Angewandte
International Edition Chemie

Group 14 Compounds

DOI: 10.1002/anie.201408347

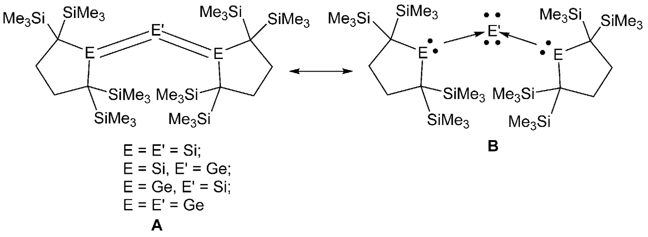
An N-Heterocyclic Silylene-Stabilized Digermanium(0) Complex[**]

Yu-Liang Shan, Wai-Leung Yim, and Cheuk-Wai So**

Abstract: *The synthesis of an N-heterocyclic silylene-stabilized digermanium(0) complex is described. The reaction of the amidinate-stabilized silicon(II) amide* $[\mathrm{LSiN(SiMe_3)_2}]$ (**1**; $L = \mathrm{PhC(N}t\mathrm{Bu)_2}$) *with* $\mathrm{GeCl_2{\cdot}dioxane}$ *in toluene afforded the* $\mathrm{Si^{II}{-}Ge^{II}}$ *adduct* $[\mathrm{L\{(Me_3Si)_2N\}Si\rightarrow GeCl_2}]$ (**2**). *Reaction of the adduct with two equivalents of* $\mathrm{KC_8}$ *in toluene at room temperature afforded the N-heterocyclic carbene silylene-stabilized digermanium(0) complex* $[\mathrm{L\{(Me_3Si)_2N\}Si\rightarrow Ge{=}Ge\leftarrow Si\{N(SiMe_3)_2\}L}]$ (**3**). *X-ray crystallography and theoretical studies show conclusively that the N-heterocyclic silylenes stabilize the singlet digermanium(0) moiety by a weak synergic donor–acceptor interaction.*

The utilization of N-heterocyclic carbenes (NHCs) for the stabilization of Group 14 elements in the zero oxidation state (Group 14 element(0) complex) has attracted much attention.[1] The most spectacular example of such a complex is $[\mathrm{IPr\rightarrow Si{=}Si\leftarrow IPr}]$ ($\mathrm{IPr} = \mathrm{{:}C\{N(Ar)CH\}_2}$; $\mathrm{Ar} = 2,6\text{-}i\mathrm{Pr_2C_6H_3}$), which is considered as an NHC adduct of the singlet disilicon(0) fragment $\{\mathrm{{:}Si{=}Si{:}}\}$ comprising a Si=Si double bond and a lone pair of electrons on each Si atom. The molecule $[\mathrm{IPr\rightarrow Si{=}Si\leftarrow IPr}]$ can be synthesized by the reduction of $[\mathrm{IPr\rightarrow SiCl_4}]$ with $\mathrm{KC_8}$.[2] Its unique electronic properties were determined by both X-ray crystallography and theoretical studies, which showed that the stability of an NHC adduct of a Group 14 element(0) can be rationalized purely by the superior σ-donating ability of the NHC.[3] The reactivity of $[\mathrm{IPr\rightarrow Si{=}Si\leftarrow IPr}]$ was recently examined.[4] Following this pioneer work, the heavier analogues $[\mathrm{IPr\rightarrow E{=}E\leftarrow IPr}]$ (E = Ge, Sn) were synthesized by the reaction of the NHC-stabilized germanium or tin dichloride $[\mathrm{IPr\rightarrow ECl_2}]$ (E = Ge, Sn) with the magnesium(I) dimer $[\mathrm{HC(CMeNMes)_2Mg}]_2$ (Mes = mesityl).[5] The chemistry of the Group 14 element(0) complex was further extended by modifying the electronic structure of the NHC, which results in the formation of a monoatomic Group 14 element(0) complex. The bis(NHC)-stabilized silylone and germylone complexes of composition $[\{\mathrm{bis(NHC)}\}\rightarrow \mathrm{E}]$ (where $\mathrm{bis(NHC)} = \mathrm{H_2C[\{NC(H)C(H)N(Ar)\}C{:}]_2}$; E = Si, Ge) were synthesized by the reduction of the corresponding silyliumylidene and germyliumylidene cation, in which the $\mathrm{E^0}$ atom retains its valance electrons as two lone pairs.[6] When the IPr and bis(NHC) were replaced by two cyclic alkyl amino carbene ligands (cAAC) with enhanced nucleophilicity and electrophilicity, the resulting Group 14 element(0) complexes $[\mathrm{cAAC\rightleftarrows Si{=}Si\rightleftarrows cAAC}]$ and $[\mathrm{cAAC\rightleftarrows E\rightleftarrows cAAC}]$ (E = Si and Ge) exhibit different electronic properties and $[\mathrm{cAAC\rightleftarrows E\rightleftarrows cAAC}]$ (E = Si and Ge) have a biradicaloid character.[7,8]

