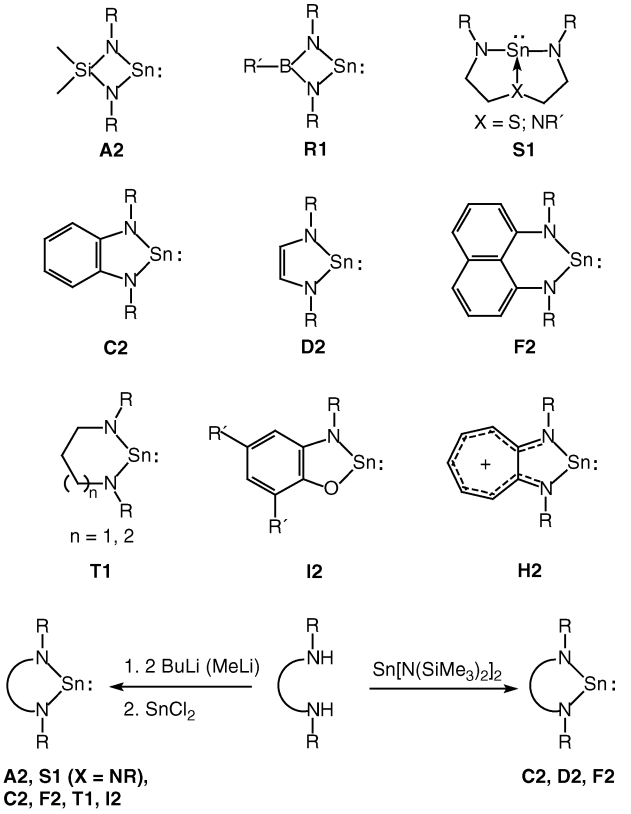
13 **15** **14**

Figure 6. Molecular structures of complex **13** and one of the conformers of **14** and schematic drawing of **15**.

Stannylenes

Monodentate Stannylenes

The tin analogues of germylenes **A1** – stannylenes **A2** (Scheme 9) – were the first representatives for N-heterocyclic stannylenes (NHSn). They were prepared first in 1975 by Veith.[57] Stannylenes of type **A2** are monomeric or dimerize in solution or in the solid state depending on the substituents at the nitrogen atom.[58] They coordinate to transition metals with formation of homo- and heteroleptic complexes.[59] The molecular structure and the dynamic behaviour of the related diazastannaboretine **R1** were investigated later.[60] Compound **R1** was prepared by the cyclization of $Sn[N(R)(BR'_2)]_2$ with elimination of BR'_3. An X-ray diffraction study revealed the formation of bimolecular aggregates of stannylene **R1** built from three four-membered rings and exhibiting intermolecular Sn···N and N···B interactions.

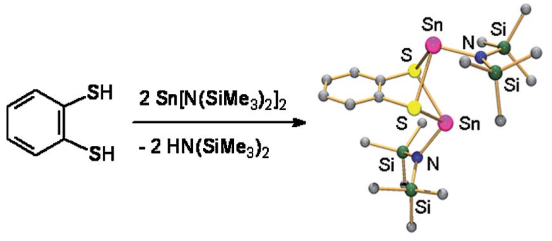


Scheme 9. N-heterocyclic stannylenes and their preparation.

Multinuclear NMR, Mössbauer and X-ray diffraction investigations on base-stabilized cyclic stannylenes of type **S1** with an intramolecular Sn···S or Sn···N interaction showed these molecules to be monomeric in the solid state and in solution.[61] While the first NHSn compounds of type **C2** with the tin atom being part of a conjugated π-system were prepared and unambiguously characterized in 1995 by Braunschweig et al.,[62] stannylenes of types **C2** and **F2** were first mentioned in the literature as early as 1974.[63] Structural and spectroscopic investigations have been carried out for symmetrically and unsymmetrically substituted stannylenes of type **C2** by using various alkyl- and donor-functionalized *N*,*N*′-substituents.[64] The tin analogue of Arduengo's carbene **D2** has recently been isolated.[16] It undergoes some unusual chemical reactions such as the reaction with diazadienes, which proceeds under exchange of the tin atom between the nitrogen ligands.[17] Stannylenes

F2 can act as Lewis acids coordinating a dialkylstannylene, which acts as a Lewis base.[65] The free stannylenes of type **F2** are not planar but exhibit a tin atom strongly deviated from the plane of the 1,8-naphthalenediyl moiety.[66] For stannylene **F2** with R = *i*Pr a one-dimensional head-to-tail chain structure with short intermolecular Sn···C_6(aryl) interaction was observed in the solid state.[66a] Saturated NHSn compounds of type **T1** possessing six- or seven-membered heterocycles exhibit a monomer/dimer equilibrium in solution.[67] Stannylene **T1** with the seven-membered heterocycle was observed as a dimer with intermolecular Sn···N contacts in the solid state by X-ray diffraction analysis. In addition, stannylenes of type **T1** undergo heterocumulene metathesis with *tert*-butyl isocyanates to produce α,ω-bis(carbodiimides). The *N*,*O*-stabilized cyclic stannylene **I2** has recently been prepared.[68] Cationic NHSn compounds **H2** containing a 10π-electron system feature a planar heterobicyclic C_7N_2Sn ring. They act as Lewis acids towards suitable donor ligands.[39,69] The majority of the known N-heterocyclic stannylenes have been prepared by either of two general methods: (i) the reaction of lithiated diamines with $SnCl_2$ or by (ii) the transamination reaction between a suitable diamine and $Sn[N(SiMe_3)_2]_2$ (Scheme 9).

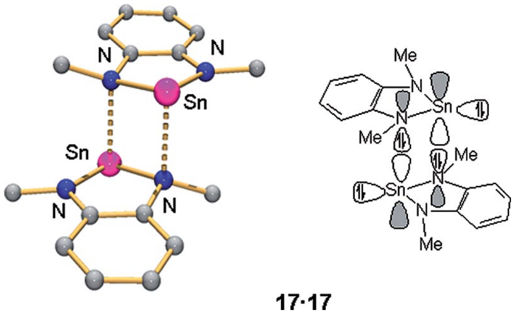
It has been proposed that benzannulated N-heterocyclic stannylenes of type **C2** are formed in a trimolecular reaction between a suitably *N*,*N*′-substituted *o*-phenylenediamine and 2 equiv. of $Sn[N(SiMe_3)_2]_2$. The distannylene 1,2-$[(Me_3Si)_2NSnNR]_2C_6H_4$ has been postulated as an intermediate in this reaction which upon rearrangement gives the N-heterocyclic stannylene and 1 equiv. of $Sn[N(SiMe_3)_2]_2$.[62] We have isolated and characterized the related bis(stannylene) **16**, which was obtained in the reaction of *ortho*-benzodithiol instead of *o*-phenylenediamine (Scheme 10).[70] The X-ray diffraction analysis with single crystals of **16** revealed the presence of two three-coordinate tin(II) atoms stabilized by Sn–N and Sn–S interactions confirming the trimolecular nature of the reaction.



16

Scheme 10. Preparation and molecular structure of stannylene **16**.

The *N*,*N*′-$(CH_3)_2$ substituted benzannulated stannylene **17** forms a dimer in the solid state, which exhibits strong intermolecular interactions {distance Sn···N [2.361(2) Å] (Figure 7)}.[64] This behaviour is in contrast to the situation found for its carbene analogue, which exists as dimer with a *trans*-bent C=C double bond. We take this difference as an indication for an enhanced Lewis acidity of tin(II) compared to the carbon(II) atom. A related but much weaker Ge···N interaction was found for bis(germylene) **10** (Figure 4). Only one signal was observed for the methylene protons of **17** in the ^1H NMR spectrum which is consistent with a fast exchange of the stannylene moieties of the dimer or dissociation of the dimer in solution.



17·17

Figure 7. Molecular structure and schematic representation of the bonding situation in the dimolecular aggregate **17·17**.

In contrast to the situation found for **17**, stannylene **18** with the sterically more demanding *N*,*N*′-$(CH_2tBu)_2$ substituents does also dimerize in the solid state but by formation of intermolecular $[\eta^6\text{-}(C_6H_4)\cdots Sn]_2$ interactions between parallel oriented stannylene molecules.[62] In this case the aromatic π-system of the benzene ring donates electron density to the vacant p-orbital at the tin atom. The intermolecular Sn···C_6(centroid) distance measures 3.23 Å This value compares well to the values found for π-complexes of divalent tin derivatives with neutral arenes.[71]

Stannylenes **19**–**21** with Lewis base functionalized *N*,*N*′-substituents exhibit different types of aggregation in the solid state (Figure 8).[64] Stannylene **19** with *N*,*N*′-$(CH_2CH_2OCH_3)_2$ substituents is monomeric with weak intramolecular Sn···O interactions [distances Sn···O 3.060(3) and 3.120(3) Å].

