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A Cyclic Germadycarbene ("Germylone") from Germyliumylidene

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Supporting Information

ABSTRACT: By employing the chelate dicarbene **1**, the new chlorogermyliumylidene complex **2** could be synthesized and isolated in 95% yield. Dechlorination of **2** with sodium naphthalenide furnishes the unique cyclic germadycarbene **3** which could be isolated in 45% yield. Compound **3** is the first isolable Ge(0) complex with a single germanium atom stabilized by a dicarbene. Its molecular structure is in accordance with DFT calculations which underline the peculiar electronic structure of **3** with two lone pairs of electrons at the Ge atom.

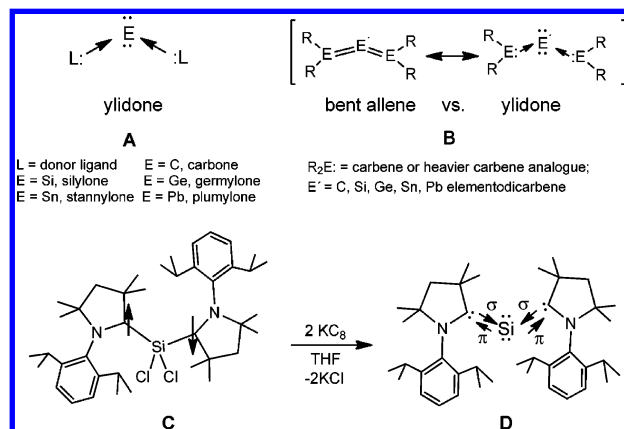
Recently, the use of N-heterocyclic carbenes (NHCs) as ligands to stabilize Group 14 elements in the zero oxidation state has attracted significant research interest. For example, through dechlorination of the NHC-stabilized compounds $\text{NHC} \rightarrow \text{SiCl}_4$ and $\text{NHC} \rightarrow \text{GeCl}_2$ (NHC = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) the groups of Robinson¹ and Jones² were able to isolate the fascinating Si(0) and Ge(0) species $\text{L} \rightarrow \text{Si} \leftarrow \text{Si} \leftarrow \text{L}$ and $\text{L} \rightarrow \text{Ge} \leftarrow \text{Ge} \leftarrow \text{L}$ (L = NHC), respectively. In the latter compounds each Si(0) and Ge(0) atom features one lone pair of electrons. Another striking new class of compounds with Group 14 atoms represents the so-called ylidenes $\text{L} \rightarrow \text{E} \leftarrow \text{L}$ (Scheme 1, A), (L = donor ligand, E = C – Pb),³ in which the E atom retains its valence electrons as two lone pairs and the bonding situation between the two donor ligands L: and the single atom E can be best described in terms of donor–acceptor interactions; they are expected to possess unusual reactivity owing to the peculiar electronic structures in accordance with results from theoretical

calculations reported by the research groups of Frenking^{3a–g} and Apeloig.^{3h} Accordingly, the isolated and structurally characterized bent allenes reported by the groups of Bertrand^{4a} and Regitz,^{4b} as well as the heavier Group 14 analogues (trisilaallene, trigermaallene, and 1,3-digermasilaallene) published by the groups of Kira⁵ and Wiberg (tristannaallene),⁶ should rather be interpreted as ylidenes (Scheme 1, B), since these compounds have bent structures with nonlinear E–E–E bond angles (E = C – Sn) ranging from 122 to 156°, and the four substituents at the terminal E atoms deviate from orthogonal arrangement as in genuine allenes.^{3–6}