In sharp contrast to $[\mathrm{IPr\rightarrow E{=}E\leftarrow IPr}]$ and $[\{\mathrm{bis(NHC)}\}\rightarrow \mathrm{E}]$ complexes (E = Si, Ge), the chemical bonding situation in heavier analogues $[\mathrm{R_2E{:}\rightarrow E\leftarrow{:}ER_2}]$ (E = Si, Ge) is still open to debate. Recently, Kira and co-workers synthesized a series of stable heavier allene analogues **A**, which are strongly bent at the central E′ atom of the allene skeleton (122–137°) and the E=E′ bonds have double bond character (Scheme 1).[9] Their theoretical studies rationalized the strongly bent skeleton in these compounds which results from the Jahn–Teller distortion associated with the π–σ* mixing.[9] In contrast, Frenking et al. disputed that the heavier allene analogues should be interpreted as a ylidone **B** stabilized by two silylene or germylene moieties (Scheme 1).[10] Further calculations by Apeloig and co-workers and Veszprémi et al. showed that the parent trisilaallene $[\mathrm{H_2Si{=}Si{=}SiH_2}]$ has a very complex mixture of isomers which have different electronic structures, such as zwitterionic allylium and trisilacyclopropylidene.[11] These theoretical studies revealed that both structural and electronic properties of heavier allene analogues greatly depend on the substituent effects at the terminal E atoms. In this context, Sekiguchi et al. synthesized the trisilaallene $[(t\mathrm{Bu_2MeSi})_2\mathrm{Si{=}Si{=}Si(SiMe}t\mathrm{Bu_2)_2}]$ bearing bulkier silyl ligands.[9f] The molecule is slightly bent (164.3°), which greatly influences its electronic properties resulting in different reactivity for regioselective addition compared with that of **A**. To date, no solid experimental evidence has been reported for the existence of a ylidone **B** stabilized by two silylene or germylene moieties. In other words, the ability of a low-valent Group 14 carbene analogue $\{\mathrm{R_2E{:}}\}$ to stabilize a Group 14 element(0) fragment has not yet been established.



Scheme 1. Stable heavier allene analogues **A**.

---

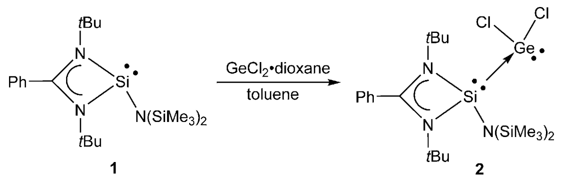
[*] Y.-L. Shan, Dr. C.-W. So
Division of Chemistry and Biological Chemistry
Nanyang Technological University
21 Nanyang Link, 637371 (Singapore)
E-mail: CWSo@ntu.edu.sg
Dr. W.-L. Yim
Institute of High Performance Computing
Agency for Science, Technology, and Research
1 Fusionopolis Way, No. 16-16 Connexis, 138632 (Singapore)
E-mail: yimwl@ihpc.a-star.edu.sg

[**] This work is supported by an AcRF Tier 1 Grant. W.-L.Y. acknowledges the A*STAR Computational Resource Centre (A*CRC) for computing facilities.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201408347.