The structure analyses for stannylenes **20** and **21** with the $CH_2CH_2NMe_2$ and $CH_2CH_2CH_2NMe_2$ arms at the ring nitrogen atoms revealed the existence of inter- and intramolecular Sn···N interactions. In **20** the ethylene side chain is too short to allow for a strain-free interaction of the Me_2N donor with the p-orbital at the tin atom. Stannylene **21** possesses longer *N*,*N*′-$(CH_2CH_2CH_2NMe_2)_2$ substituents which enables a strain-free intramolecular coordination of the Me_2N donor group. The coordinative Sn···N bond lengths for **20** and **21** fall in the range 2.497(2)–2.612(2) Å.

^{119}Sn NMR investigations performed for the symmetrically and unsymmetrically *N*,*N*′-substituted N-heterocyclic stannylenes showed a strong dependence of the chemical shift $\delta(^{119}Sn)$ on the type of *N*,*N*′-substituents and on the solvent used.[64] The ^{119}Sn NMR resonances for **17**–**21** fall in a broad range between δ = 49 and 269 ppm (Table 1). The value of $\delta(^{119}Sn)$ reflects the amount of electron density at the tin atom. The variation of the ^{119}Sn chemical shift in dependence on the solvent can thus serve as a probe for the presence of additional donor interactions with the stannylene tin atom.

Stannylene **17** shows a strong dependence of the ^{119}Sn NMR resonance on the solvent used. The strong upfield

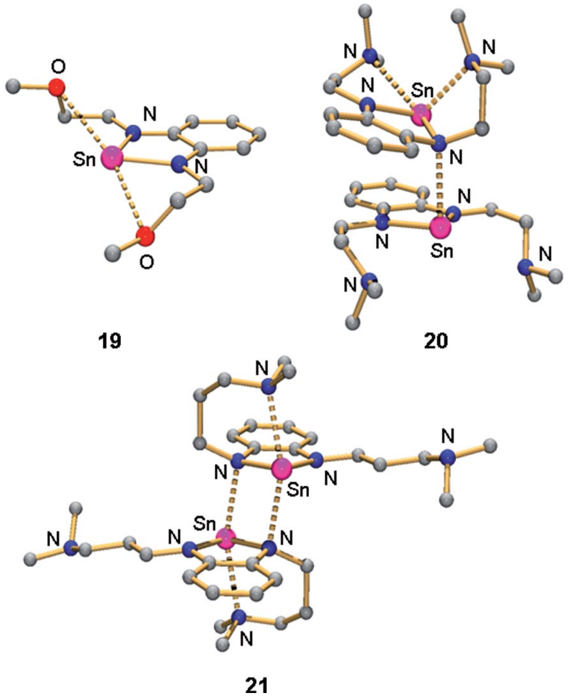


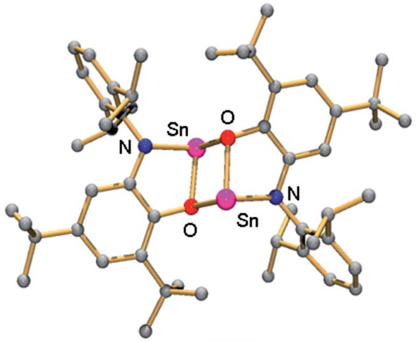
Figure 8. Molecular structures of stannylenes **19**–**21**.

Table 1. $\delta(^{119}Sn)$ chemical shifts for the benzannulated stannylenes **C2** in C_6D_6 and $[D_8]$thf.

R	C_6D_6	$[D_8]$thf
Me (**17**)	222	107
CH_2tBu (**18**)	269	–
CH_2CH_2OMe (**19**)	148	89
$CH_2CH_2NMe_2$ (**20**)	49	51
$CH_2CH_2CH_2NMe_2$ (**21**)	52	51

shift in thf is apparently caused by coordination of thf to the electron-deficient tin(II) center. The chemical shift of the ^{119}Sn resonance for stannylene **19** in benzene indicates the presence of a weak intramolecular Sn···O coordination in solution. In thf the ^{119}Sn resonance is again shifted upfield, which was taken as an indication for thf coordination to the tin(II) atom. The ^{119}Sn NMR spectra measured for stannylenes **20** and **21** bearing amino-functionalized *N*,*N′*-substituents show resonances at high field when compared to the stannylenes **17**–**19**. Both **20** and **21** give ^{119}Sn resonances with almost identical chemical shifts in C_6D_6 and $[D_8]$thf. The tin centers in both stannylenes are stabilized by intra- and intermolecular coordination of nitrogen donors in the solid state (Figure 8), and this coordination appears to prevail in solution thereby rendering the chemical shift of the ^{119}Sn resonance non-dependent on the type of solvent used.

An X-ray diffraction study of the *N*,*O*-stabilized benzannulated stannylene **22** shows also strong intermolecular Sn···O interactions [distance Sn···O 2.240(2) and 2.235(2) Å] leading to the dimer **22·22** (Figure 9).[68] The preferred coordination of the oxygen atoms to the tin atoms in **22** can be rationalized by the strong Lewis basicity of the oxygen atoms and/or by the bulky substituent at the ring nitrogen atom, which prevents nitrogen coordination.



22·22

Figure 9. Molecular structure of the dimeric stannylene **22·22**.

Benzannulated stannylenes are capable of forming adducts with various Lewis bases such as tmeda[62] and benzannulated N-heterocyclic carbenes.[43,72] The dinuclear tmeda adduct **23** was prepared by the addition of the Lewis base tmeda to a benzannulated N-heterocyclic stannylene of type **C2** (R = $SiMe_3$). The molecular structure analysis for **23** shows a tmeda molecule coordinated in a bridging fashion between two tin(II) centers (Figure 10). The $Sn\cdots N_{tmeda}$ separation measures 2.516(5) Å, which is a value similar to the equivalent Sn···N distances in stannylenes **20** and **21**. The carbene adduct **24** (Figure 10) was prepared by the reaction of the benzannulated stannylene **20** with the dibenzotetraazafulvalene of a benzannulated N-heterocyclic carbene (Scheme 7).[72] Carbene–stannylene adduct **24** is not stable in solution but crystallizes from solutions containing equimolar amounts of the carbene and the stannylene. Both carbene adducts **4** (Scheme 7) and **24** contain a carbene ligand coordinated in perpendicular fashion relative to the stannylene plane again demonstration the Lewis acidity of the empty p-orbital at the tin center.

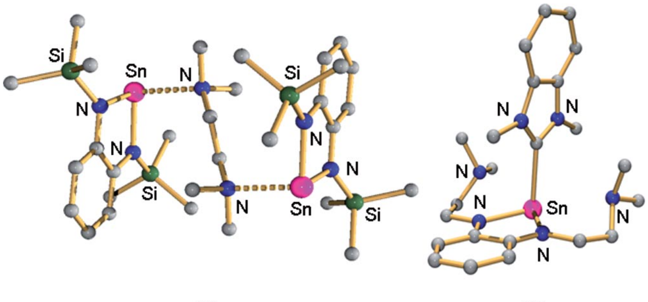


Figure 10. Molecular structures of the stannylene adducts **23** (with tmeda) and **24** (with an N-heterocyclic carbene).