In order to synthesize isolable ylidenes, carbenes have proven to serve as suitable donors, although even phosphanes⁷ and heavier carbene analogues have been employed successfully as mentioned above. Very recently, Roesky and Frenking et al. reported the first silylone $(\text{L})_2\text{Si}$ **D** (Scheme 1),^{8a} bearing the cyclic alkyl amino carbene (cAAC) L: . Compound **D** results from dechlorination of the precursor **C** with KC_8 (Scheme 1).^{8b} The latter investigations revealed that, in contrast to the remarkable biradical electronic structure of precursor **C**, the siladycarbene **D** is a silylone instead of a Si(II) silylene. However, **D** has a closed-shell singlet ground state with a non-negligible contribution from the singly excited state owing to the low electronic excitation energy (small HOMO–LUMO gap). In other words, **D** has a biradicaloid character. The two carbene ligands L: in **D** coordinate to the Si atom in a much more acute C–Si–C bond angle of 117° compared with those observed for **B** (122–156°). The slightly shorter Si–C bond distance of 1.841(2) Å in **D** than the calculated value for $(\text{NHC})_2\text{Si}$ (1.869 Å)^{3e–g} exhibits the better π acceptor properties of the cAAC ligand than NHC,^{8a} which is reflected by its frontier orbitals: its HOMO is a π -type orbital which has the largest extension at Si but exhibits significant Si–C π bonding. NBO analysis of the siladycarbene **D** gives one σ lone-pair orbital and a three-center C–Si–C π orbital with 40% at Si and 30% at each C atom as shown in Scheme 1.^{8a}

Taking into account that chelate ligands with strong push–pull effect^{4a,9} will lead automatically to acute bending angles, we planned to synthesize ylidenes of type E (Scheme 2). Recently, we described the coordination properties of the chelate ligand 1,8-bis(tributylphosphazenylnaphthalene toward Si(II) and Ge(II) which furnishes the potential chlorosilyliumylidene precursors **F** and its Ge analogue **G**, respectively (Scheme 2).¹⁰ However, their reduction reactions with KC_8 did not lead to the desired ylide **H** but to reduction of the chelate ligand. This can be explained by DFT calculations which revealed that the

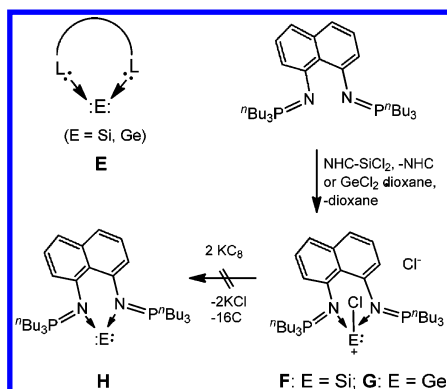
Scheme 1. Dicoordinate E(0) Complexes



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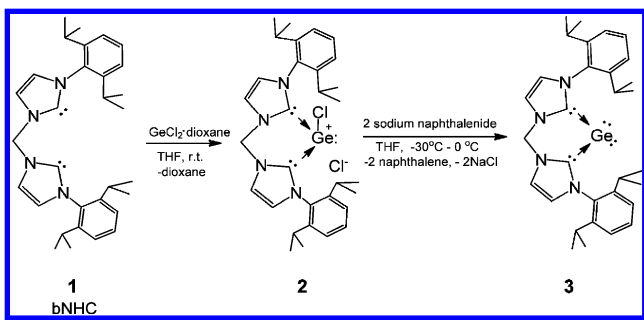
Scheme 2. Attempts To Prepare Ylidones Featuring Chelate Ligands



LUMOs of F and G are mainly represented by the π system of the naphthalene moiety.

Based on the formation of F and G and inspired by the successful preparation of D we explored the reactivity of the bis-N-heterocyclic carbene (bNHC) 1 (Scheme 3) toward

Scheme 3. Generation of the Chlorogermylumylidene Chloride 2, Starting from bNHC 1, and Its Dechlorination to the Cyclic Germadycarbene (“Germylone”) 3



$\text{GeCl}_2 \cdot \text{dioxane}$, aiming at synthesizing the first germadycarbene (“germylone”) E through dehalogenation (Scheme 2). To our best knowledge, the coordination ability of 1 has merely been investigated toward a few transition metals such as chromium¹¹ and iron,¹² but its utilization to stabilize low-valent p-block main-group elements has not yet been reported.