Recently, N-heterocyclic silylene (NHSi) ligands have emerged as a prominent ligand class in the coordination chemistry of transition metals in the zero oxidation state.[12] The application of transition metal(0)–NHSi complexes toward the activation of small molecules and catalytic transformations was also investigated.[13,14] In parallel with their coordination chemistry, we anticipate that a NHSi ligand is capable of stabilizing main-group elements in the zero oxidation state, although such chemistry is unknown. Additionally, it is highly beneficial to explore whether and how a NHSi ligand stabilizes a Group 14 element(0) compound as the NHSi exhibits different structural and electronic properties compared with those of silylene moieties, $[Si(SiMe\mathit{t}Bu_2)_2]$ and $[Si\{C(SiMe_3)_2CH_2\}_2]$, in the heavier allene analogues. Thus, a NHSi-stabilized Group 14 element(0) complex should be a worthwhile synthetic target not only for fundamental bonding studies but also for its possible application in the activation of small molecules. Herein, we report the utilization of an amidinate-stabilized silicon(II) amide $[LSiN(SiMe_3)_2]$ ($L = PhC(N\mathit{t}Bu)_2$) to stabilize a digermanium(0) moiety by a weak synergic donor–acceptor interaction.

The reaction of the amidinate-stabilized silicon(II) amide $[LSiN(SiMe_3)_2]$ (**1**)[15] with $GeCl_2$·dioxane in toluene afforded the silicon(II)–germanium(II) adduct $[L\{(Me_3Si)_2N\}Si\rightarrow GeCl_2]$ (**2**; Scheme 2), which was isolated as an air- and moisture-sensitive colorless crystalline solid in high yield (73 %).[16] Although the coordination chemistry of NHSi toward transition metals and of the NHC-stabilized silylene toward main-group elements have been investigated extensively,[12,17] compound **2** is the first NHSi adduct of Group 14 compounds. The ^1H NMR spectrum displays one set of resonance signals which can be attributed to protons on the amidinate ligand and $SiMe_3$ substituents. The ^{29}Si NMR spectrum shows a resonance signal for the Si^{II} center ($\delta = 2.76$ ppm) which has undergone an expected downfield shift compared with that of **1** ($\delta = -8.07$ ppm) as the lone-pair electrons on the Si^{II} center are donated to the vacant orbital on the Ge^{II} atom. The signal also shows a downfield shift compared with that of the NHC/tungsten-stabilized Si^{II}–Ge^{II} adduct $[IPrSi(Cl_2)Ge(Cl_2)W(CO)_5]$ ($\delta = -6.1$ ppm).[18]



Scheme 2. Synthesis of the silicon(II)–germanium(II) adduct $[L\{(Me_3Si)_2N\}Si\rightarrow GeCl_2]$ (**2**). $L = PhC(N\mathit{t}Bu)_2$.

The single-crystal X-ray structure of **2** (Figure 1) shows that the amidinate ligand is bidentate coordinated to the Si1 atom, which adopts a tetrahedral geometry. The Ge1 atom displays a distorted trigonal pyramidal geometry (the sum of the bond angles = 281.8°), which indicates the presence of a lone pair on the Ge1. The Si1–Ge1 bond (2.5259(13) Å) is significantly longer than typical Si–Ge single bonds (2.40–2.45 Å)[19] and is also longer than the Si–Ge bond in the NHC/tungsten-stabilized Si^{II}–Ge^{II} adduct $[IPrSi(H_2)Ge(H_2)W(CO)_5]$ (2.3717(14) Å),[18] which indicates that the Si1–Ge1 bond is a coordinative covalent bond.

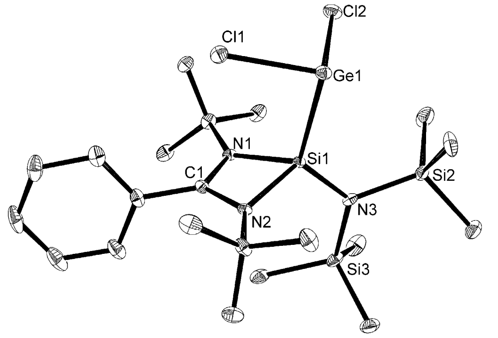
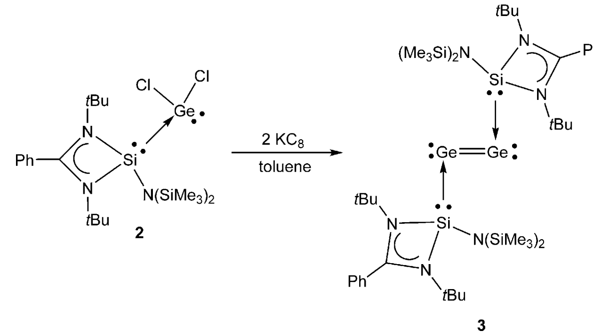