Bis- and Polydentate Stannylenes

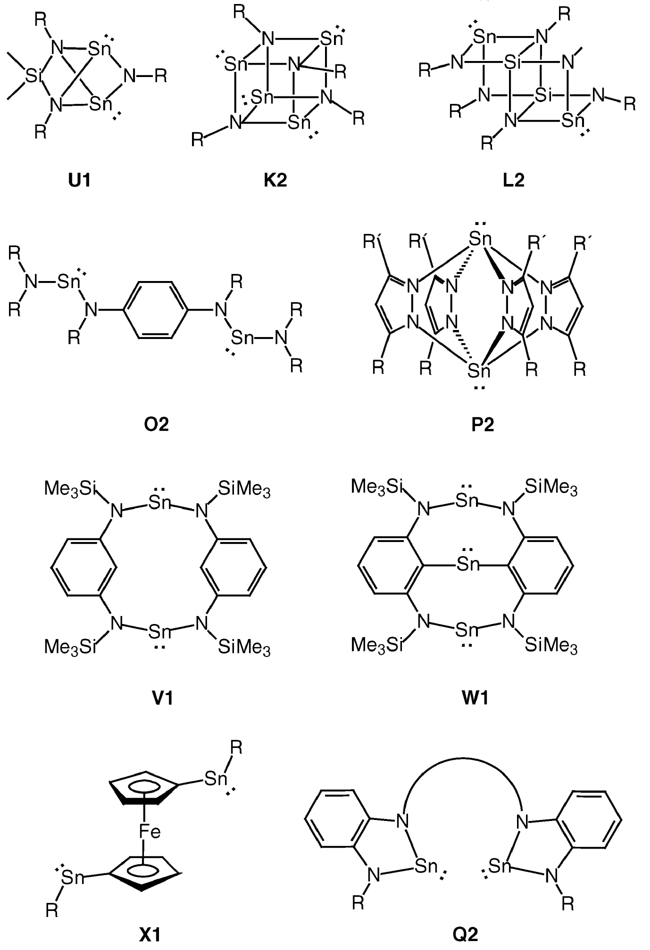
A selection of polydentate *N*-substituted and N-heterocyclic stannylenes is depicted in Scheme 11. Bis(stannylene) **U1** was prepared by the reaction of compound **A2**

(Scheme 9) with the reactive tin derivative Sn=N–R generated in situ.[27] Upon heating compound **U1** transforms into the cubane-type tetrakis(stannylene) **K2**.[27,73] Each tin atom in **K2** possesses a chemically active unshared electron pair, which can act as a Lewis base towards Lewis acids like $AlCl_3$.[74] Various related mixed cubane-type compounds with tin(II) and germanium(II) or lead(II) have been described.[27] Compared to the bis(germylene) derivative **L1** (Scheme 8) bis(stannylene) **L2** exhibits two additional intramolecular Sn···N interactions, which lead to a pseudo-bis-(cubane) skeleton.[47] The macrocyclic bis(stannylene) **V1** was prepared by the reaction of $1,3\text{-}(RLiN)_2C_6H_4$ with $[Sn(\mu\text{-}Cl)(SiMe_3)]_2$.[75] $Sn[N(SiMe_3)_2]_2$ can activate the C–H and N–H bonds in $1,3\text{-}(RHN)_2C_6H_4$ to give compound **W1** with two diamino- and one (dialkylstannyl)stannylene.[75] Bis(stannylenes) of type **O2** can be prepared in a fashion similar to the one used for the preparation of the germanium analogues of type **O1** (Scheme 8).[50,51] Neutral and positively charged bis(stannylenes) **P2** bearing three or four pyrazolyl ligands are known.[52] The stannylene-substituted ferrocene **X1** can coordinate in a chelating fashion to transition metals.[76] N-heterocyclic bis(stannylenes) **Q2** with various bridging units and substituents R were isolated recently.[24,77,78] They have been prepared by the reaction of suitable tetraamines and $Sn[N(SiMe_3)_2]_2$.

Bis(stannylene) **26** with a $–CH_2C(CH_3)_2CH_2–$ linking unit between the stannylene moieties and *N*-$CH_2CH_2CH_2NMe_2$ substituents exhibits intramolecular $Sn\cdots NMe_2$ contacts [Sn···N distances 2.561(4) and 2.530(4) Å] along with an intermolecular interaction between the tin(II) centers and the aromatic benzene π-system of an adjacent molecule (Figure 11).[24] This interaction leads to a polymeric arrangement of bis(stannylene) molecules in the solid state. The molecular structure of the *N*-$CH_2C(CH_3)_3$ substituted bis(stannylene) **25**[24] has not yet been determined.

Both bis(stannylene) **25** and **26** containing the $–CH_2C(CH_3)_2CH_2–$ linking unit react with $[Mo(nbd)(CO)_4]$ with formation of the heteroleptic complexes **27** and **28** (Figure 12).[24] An X-ray diffraction study for complex **28** showed an intramolecular $Sn\cdots NMe_2$ interaction [$Sn\cdots NMe_2$ distance 2.390(2) Å], which is significantly shorter than the corresponding value in the free bis(stannylene) **26** [$Sn\cdots NMe_2$ distances 2.561(4) and 2.530(4) Å]. The coordination of amino arms to the tin atoms in **28** leads to an elongation of the Mo–Sn bonds [2.7046(6) Å] compared to complex **27** [2.6850(3) and 2.6736(4) Å].

The Mo–E and E–N bond lengths and the wavenumbers for the *ν*(CO) stretching modes for bis(carbene) (**15**),[6a] bis(germylene) (**13**)[53a] and bis(stannylene) (**27**)[24] complexes are listed in Table 2. As expected and according to the increase of the atomic radii, the intracycle E–N bond lengths increase in the following order: bis(carbene) complex **15**, bis(germylene) complex **13**, bis(stannylene) complex **27**. This increase, however, is much stronger than the observed lengthening the Mo–E bonds for the transition E = C → E = Sn. On first sight it appears conceivable that the heavier analogues of benzannulated carbenes act not exclusively as σ-donors but, owing to the Lewis acidity of the empty p-orbital particularly at the stannylenes, also function as π-acceptor ligands. Such π-acceptor properties would also explain the higher wavenumbers observed for the stretching frequencies *ν*(CO) of the carbonyl groups



Scheme 11. Polydentate stannylenes.

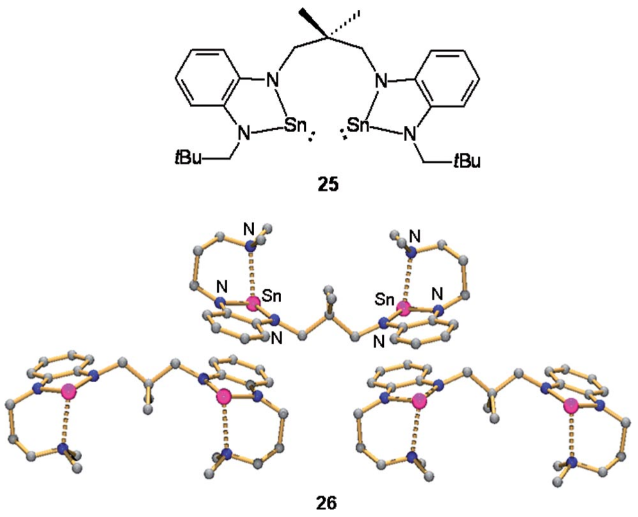


Figure 11. Schematic representation of bis(stannylene) **25** and molecular structure and packing of stannylene **26** in the solid state.

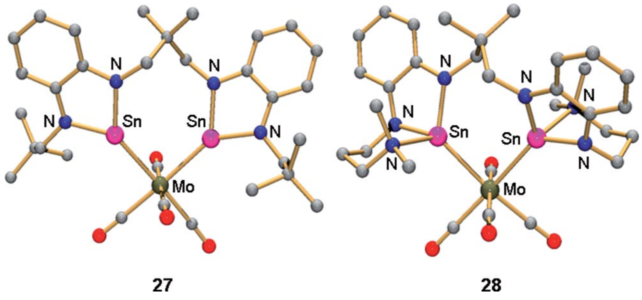
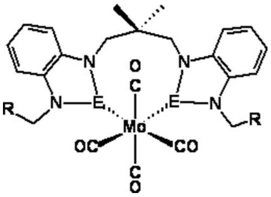


Figure 12. Molecular structures of complexes **27** and **28**.

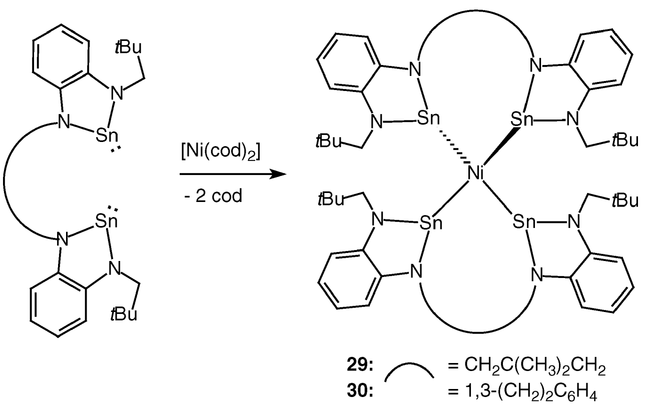
trans to the group 14 element E measured for complexes **13** and **27** compared to complex **15**. DFT calculations performed for model complexes **13**, **15** and **27** indicated, however, that the bis(germylene) and bis(stannylene) ligands act not only as σ-donors and π-acceptors but also as π-donors.[24] This provides an alternative explanation for the measured geometric and spectroscopic parameters of complexes **13**, **15** and **27**. The elongated Mo–Sn bonds and the lowered ν(CO) frequencies for **28** compared to complex **27** indicate a reduced Mo–Sn bond order in **28** due to coordination of the donor-functionalized *N*-substituent.