Similar to the formation of G, treatment of an equimolar amount of bNHC 1 with $\text{GeCl}_2 \cdot \text{dioxane}$ in THF at room temperature furnished the desired Ge(II) salt $[\text{bNHC-GeCl}]^+\text{Cl}^-$ 2 as an off-white powder in 95% yield (Scheme 3). Compound 2 is the first germylumylidene cation supported by a chelating bis-carbene. In contrast to G, compound 2 is insoluble in THF but soluble in acetonitrile, exhibiting its stronger ionicity. The high-resolution ESI-mass spectrum of 2 dissolved in acetonitrile gives in the positive mode a peak at $m/z = 577.21484$ (calcd 577.21478) corresponding to the $[\text{bNHC-GeCl}]^+$ cation. In comparison to 1, the donor ^{13}C carbene nuclei in 2 show an upfield shift ($\delta = 166$ ppm for 2 vs 220 ppm for 1) in the ^{13}C NMR spectrum. Single crystals of 2 suitable for X-ray diffraction analysis were grown in acetonitrile solutions at -20°C . Similar to G, the Ge(II) atom in 2 is three-fold coordinated by two carbon atoms from the bis-carbene ligand 1 and one chlorine atom (Figure 1); the chloride counterion is located far away from the Ge center (6.53 Å). The six-membered $\text{C}_3\text{N}_2\text{Ge}$ ring is puckered in a boat

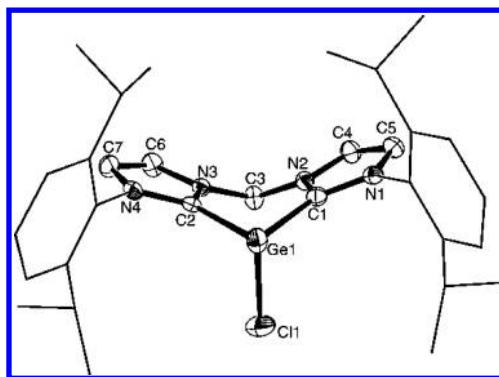


Figure 1. Molecular structure of the chlorogermylumylidene cation in 2. Thermal ellipsoids are drawn at the 50% probability level. H atoms, counteranion (Cl^-), and one acetonitrile lattice solvent molecule are omitted for clarity. Selected interatomic distances (Å) and angles ($^\circ$): Ge1–Cl1 2.310(1), Ge1–C1 2.058(3), Ge1–C2 2.057(3), C1–N1 1.349(4), C1–N2 1.341(4), C2–N3 1.347(4), C2–N4 1.385(5), C1–Ge1–C2 85.2(1), C1–Ge1–Cl1 91.8(1), C2–Ge1–Cl1 90.5(1), Ge1–C1–N1 129.1(2), Ge1–C1–N2 126.0(2), N1–C1–N2 104.8(3), Ge1–C2–N3 126.2(2), Ge1–C2–N4 128.8(2), N3–C2–N4 104.9(3).

conformation with N2, N3, C1, and C2 being nearly coplanar, and Ge1 and C3 displaced away from that plane in the same direction as the Ge–Cl bonding vector is pointing. The dihedral angle between the plane defined by C3, N2, N3 and the plane defined by N2, N3, C2, C1 is 38.7° , whereas the dihedral angle between the plane defined by Ge1, C1, C2 and the plane defined by N2, N3, C2, C1 is 18.4° . The Ge1–Cl1 bond in 2 is oriented nearly perpendicular to both Ge–C bonds, with Cl1–Ge1–C1 and Cl1–Ge1–C2 bond angles of 90.1° and 91.8° , respectively, which are smaller than those in G (average 95.8°). The sum of angles around the carbene carbon atoms in 2 is 359.90° and 359.88° , respectively, indicating a nearly ideal trigonal-planar geometry. The Ge1–Cl1 distance of 2.310(1) Å in 2 is longer than those in G (2.278(1) Å), in the NHC– GeCl_2 adduct (average 2.277 Å¹³), and in the related four-coordinate Ge(II) species 1,2,3,4-tetrakis(di-*tert*-butylmethylsilyl)-3,4-dichlorotetragermene (2.248(1) Å¹⁴) and $[\text{GeCl}(\text{pmdta})][\text{GeCl}_3]$ (2.266(2) Å¹⁵). In contrast, the Ge1–C1 (2.058(3) Å) and Ge1–C2 (2.057(3) Å) bond lengths in 2 are significantly shorter than that in NHC– GeCl_2 (2.112(2) Å),¹³ indicating a stronger interaction of the chelate carbene carbon atoms toward the Ge atom in 2 than that in NHC– GeCl_2 .