Figure 1. Molecular structure of compound **2** (thermal ellipsoids set at 30% probability). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1–Ge1 2.5259(13), Si1–N1 1.825(4), Si1–N2 1.823(4), Si1–N3 1.717(5); Cl1-Ge1-Cl2 97.36(6), Cl1-Ge1-Si1 91.53(5), Cl2-Ge1-Si1 92.89(5), N1-Si1-N2 71.93(19), N1-Si1-N3 115.3(2), N2-Si1-N3 114.3(2).

Compound **2** reacted with two equivalents of KC_8 in toluene at room temperature to afford the complex $[L\{(Me_3Si)_2N\}Si\rightarrow Ge{=}Ge\leftarrow Si\{N(SiMe_3)_2\}L]$ (**3**; Scheme 3), which was isolated as an air- and moisture-sensitive dark-red crystalline solid in low yield (16 %). The NHC analogue $[IPr\rightarrow Ge{=}Ge\leftarrow IPr]$ has been reported by Jones et al.[5a] Compound **3** decomposes at 154 °C. The ^1H NMR spectrum shows one set of resonance signals for protons on the amidinate and $N(SiMe_3)_2$ ligands. The ^{29}Si NMR spectrum shows a resonance signal for the Si^{II} center ($\delta = 30.8$ ppm) which is shifted more downfield compared with that of **2**. A similar downfield shift is detected by comparing the resonance signals in the ^{13}C NMR spectrum which are attributable to the $C_{carbene}$ centers in $[IPr\rightarrow Ge{=}Ge\leftarrow IPr]$ ($\delta = 203.3$ ppm) and $[IPr\rightarrow GeCl_2]$ ($\delta = 175.3$ ppm).[5a]



Scheme 3. Synthesis of $[L\{(Me_3Si)_2N\}Si\rightarrow Ge{=}Ge\leftarrow Si\{N(SiMe_3)_2\}L]$ (**3**). $L = PhC(N\mathit{t}Bu)_2$.

The X-ray crystal structure of **3** (Figure 2) shows that the SiGeGeSi skeleton has a *trans*-bent (Ge1-Ge1A-Si: 91.95(6)°) and planar geometry. A similar *trans*-bent geometry is found in $[IPr\rightarrow Ge{=}Ge\leftarrow IPr]$ (C-Ge-Ge: 89.87(8)°).[5a] Additionally, the Si1 atom adopts a tetrahedral geometry

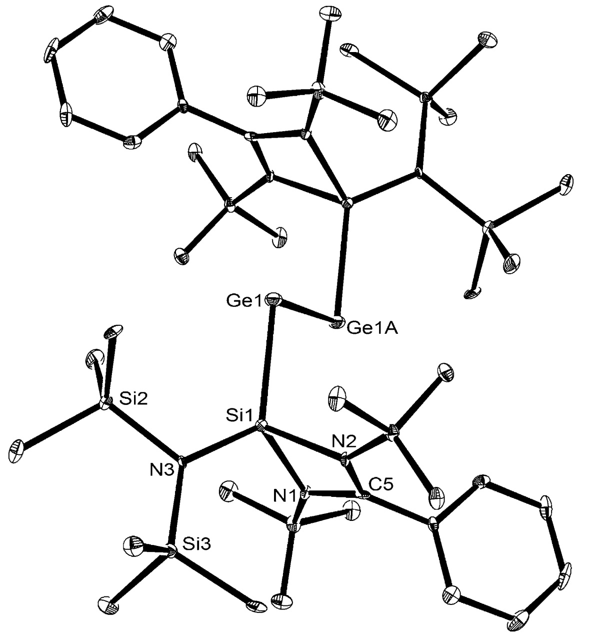


Figure 2. Molecular structure of compound **3** (thermal ellipsoids set at 30% probability). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ge1–Ge1A 2.3518(16), Si1–Ge1 2.406(2), Si1–N1 1.859(6), Si1–N2 1.866(5), Si1–N3 1.741(5); Si1-Ge1-Ge1A 91.95(6), N1-Si1-Ge1 123.2(2), N2-Si1-Ge1 108.67(18), N3-Si1-Ge1 121.2(2), N1-Si1-N2 70.2(2).