Table 2. Bond lengths [Å] and wavenumbers for the ν(CO) stretching modes of complexes **13**, **15**, **27** and **28**.

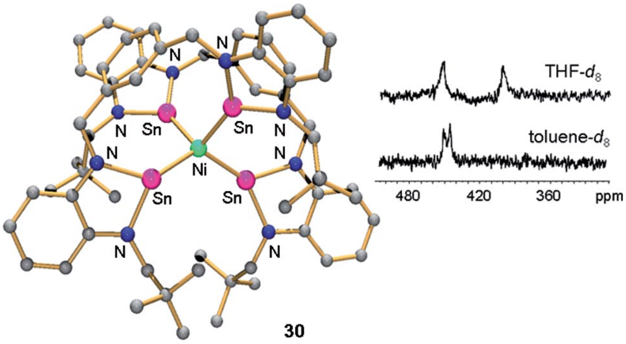


	15 E = C R = *t*Bu	**13** E = Ge R = *t*Bu	**27** E = Sn R = *t*Bu	**28** E = Sn R = $(CH_2)_2NMe_2$
r(Mo–E)	2.324(3)	2.5204(6), 2.5189(6)	2.6850(3), 2.6736(4)	2.7046(6)
r(E–N)	1.385(4), 1.367(4)	1.823(3)– 1.827(3)	2.0182(2)– 2.0398(2)	2.033(2), 2.0586(2)
ν(CO), A_1	1889	1950	1947	1928
ν(CO), A_1	2002	2029	2038	2008

The intensely coloured homoleptic bis(stannylene)Ni^0 complexes **29** and **30** were prepared by the reaction of bis(stannylenes) with [Ni(cod)$_2$] (cod = cyclooctadiene) (Scheme 12).[78] The ^{119}Sn NMR spectrum of complex **29** shows only one resonance signal both in thf (δ = 440.1 ppm) and downfield-shifted in toluene (δ = 492.3 ppm). Two only slightly separated resonances were observed in the ^{119}Sn NMR spectrum of complex **30** measured in toluene (δ = 439.0 and 434.0 ppm, Figure 13). One of these ^{119}Sn resonances is significantly shifted upfield in thf (δ = 328.4 ppm), whereas the other one shows an almost unchanged chemical shift (δ = 444.5 ppm) compared to the resonances observed for **30** in toluene.



Scheme 12. Preparation of the homoleptic complexes **29** and **30**.

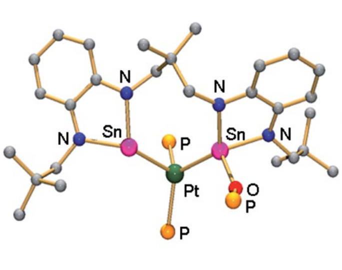


30

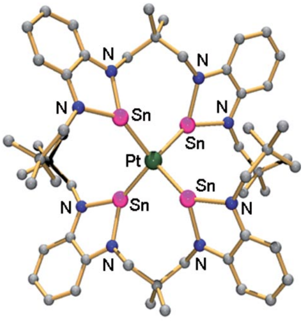
Figure 13. Molecular structure and ^{119}Sn NMR spectra for complex **30**.

The observation of two ^{119}Sn resonances indicates the presence of two different types of tin atoms in complex **30**. X-ray diffraction studies confirmed the presence of four identical tin atoms in **29**, all of which are accessible for thf coordination leading to the upfield shift in this solvent. The X-ray diffraction analysis shows two different types of tin atoms in complex **30**. Two of these are accessible for thf coordination, whereas the other two are efficiently shielded by the 1,3-$(CH_2)C_6H_4$ bridging units linking the stannylene donors (Figure 13).

It has been demonstrated that bis(stannylene) ligands in the presence of a Lewis base are capable of replacing transition metal coordinated triphenylphosphane.[79] Bis(stannylene) **25** (Figure 11) reacts with [Pt(PPh$_3$)$_4$] in the presence of OPPh$_3$ to give the heteroleptic Pt^0 complex **31**. The molecular structure analysis (Figure 14) shows one O=PPh$_3$ ligand coordinated to one tin atom. Surprisingly, only one resonance was found in the ^{119}Sn NMR spectrum exhibiting the characteristic coupling constants [$^1J(^{119}Sn–^{195}Pt)$ and $^2J(^{119}Sn–^{31}P)$]. Apparently, the O=PPh$_3$ ligand in **31** dissociates from the tin center or is fast exchanged. Both Pt–Sn bond lengths [2.5734(9) and 2.5868(8) Å] are almost equidistant in **31**. The significant deviation of Sn–Pt vectors from the N$_2$Sn planes indicates that an interaction of the empty p-orbital at the tin atoms with the d-orbitals at the platinum atom is not feasible. Thus, geometric factors preventing d→p π-interaction between the tin and platinum atoms are responsible for the almost equidistant Pt–Sn bonds in spite of the fact that one tin atom is coordinated by phosphane oxide and the other one is not.



31



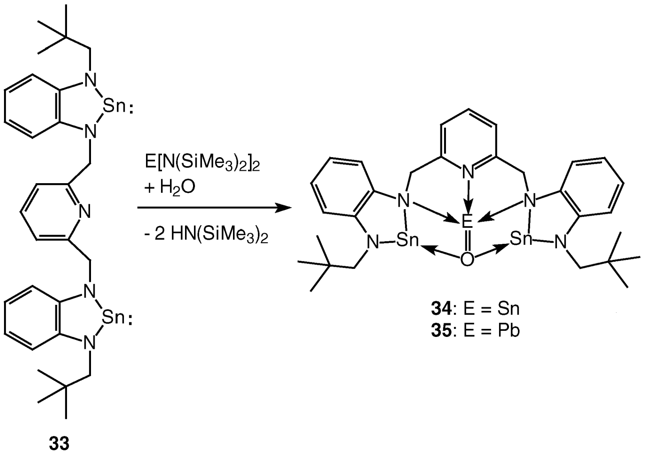
32

Figure 14. Molecular structures of hetero- (**31**) and homoleptic (**32**) platinum(0) complexes with bis(stannylene) ligands; thf molecules coordinated to the tin atoms in **32** and the phenyl groups of the PPh_3 and $O=PPh_3$ ligands in **31** are omitted for clarity.

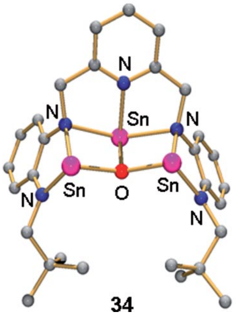
Homoleptic Pt^0 complexes with bis(stannylene) ligands were synthesized by the reaction of the ligands with $[Pt(nbe)_3]$ (nbe = norbornene).[79] An X-ray diffraction study for complex **32** (Figure 14) shows a tetrahedral Sn_4Pt core and coordination of thf molecules to the sterically unprotected tin atoms. The molecular structures of the nickel(0) complex **29** (Scheme 12) and the analogous platinum(0) complex **32** are quite similar in the solid state. ^{119}Sn NMR spectra of the platinum analogue of complex **30** indicate the presence of an equilibrium between complexes with three- and four-coordinate platinum atoms in solution.[79]

The lutidine-bridged bis(stannylene) **33** (Scheme 13) has been prepared in analogy to the corresponding bis(germylene) **11** (Figure 5). It was found that bis(stannylene) **33** reacts with in situ generated tin and lead homologues of carbon monoxide with formation of the Sn=O and Pb=O adducts **34** and **35**, respectively (Scheme 13).[77] Tin(II) monoxide for the adduct formation has been generated by the reaction of water with the benzannulated bis(stannylene) **33** or, more simply, by the reaction of water with $Sn[N(SiMe_3)_2]_2$. Pb=O was generated in situ by hydrolysis of $Pb[N(SiMe_3)_2]_2$. The formation of various clusters exhibiting Sn–O bonds during the hydrolysis of diaminostannylenes has been discussed previously by Veith and Lange.[80] The valence states of the tin atoms in complexes **34** and **35** were estimated by Mössbauer spectroscopy. The ^{119}Sn Mössbauer spectrum for **34** shows the presence of nonequivalent tin(II) atoms and can be simulated as addition of two signals at δ = 2.66(1) and 2.84(3) mm/s with relative intensities 2:1. These values as well as the isomer shift observed for **35** [δ = 2.63(1) mm/s] are also typical for divalent tin atoms. The ^{119}Sn NMR resonance signal for the Sn=O tin atom in **34** was observed at δ = –95.1 ppm (in toluene).