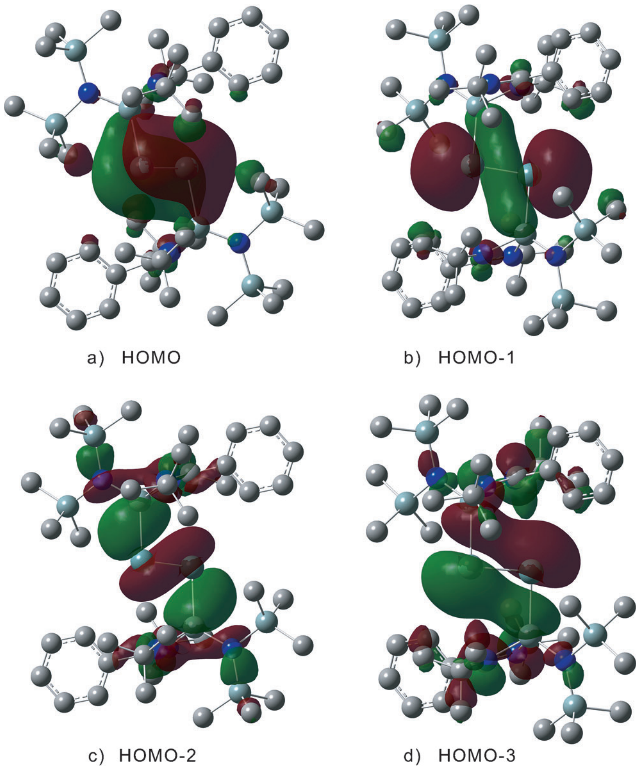


Figure 3. Selected molecular orbitals of **3** as determined by density functional calculations.

comparable to that in **2**. The Ge1–Ge1A bond (2.3518(16) Å) is comparable in length with that in [IPr→Ge=Ge←IPr] (2.3490(8) Å) and typical >Ge=Ge< double bonds in digermenes (2.344 Å).[5a] It is noteworthy that the Ge1–Si1 bond (2.406(2) Å) is significantly longer than that in the 2-germadisilaallene (2.2370(7) Å).[9] It is slightly shorter than that in **2** and is well within typical Si–Ge single bond lengths (2.40–2.45 Å).[19]

To understand the bonding nature in compound **3**, density functional calculations were conducted.[20] The optimized geometry (PBE-vdW-DF level; see Table S1 in the Supporting Information) is in good agreement with the X-ray crystallographic data. The HOMO (highest occupied molecular orbital) shows the Ge–Ge π orbital interacting with the empty p orbital on the Si atoms (Figure 3). Such π-backbonding interactions, which are absent in [IPr→Ge=Ge←IPr],[5a] are considered to be key for the stabilization of a NHSi adduct of a Group 14 element(0) and allow for its isolation. This also results in the shortening of the Ge–Si bonds, which is consistent with the X-ray crystallographic data. Similar π-back-bonding interactions can be detected in the cAAC-stabilized Group 14 element(0) complexes.[7,8] The HOMO-1 is located primarily on the Ge–Ge σ orbital, whereas the HOMO-2 shows the donor–acceptor interaction between the lone-pair orbitals on the Si atoms and the vacant p orbitals on the Ge atoms. The HOMO-3 is located primarily on the lone-pair orbitals of the Ge atoms.