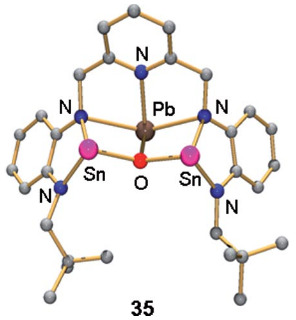
An X-ray diffraction study of adduct **34** shows the bis(stannylene) **33** as a pentadentate ligand. The Sn=O tin atom gains electron density from three nitrogen atoms of the bis(stannylene) moiety (Figure 15). The coordination geometry of the central core in **34** is similar to that found



Scheme 13. Formation of the Sn=O and Pb=O adducts **34** and **35**.

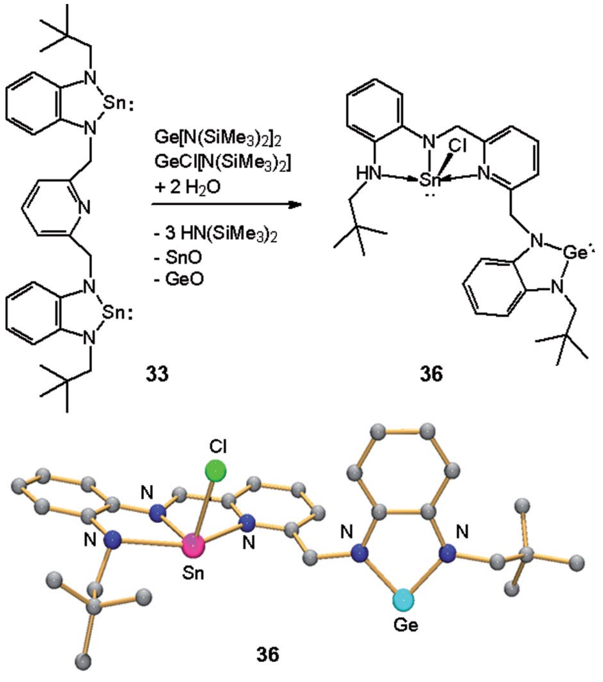


34



35

Figure 15. Molecular structures of the complexes of bis(stannylene) **33** with tin(II) (**34**) and lead(II) (**35**) monoxides.



Scheme 14. Preparation and molecular structure of the mixed germylene–stannylene **36**.

in polymeric $(SnO)_\infty$,[81] which like **34** also contains square-pyramidal coordinated Sn atoms. The Sn=O bond length [2.079(2) Å] is slightly shorter than the $Sn_{stannylene}$–O bonds [2.114(2) and 2.135(2) Å].

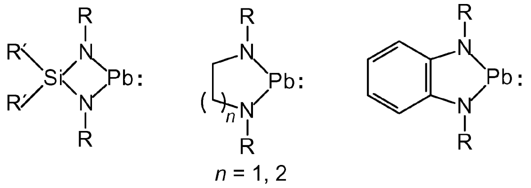
The bis(stannylene) ligand **33** in adduct **35** coordinates to the lead(II) monoxide in a fashion similar to its coordination to Sn=O in complex **34**. The bond of Pb=O measures 2.157(5) Å.

The hydrolysis of bis(stannylene) **33** in the presence of a mixture of $ClGeN(SiMe_3)_2$[50,51] and $Ge[N(SiMe_3)_2]_2$ gave the unsymmetrical molecule **36** (Scheme 14) containing an N,Cl-substituted stannylene and a benzannulated N-heterocyclic germylene (Scheme 14).[82] The X-ray diffraction study of **36** shows an intramolecular donor–acceptor stabilization of the tin(II) atom by the nitrogen atoms of the lutidine and NH–CH_2*t*Bu groups. Related N,Cl-substituted stannylenes featuring additional intramolecular Sn···N interactions have been isolated by the reaction of stannylenes of type **A2** (Scheme 9) with HCl.[83]

Plumbylenes

Benzannulated Plumbylenes and Their Adducts

In contrast to the chemistry of N-heterocyclic germylenes and stannylenes, much less is known about their lead analogues. The first representative of an N-heterocyclic plumbylene, compound **A3** (Scheme 15), was prepared by Veith and Grosser[27] by the reaction of the appropriate dilithiated diamine with $PbCl_2$. Multinuclear NMR studies indicated the formation of dimeric aggregates of **A3** in solution. In the presence of the related stannylene **A2** (Scheme 9) the formation of mixed dimers **A2·A3** has also been described.[84] X-ray diffraction studies on spirocyclic plumbylene of type **A3** with R′,R′ = –$(CH_2)_3$– demonstrated the existence of intermolecular Pb···N interactions again leading to dimeric aggregates in the solid state.[85]

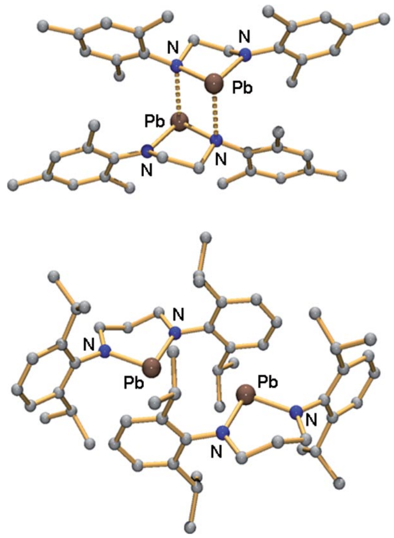


A3 **T2** **C3**

Scheme 15. N-heterocyclic plumbylenes.

Saturated N-heterocyclic plumbylenes of type **T2** with five- or six-membered heterocycles have been prepared recently by the transamination method or by the reaction of $PbCl_2$ with dilithiated diamines.[86] The first benzannulated N-heterocyclic plumbylene **C3** was isolated as a carbene–plumbylene adduct of type **5** (Scheme 7) in 2000.[43] No NMR or structural data of the free benzannulated plumbylene were reported. More recently two benzannulated N-heterocyclic plumbylenes of type **C3** (R = CH_2*i*Pr, CH_2*t*Bu) have been synthesized and characterized including molecular structure determination by X-ray diffraction.[87] Up to now, only for the benzannulated N-heterocyclic compounds has the complete series of group 14 derivatives (carbene,[31] silylene,[88] germylene,[30a] stannylene[62,64] and plumbylene[87]) been isolated and fully characterized in the free state. The lead analogue of the cubane-type stannylene **K2** (Scheme 11) has also been described.[27]

The saturated plumbylene of type **T2** featuring a five-membered heterocycle and *N*,*N*′-$(dipp)_2$ substituents (dipp = 2,6-diisopropylphenyl) is monomeric in the solid state, whereas the plumbylene **37** (Figure 16) bearing the sterically less demanding *N*,*N*′-mesitylene substituents crystallized as a dimer with strong intermolecular Pb···N interactions [intermolecular distance Pb···N 2.471(2) Å].[86]



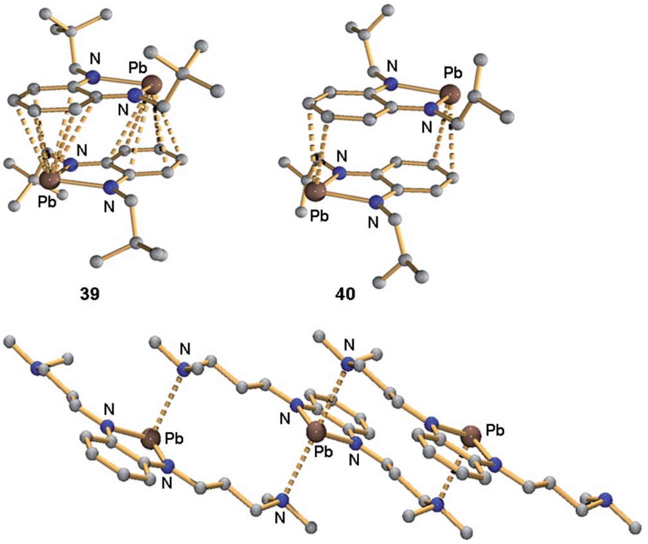
37

38

Figure 16. Molecular structures of the saturated N-heterocyclic plumbylenes **37** and **38**.