Bader analysis was performed (Table S2), which shows bond critical points (BCPs) with (3,−1) character along the Si–Ge and Ge–Ge bonds. The high ellipticity (ε_{BCP}) and delocalization index (DI) of the Ge1–Ge1A bond ($\varepsilon_{BCP} = 0.191$, DI = 1.679), which are comparable with those of $H_2Ge{=}GeH_2$ ($\varepsilon_{BCP} = 0.243$, DI = 1.821), imply that the Ge1–Ge1A bond has a significant double-bond character. Additionally, the ellipticity of the Si1–Ge1 bond ($\varepsilon_{BCP} = 0.073$) is intermediate between that of $H_2Si{=}GeH_2$ ($\varepsilon_{BCP} = 0.623$) and $H_3Si{-}GeH_3$ ($\varepsilon_{BCP} = 1.19\times10^{-5}$), suggesting that there is a weak π-back-bonding interaction from the digermanium(0) {:Ge=Ge:} to the NHSi, which is consistent with the HOMO. The small Laplacian $\nabla^2\rho_{BCP}$ value (−0.0104 a.u.) and NPA charges (Si = 1.68, Ge = −0.53) also imply a donor–acceptor character of the Si–Ge bonds. It is noteworthy that the electron density of the Si–Ge bonds ($\rho_{BCP} = 0.070$ a.u.) is smaller than that of $H_3Si{-}GeH_3$ ($\rho_{BCP} = 0.090$ a.u.) and $H_2Si{=}GeH_2$ ($\rho_{BCP} = 0.103$), which reveals that the bond strength of the $Si\rightleftarrows Ge$ donor–acceptor interaction in **3** is significantly weaker than that of a Si–Ge single bond.

In conclusion, we have reported the synthesis of the first NHSi adduct of digermanium(0) by a simple procedure. X-ray crystallography and theoretical studies show conclusively that a singlet germanium(0) dimer {:Ge=Ge:} is stabilized by two NHSi ligands through a weak synergic donor–acceptor interaction. These results provide a confirmation of Frenking's prediction that the stabilization of a ylidone by low-valent heavier Group 14 carbene moieties should be possible. We will report this type of complex and other NHSi adducts of metals in their zero oxidation state in due course.

Received: August 18, 2014
Revised: September 11, 2014

Keywords: carbene homologues · density functional calculations · germanium · silicon · zero oxidation state

[1] a) Y. Wang, G. H. Robinson, *Inorg. Chem.* **2011**, *50*, 12326–12337; b) Y. Wang, G. H. Robinson, *Dalton Trans.* **2012**, *41*, 337–345.

[2] Y. Wang, Y. Xie, P. Wei, R. B. King, H. F. Schaefer III, P. v. R. Schleyer, G. H. Robinson, *Science* **2008**, *321*, 1069–1071.

[3] D. J. D. Wilson, S. A. Couchman, J. L. Dutton, *Inorg. Chem.* **2012**, *51*, 7657–7668.

[4] a) M. Y. Abraham, Y. Wang, Y. Xie, P. Wei, H. F. Schaefer, P. v. R. Schleyer, G. H. Robinson, *J. Am. Chem. Soc.* **2011**, *133*, 8874–8876; b) M. Chen, Y. Wang, Y. Xie, P. Wei, R. J. Gilliard, Jr., N. A. Schwartz, H. F. Schaefer III, P. v. R. Schleyer, G. H. Robinson, *Chem. Eur. J.* **2014**, *20*, 9208–9211.

[5] a) A. Sidiropoulos, C. Jones, A. Stasch, S. Klein, G. Frenking, *Angew. Chem. Int. Ed.* **2009**, *48*, 9701–9704; *Angew. Chem.* **2009**, *121*, 9881–9884; b) C. Jones, A. Sidiropoulos, N. Holzmann, G. Frenking, A. Stasch, *Chem. Commun.* **2012**, *48*, 9855–9857.

[6] a) Y. Xiong, S. Yao, S. Inoue, J. D. Epping, M. Driess, *Angew. Chem. Int. Ed.* **2013**, *52*, 7147–7150; *Angew. Chem.* **2013**, *125*, 7287–7291; b) Y. Xiong, S. Yao, G. Tan, S. Inoue, M. Driess, *J. Am. Chem. Soc.* **2013**, *135*, 5004–5007.