Another mode of dimerization was found for plumbylene **38** derived from a six-membered heterocycle and also bearing *N*,*N*′-$(dipp)_2$ substituents (Figure 16). Dimeric **38** is formed by weak intermolecular interactions of the lead atoms of one plumbylene with the benzene ring of an adjacent molecule.

The benzannulated N-heterocyclic plumbylenes of type **C3** were prepared by the transamination reaction between a suitable *o*-phenylenediamine and $Pb[N(SiMe_3)_2]_2$.[87] X-ray diffraction analyses demonstrated that the plumbylenes with the sterically demanding *N*,*N*′-$(CH_2tBu)_2$ (**39**) and *N*,*N*′-$(CH_2iPr)_2$ (**40**) substituents exist as dimers in the solid state. The modes of dimerization are slightly different with intermolecular $[\eta^6\text{-}(C_6H_4)\cdots Pb]_2$ contacts for **39** and $[\eta^2\text{-}(C_6H_4)\cdots Pb]_2$ contacts for **40** (Figure 17). Similar intermolecular interactions have been observed for the benzannulated N-heterocyclic tin(II) analogue **18**.[62] The plumbylene **41** with donor-functionalized *N*,*N*′-substituents crystallizes as a polymer with strong intermolecular $Pb\cdots NMe_2$ contacts [intermolecular distance $Pb\cdots NMe_2$ 2.826(3) Å] (Figure 17).[89] This behaviour is in contrast to the situation found for the stannylene analogue **21** (Figure 8) which dimerizes in the solid state with formation of intermolecular Sn···N_{ring} and intramolecular Sn···NMe_2 interactions.

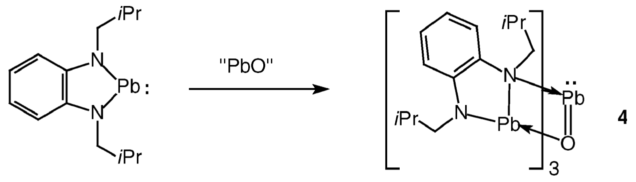


39 **40**

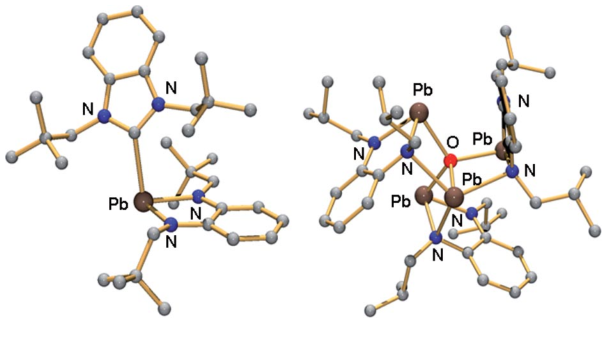
41

Figure 17. Molecular structures of N-heterocyclic benzannulated plumbylenes **39**–**41**.

The benzannulated plumbylenes of type **C3** are capable of forming donor–acceptor adducts with benzannulated carbenes giving **5**[43] or with lead monoxide leading to **42**[90] (Scheme 16, Figure 18). Complex **42** containing a Pb=O molecule stabilized by three plumbylenes **40** was prepared in a fashion similar to that of the bis(stannylene) adduct of Pb=O **35** (Scheme 13, Figure 15).



Scheme 16. Reaction of **40** with “Pb=O” to give adduct **42**.



5 **42**

Figure 18. Molecular structures of the adducts of plumbylenes with a benzannulated carbene (**5**) and with Pb=O (**42**).

The unshared electron pairs at the oxygen atom of the Pb=O moiety in **42** donate electron density to the vacant p-orbitals at the lead atoms of the three plumbylenes (Figure 18). In turn, the reactive Pb^{II}=O species is stabilized by electron donation from three ring nitrogen atoms to the lead center. The Pb–O bond in **42** [2.313(7) Å] is longer than that in the bis(stannylene) adduct **35** [2.157(5) Å] indicating a reduced Pb=O double-bond character in **42**.

Conclusions

Some of the heavier analogues of diaminocarbenes have been studied long before the first N-heterocyclic carbenes were prepared. The properties and the coordination chemistry of the heavier NHC analogues differ significantly from those of NHCs. Benzannulated N-heterocyclic stannylenes and plumbylenes have been used to trap reactive intermediates such as Sn=O and Pb=O. The heavier analogues of NHCs also exhibit an ambiphilic character with a Lewis basic filled sp^2-orbital and perpendicular to this a Lewis acidic empty p-orbital. They are promising ligands for transition metals, and both homoleptic and heteroleptic complexes with monodentate or bidentate NHC analogues are known. Given the significance of NHCs as ligands for catalytically active metal complexes, it will be interesting to see whether catalytically active complexes with N-heterocyclic germylene, stannylene or plumbylene ligands emerge in the future.

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. J. Arduengo III, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1991**, *113*, 361–363.
[2] a) F. E. Hahn, M. C. Jahnke, *Angew. Chem.* **2008**, *120*, 3166–3216; *Angew. Chem. Int. Ed.* **2008**, *47*, 3122–3172; b) O. Kaufhold, F. E. Hahn, *Angew. Chem.* **2008**, *120*, 4122–4126; *Angew. Chem. Int. Ed.* **2008**, *47*, 4057–4061; c) F. E. Hahn, *Angew. Chem.* **2006**, *118*, 1374–1378; *Angew. Chem. Int. Ed.* **2006**, *45*, 1348–1352; d) D. Bourissou, O. Guerret, F. P. Gabbaï, G. Bertrand, *Chem. Rev.* **2001**, *101*, 39–91.
[3] For recent reviews on N-heterocyclic silylenes, see: a) B. Gehrhus, M. F. Lappert, *J. Organomet. Chem.* **2001**, *617–618*, 209–223; b) M. Haaf, T. A. Schmedake, R. West, *Acc. Chem. Res.* **2000**, *33*, 704–714; c) N. J. Hill, R. West, *J. Organomet. Chem.* **2004**, *689*, 4165–4183.
[4] O. Kühl, *Coord. Chem. Rev.* **2004**, *248*, 411–427.
[5] a) W. A. Herrmann, *Angew. Chem.* **2002**, *114*, 1342–1363; *Angew. Chem. Int. Ed.* **2002**, *41*, 1290–1309; b) *N-Heterocyclic Carbenes in Synthesis* (Ed.: S. P. Nolan), Wiley-VCH, Weinheim, Germany, **2006**; c) N-Heterocyclic Carbenes in Transition Metal Catalysis (Ed.: F. Glorius), *Top. Organomet. Chem.* **2007**, *21*.
[6] a) D. M. Khramov, A. J. Boydston, C. W. Bielawski, *Angew. Chem.* **2006**, *118*, 6332–6335; *Angew. Chem. Int. Ed.* **2006**, *45*, 6186–6189; b) F. E. Hahn, L. Wittenbecher, D. Le Van, R. Fröhlich, *Angew. Chem.* **2000**, *112*, 551–554; *Angew. Chem. Int.*

Ed. **2000**, *39*, 541–544; c) F. E. Hahn, M. Foth, *J. Organomet. Chem.* **1999**, *585*, 241–245; d) F. E. Hahn, T. von Fehren, T. Lügger, *Inorg. Chim. Acta* **2005**, *358*, 4137–4144.

[7] O. Kaufhold, A. Stasch, P. G. Edwards, F. E. Hahn, *Chem. Commun.* **2007**, 1822–1824.

[8] 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.

[9] B. Gehrhus, P. B. Hitchcock, M. F. Lappert, *Z. Anorg. Allg. Chem.* **2005**, *631*, 1383–1386.

[10] a) J. D. Cotton, C. S. Cundy, D. H. Harris, A. Hudson, M. F. Lappert, P. W. Lednor, *J. Chem. Soc., Chem. Commun.* **1974**, 651–652; b) D. H. Harris, M. F. Lappert, *J. Chem. Soc., Chem. Commun.* **1974**, 895–896; c) D. H. Harris, M. F. Lappert, J. B. Pedley, G. J. Sharp, *J. Chem. Soc., Dalton Trans.* **1976**, 945–950.

[11] W. A. Herrmann, C. Köcher, *Angew. Chem.* **1997**, *109*, 2256–2282; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2162–2187.

[12] C. Heinemann, T. Müller, Y. Apeloig, H. Schwarz, *J. Am. Chem. Soc.* **1996**, *118*, 2023–2038.

[13] C. Heinemann, W. A. Herrmann, W. Thiel, *J. Organomet. Chem.* **1994**, *475*, 73–84.