[7] a) K. C. Mondal, H. W. Roesky, M. C. Schwarzer, G. Frenking, B. Niepoetter, H. Wolf, R. Herbst-Irmer, D. Stalke, *Angew. Chem. Int. Ed.* **2013**, *52*, 2963–2967; *Angew. Chem.* **2013**, *125*, 3036–3040; b) K. C. Mondal, P. P. Samuel, M. Tretiakov, A. P. Singh, H. W. Roesky, A. C. Stueckl, B. Niepoetter, E. Carl, H. Wolf, R. Herbst-Irmer, D. Stalke, *Inorg. Chem.* **2013**, *52*, 4736–4743; c) Y. Li, K. C. Mondal, H. W. Roesky, H. Zhu, P. Stollberg, R. Herbst-Irmer, D. Stalke, D. M. Andrada, *J. Am. Chem. Soc.* **2013**, *135*, 12422–12428.

[8] K. C. Mondal, P. P. Samuel, H. W. Roesky, R. R. Aysin, L. A. Leites, S. Neudeck, J. Luebben, B. Dittrich, N. Holzmann, M. Hermann, G. Frenking, *J. Am. Chem. Soc.* **2014**, *136*, 8919–8922.

[9] a) S. Ishida, T. Iwamoto, C. Kabuto, M. Kira, *Nature* **2003**, *421*, 725–727; b) T. Iwamoto, T. Abe, C. Kabuto, M. Kira, *Chem. Commun.* **2005**, 5190–5192; c) T. Iwamoto, H. Masuda, C. Kabuto, M. Kira, *Organometallics* **2005**, *24*, 197–199; d) M. Kira, T. Iwamoto, S. Ishida, H. Masuda, T. Abe, C. Kabuto, *J. Am. Chem. Soc.* **2009**, *131*, 17135–17144. For other examples of heavier allene analogues, see: e) N. Wiberg, H.-W. Lerner, S.-K. Vasisht, S. Wagner, K. Karaghiosoff, H. Noth, W. Ponikwar, *Eur. J. Inorg. Chem.* **1999**, 1211–1218; f) H. Tanaka, S. Inoue, M. Ichinohe, M. Driess, A. Sekiguchi, *Organometallics* **2011**, *30*, 3475–3478.

[10] a) N. Takagi, T. Shimizu, G. Frenking, *Chem. Eur. J.* **2009**, *15*, 3448–3456; b) N. Takagi, T. Shimizu, G. Frenking, *Chem. Eur. J.* **2009**, *15*, 8593–8604; c) G. Frenking, R. Tonner, S. Klein, N. Takagi, T. Shimizu, A. Krapp, K. K. Pandey, P. Parameswaran, *Chem. Soc. Rev.* **2014**, *43*, 5106–5139.

[11] a) M. Kosa, M. Karni, Y. Apeloig, *J. Chem. Theory Comput.* **2006**, *2*, 956–964; b) M. Kosa, M. Karni, Y. Apeloig, *J. Am. Chem. Soc.* **2004**, *126*, 10544–10545; c) T. Veszprémi, K. Petrov, C. T. Nguyen, *Organometallics* **2006**, *25*, 1480–1484.

[12] B. Blom, M. Stoelzel, M. Driess, *Chem. Eur. J.* **2013**, *19*, 40–62.

[13] A. Meltzer, S. Inoue, C. Präsang, M. Driess, *J. Am. Chem. Soc.* **2010**, *132*, 3038–3046.

[14] A. Fürstner, H. Krause, C. W. Lehmann, *Chem. Commun.* **2001**, 2372–2373.

[15] S. S. Sen, J. Hey, R. Herbst-Irmer, H. W. Roesky, D. Stalke, *J. Am. Chem. Soc.* **2011**, *133*, 12311–12316.

[16] For details of the experimental procedure, see the Supporting Information.

[17] E. Rivard, *Dalton Trans.* **2014**, *43*, 8577–8586.

[18] S. M. I. Al-Rafia, A. C. Malcolm, R. McDonald, M. J. Ferguson, E. Rivard, *Angew. Chem. Int. Ed.* **2011**, *50*, 8354–8357; *Angew. Chem.* **2011**, *123*, 8504–8507.

[19] K. M. Baines, W. G. Stibbs, *Coord. Chem. Rev.* **1995**, *145*, 157–200.

[20] For details of theoretical studies and references, see the Supporting Information.