[14] a) C. Boehme, G. Frenking, *J. Am. Chem. Soc.* **1996**, *118*, 2039–2046; b) R. West, J. J. Buffy, M. Haaf, T. Müller, B. Gehrhus, M. F. Lappert, Y. Apeloig, *J. Am. Chem. Soc.* **1998**, *120*, 1639–1640; c) H. M. Tuononen, R. Roesler, J. L. Dutton, P. J. Ragogna, *Inorg. Chem.* **2007**, *46*, 10693–10706.

[15] a) A. J. Arduengo III, H. Bock, H. Chen, M. Denk, D. A. Dixon, J. C. Green, W. A. Herrmann, N. L. Jones, M. Wagner, R. West, *J. Am. Chem. Soc.* **1994**, *116*, 6641–6649; b) J. F. Lehmann, S. G. Urquhart, L. E. Ennis, A. P. Hitchcock, K. Hatano, S. Gupta, M. K. Denk, *Organometallics* **1999**, *18*, 1862–1872; c) S. G. Urquhart, A. P. Hitchcock, J. F. Lehmann, M. Denk, *Organometallics* **1998**, *17*, 2352–2360; d) M. Denk, J. C. Green, N. Metzler, M. Wagner, *J. Chem. Soc., Dalton Trans.* **1994**, 2405–2410; e) L. A. Leites, S. S. Bukalov, M. Denk, R. West, M. Haaf, *J. Mol. Str.* **2000**, *550–551*, 329–335; f) L. A. Leites, S. S. Bukalov, A. V. Zabula, I. A. Garbuzova, D. F. Moser, R. West, *J. Am. Chem. Soc.* **2004**, *126*, 4114–4115; g) L. Pause, M. Robert, J. Heinicke, O. Kühl, *J. Chem. Soc., Perkin Trans. 2* **2001**, 1383–1388.

[16] T. Gans-Eichler, D. Gudat, M. Nieger, *Angew. Chem.* **2002**, *114*, 1966–1969; *Angew. Chem. Int. Ed.* **2002**, *41*, 1888–1891.

[17] T. Gans-Eichler, D. Gudat, K. Nättinen, M. Nieger, *Chem. Eur. J.* **2006**, *12*, 1162–1173.

[18] O. Kühl, P. Lönnecke, J. Heinicke, *Polyhedron* **2001**, *20*, 2215–2222.

[19] J. Heinicke, A. Oprea, *Heteroat. Chem.* **1998**, *9*, 439–444.

[20] J. Heinicke, A. Oprea, M. K. Kindermann, T. Karpati, L. Nyulászi, T. Veszprémi, *Chem. Eur. J.* **1998**, *4*, 541–545.

[21] F. Ullah, G. Bajor, T. Veszprémi, P. G. Jones, J. W. Heinicke, *Angew. Chem. Int. Ed.* **2007**, *46*, 2697–2700.

[22] a) W. Petz, *Chem. Rev.* **1986**, *86*, 1019–1047; b) M. S. Holt, W. L. Wilson, J. H. Nelson, *Chem. Rev.* **1989**, *89*, 11–49; c) M. F. Lappert, R. S. Rowe, *Coord. Chem. Rev.* **1990**, *100*, 267–292.

[23] a) C. Boehme, G. Frenking, *Organometallics* **1998**, *17*, 5801–5809; b) J. E. Bender IV, A. J. Shusterman, M. M. Banaszak Holl, J. W. Kampf, *Organometallics* **1999**, *18*, 1547–1552.

[24] F. E. Hahn, A. V. Zabula, T. Pape, A. Hepp, R. Tonner, R. Haunschild, G. Frenking, *Chem. Eur. J.*, DOI: 10.1002/chem.200801128.

[25] O. Kühl, K. Lifson, W. Langel, *Eur. J. Org. Chem.* **2006**, 2336–2343.

[26] C. W. Tolman, *Chem. Rev.* **1977**, *77*, 313–348.

[27] M. Veith, M. Grosser, *Z. Naturforsch.* **1982**, *37b*, 1375–1381.

[28] A. Meller, C.-P. Gräbe, *Chem. Ber.* **1985**, *118*, 2020–2029.

[29] A. Schäfer, W. Saak, M. Weidenbruch, *Z. Anorg. Allg. Chem.* **1998**, *624*, 1405–1408.

[30] a) J. Pfeiffer, W. Maringgele, M. Noltemeyer, A. Meller, *Chem. Ber.* **1989**, *122*, 245–252; b) J. Pfeiffer, M. Noltemeyer, A. Meller, *Z. Anorg. Allg. Chem.* **1989**, *572*, 145–150.

[31] F. E. Hahn, L. Wittenbecher, R. Boese, D. Bläser, *Chem. Eur. J.* **1999**, *5*, 1931–1935.

[32] 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.

[33] O. Kühl, P. Lönnecke, J. Heinicke, *Inorg. Chem.* **2003**, *42*, 2836–2838.

[34] S. Vepřek, J. Prokop, F. Glatz, R. Merica, F. R. Klingan, W. A. Herrmann, *Chem. Mater.* **1996**, *8*, 825–831.

[35] P. Bazinet, G. P. A. Yap, D. S. Richeson, *J. Am. Chem. Soc.* **2001**, *123*, 11162–11167.

[36] M. Stender, A. D. Phillips, P. P. Power, *Inorg. Chem.* **2001**, *40*, 5314–5315.

[37] M. Driess, S. Yao, M. Brym, C. van Wüllen, *Angew. Chem.* **2006**, *118*, 4455–4458; *Angew. Chem. Int. Ed.* **2006**, *45*, 4349–4352.

[38] H. V. Rasika Dias, Z. Wang, *J. Am. Chem. Soc.* **1997**, *119*, 4650–4655.

[39] a) A. E. Ayers, D. S. Marynick, H. V. Rasika Dias, *Inorg. Chem.* **2000**, *39*, 4147–4151; b) H. V. Rasika Dias, A. E. Ayers, *Polyhedron* **2002**, *21*, 611–618; c) H. V. Rasika Dias, Z. Wang, *Inorg. Chem.* **2000**, *39*, 3890–3893; d) A. E. Ayers, H. V. Rasika Dias, *Inorg. Chem.* **2002**, *41*, 3259–3268.

[40] A. V. Piskunov, I. A. Aivaz'yan, A. I. Poddel'sky, G. K. Fukin, E. V. Baranov, V. K. Cherkasov, G. A. Abakumov, *Eur. J. Inorg. Chem.* **2008**, 1435–1444.

[41] H. H. Karsch, P. A. Schlüter, M. Reisky, *Eur. J. Inorg. Chem.* **1998**, 433–436.

[42] a) D. A. Atwood, V. O. Atwood, A. H. Cowley, J. L. Atwood, E. Román, *Inorg. Chem.* **1992**, *31*, 3871–3872; b) M. C. Kuchta, G. Parkin, *J. Chem. Soc., Chem. Commun.* **1994**, 1351–1352.

[43] B. Gehrhus, P. B. Hitchcock, M. F. Lappert, *J. Chem. Soc., Dalton Trans.* **2000**, 3094–3099.

[44] a) S. Kobayashi, S. Iwata, M. Hiraishi, *J. Am. Chem. Soc.* **1994**, *116*, 6047–6048; b) S. Kobayashi, S.-I. Shoda, S. Cao, S. Iwata, M. Abe, K. Yajima, K. Yagi, M. Hiraishi, *J. Macromol. Sci., Pure Appl. Chem.* **1994**, *A31*, 1835–1845.

[45] S.-I. Shoda, S. Iwata, K. Yajima, K. Yagi, Y. Ohnishi, S. Kobayashi, *Tetrahedron* **1997**, *53*, 15281–15295.

[46] W. J. Grigsby, T. Hascall, J. J. Ellison, M. M. Olmstead, P. P. Power, *Inorg. Chem.* **1996**, *35*, 3254–3261.

[47] M. Veith, R. Lisowsky, *Angew. Chem.* **1988**, *100*, 1124–1125; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1087–1089.

[48] a) P. B. Hitchcock, M. F. Lappert, A. J. Thorne, *J. Chem. Soc., Chem. Commun.* **1990**, 1587–1589; b) J.-T. Ahlemann, H. W. Roesky, R. Murugavel, E. Parisini, M. Noltemeyer, H.-C. Schmidt, O. Müller, R. Herbst-Irmer, L. N. Markovskii, Y. G. Shermolovich, *Chem. Ber./Recueil* **1997**, *130*, 1113–1121.

[49] a) R. A. Bartlett, P. P. Power, *J. Am. Chem. Soc.* **1990**, *112*, 3660–3662; b) H. Chen, R. A. Bartlett, H. V. Rasika Dias, M. M. Olmstead, P. P. Power, *Inorg. Chem.* **1991**, *30*, 3390–3394.

[50] S. Kobayashi, S. Cao, *Chem. Lett.* **1994**, 941–944.

[51] H. Braunschweig, P. B. Hitchcock, M. F. Lappert, L. J.-M. Pierssens, *Angew. Chem.* **1994**, *106*, 1243–1245; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1156–1158.

[52] a) I. Krummenacher, F. Breher, *Z. Anorg. Allg. Chem.* **2006**, *632*, 965–971; b) I. Krummenacher, C. Oschwald, H. Rüegger, F. Breher, *Z. Anorg. Allg. Chem.* **2007**, *633*, 2354–2361.

[53] a) A. V. Zabula, F. E. Hahn, T. Pape, A. Hepp, *Organometallics* **2007**, *26*, 1972–1980; b) F. E. Hahn, A. V. Zabula, T. Pape, A. Hepp, *Eur. J. Inorg. Chem.* **2007**, 2405–2408.

[54] F. E. Hahn, A. V. Zabula, T. Pape, A. Hepp, *Z. Anorg. Allg. Chem.* **2008**, *634*, 2397–2401.

[55] F. E. Hahn, A. V. Zabula, T. Pape, F. Hupka, *Z. Anorg. Allg. Chem.*, in preparation.

[56] a) N. O. J. Malcolm, R. J. Gillespie, P. L. A. Popelier, *J. Chem. Soc., Dalton Trans.* **2002**, 3333–3341; b) M. Driess, H. Grützmacher, *Angew. Chem.* **1996**, *108*, 900–929; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 828–856.

[57] M. Veith, *Angew. Chem.* **1975**, *87*, 287–288; *Angew. Chem. Int. Ed. Engl.* **1975**, *14*, 263–264.

[58] a) M. Veith, *Z. Naturforsch.* **1978**, *33b*, 1–6; b) M. Veith, *Z. Naturforsch,* **1978**, *33b*, 7–13; c) M. Veith, O. Recktenwald, *Top. Curr. Chem.* **1982**, *104*, 1–55.

[59] a) M. Veith, L. Stahl, V. Huch, *Inorg. Chem.* **1989**, *28*, 3278–3280; b) M. Veith, L. Stahl, V. Huch, *J. Chem. Soc., Chem. Commun.* **1990**, 359–361; c) M. Veith, A. Müller, L. Stahl, M. Nötzel, M. Jarczyk, V. Huch, *Inorg. Chem.* **1996**, *35*, 3848–3855.

[60] H. Fußstetter, H. Nöth, *Chem. Ber.* **1979**, *112*, 3672–3681.

[61] a) A. Tzschach, M. Scheer, K. Jurkschat, *Z. Anorg. Allg. Chem.* **1984**, *515*, 147–150; b) J.-L. Fauré, H. Gornitzka, R. Réau, D. Stalke, G. Bertrand, *Eur. J. Inorg. Chem.* **1999**, 2295–2299.

[62] H. Braunschweig, B. Gehrhus, P. B. Hitchcock, M. F. Lappert, *Z. Anorg. Allg. Chem.* **1995**, *621*, 1922–1928.

[63] C. D. Schaeffer, J. J. Zuckerman, *J. Am. Chem. Soc.* **1974**, *96*, 7160–7162.

[64] F. E. Hahn, L. Wittenbecher, D. Le Van, A. V. Zabula, *Inorg. Chem.* **2007**, *46*, 7662–7667.

[65] C. Drost, P. B. Hitchcock, M. F. Lappert, *Angew. Chem.* **1999**, *111*, 1185–1187; *Angew. Chem. Int. Ed.* **1999**, *38*, 1113–1116.

[66] a) A. G. Avent, C. Drost, B. Gehrhus, P. B. Hitchcock, M. F. Lappert, *Z. Anorg. Allg. Chem.* **2004**, *630*, 2090–2096; b) P. Bazinet, G. P. A. Yap, G. A. DiLabio, D. S. Richeson, *Inorg. Chem.* **2005**, *44*, 4616–4621; c) I. Nowik, H. A. Spinney, D. S. Richeson, R. H. Herber, *J. Organomet. Chem.* **2007**, *692*, 5680–5682; d) V. M. Jiménez-Pérez, B. M. Muñoz-Flores, H. W. Roesky, T. Schulz, A. Pal, T. Beck, Z. Yang, D. Stalke, R. Santillan, M. Witt, *Eur. J. Inorg. Chem.* **2008**, 2238–2243.

[67] J. R. Babcock, C. Incarvito, A. L. Rheingold, J. C. Fettinger, L. R. Sita, *Organometallics* **1999**, *18*, 5729–5732.

[68] A. V. Piskunov, I. A. Aivaz'yan, G. K. Fukin, E. V. Baranov, A. S. Shavyrin, V. K. Cherkasov, G. A. Abakumov, *Inorg. Chem. Commun.* **2006**, *9*, 612–615.

[69] H. V. Rasika Dias, W. Jin, *J. Am. Chem. Soc.* **1996**, *118*, 9123–9126.

[70] A. V. Zabula, F. E. Hahn, F. Hupka, T. Pape, A. Hepp, manuscript in preparation.

[71] H. Schmidbaur, A. Schier, *Organometallics* **2008**, *27*, 2361–2395.

[72] F. E. Hahn, L. Wittenbecher, M. Kühn, T. Lügger, R. Fröhlich, *J. Organomet. Chem.* **2001**, *617–618*, 629–634.

[73] a) M. Veith, G. Schlemmer, *Chem. Ber.* **1982**, *115*, 2141–2152; b) M. Veith, O. Recktenwald, *Z. Naturforsch.* **1983**, *38b*, 1054–1061.

[74] M. Veith, W. Frank, *Angew. Chem.* **1985**, *97*, 213-214; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 223–224.

[75] H. Braunschweig, C. Drost, P. B. Hitchcock, M. F. Lappert, L. J.-M. Pierssens, *Angew. Chem.* **1997**, *109*, 285–288; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 261–263.

[76] M. Henn, M. Schürmann, B. Mahieu, P. Zanello, A. Cinquantini, K. Jurkschat, *J. Organomet. Chem.* **2006**, *691*, 1560–1572.

[77] A. V. Zabula, T. Pape, A. Hepp, F. M. Schappacher, U. C. Rodewald, R. Pöttgen, F. E. Hahn, *J. Am. Chem. Soc.* **2008**, *130*, 5648–5649.

[78] A. V. Zabula, T. Pape, A. Hepp, F. E. Hahn, *Organometallics* **2008**, *27*, 2756–2760.

[79] A. V. Zabula, T. Pape, A. Hepp, F. E. Hahn, *Dalton Trans.*, DOI: 10.1039/b809878f.

[80] a) M. Veith, H. Lange, *Angew. Chem.* **1980**, *92*, 408–409; *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 401–402; b) M. Veith, *Chem. Ber.* **1978**, *111*, 2536–2546; c) M. Veith, *Comments Inorg. Chem.* **1985**, *4*, 179–191.

[81] J. Pannetier, G. Denes, *Acta Crystallogr., Sect. B* **1980**, *36*, 2763–2765.

[82] A. V. Zabula, F. E. Hahn, unpublished work.

[83] M. Veith, M. Jarczyk, V. Huch, *Chem. Ber.* **1988**, *121*, 347–355.

[84] B. Wrackmeyer, K. Horchler, H. Zhou, M. Veith, *Z. Naturforsch.* **1989**, *44b*, 288–292.

[85] S.-J. Kim, Y.-J. Lee, S. H. Kim, J. Ko, S. Cho, S. O. Kang, *Organometallics* **2002**, *21*, 5358–5365.

[86] J. P. H. Charmant, M. F. Haddow, F. E. Hahn, D. Heitmann, R. Fröhlich, S. M. Mansell, C. A. Russell, D. F. Wass, *Dalton Trans.*, DOI: 10.1039/b808717b.

[87] F. E. Hahn, D. Heitmann, T. Pape, *Eur. J. Inorg. Chem.* **2008**, 1039–1041.

[88] B. Gehrhus, M. F. Lappert, J. Heinicke, R. Boese, D. Bläser, *J. Chem. Soc., Chem. Commun.* **1995**, 1931–1932.

[89] F. E. Hahn, M. Kühn, to be published.

[90] F. E. Hahn, D. Heitmann, T. Pape, to be published.

Received: August 29, 2008