In order to gain more insight into the electronic features, DFT calculations (B3LYP/6-31G(d) level of theory) have been performed for the chlorogermylumylidene cation in 2. Geometry optimization of the latter yielded a structure similar to that observed experimentally. Its HOMO and LUMO are depicted in Figure 2. The HOMO is essentially a σ lone-pair orbital at the Ge(II) center. Strikingly, the LUMO consists mainly of a π -type orbital at Ge, which is in marked contrast to the situation of compounds F and G. In addition, a strong interaction between the chelate carbene carbons and the Ge center in the germylumylidene in 2 is supported by the Wiberg bond index values of the Ge–C bonds (0.608 and 0.611). We expected that these features may facilitate the two-electron reduction of the Ge(II) atom of the chlorogermylumylidene in 2 to give the desired germylone 3.

In fact, the dechlorination of 2 with sodium naphthalenide leads to the cyclic germadycarbene 3 (Scheme 3). When a cold

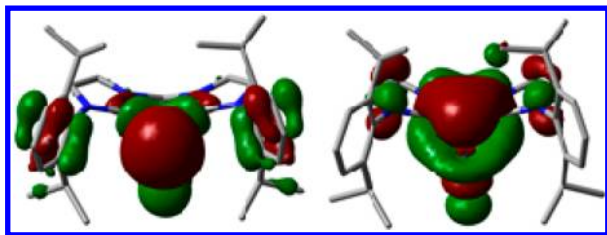


Figure 2. HOMO (left) and LUMO (right) of the chlorogermylumylidene cation in **2**. Hydrogen atoms are omitted for clarity.

solution of 2 molar equiv of sodium naphthalenide in THF ($-30\text{ }^{\circ}\text{C}$) was added to the suspension of **2** in THF ($-30\text{ }^{\circ}\text{C}$), the reaction mixture turned immediately dark red. Compound **3** could be isolated from toluene solutions of the reaction mixtures as dark red crystals in 45% yield. The dark red crystals of **3** dissolved in toluene showed UV–vis absorption bands at $\lambda = 286, 420,$ and 564 nm which are comparable with those found for the bent trigermaallene (trigermaylidone, $\lambda = 280, 380, 435, 496,$ and 630 nm)^{5b} and **D** (390 and 584 nm).^{8a} Interestingly, the chemical shift of the carbene carbons in **3**, compared to that of the precursor **2** ($\delta = 166\text{ ppm}$), appears downfield ($\delta = 196\text{ ppm}$) in the ^{13}C NMR spectrum, which is relatively close to that observed for the silylone **D** ($\delta = 210.9\text{ ppm}$).^{8a}

Compound **3** is extremely air and moisture sensitive. It exhibits also slight temperature sensitivity. Solutions of **3** in THF are stable for 2 days in a sealed NMR tube at room temperature and then show traces of “free” bNHC **1** (^1H NMR). Compound **3** crystallizes at $-20\text{ }^{\circ}\text{C}$ in toluene solutions in the monoclinic space group $P2_1/c$ (Figure 3). X-

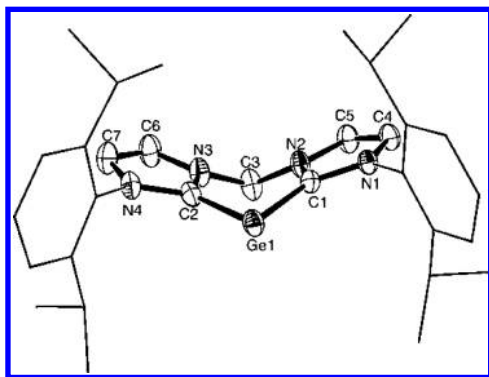


Figure 3. Molecular structure of **3**. Thermal ellipsoids are drawn at the 50% probability level. H atoms and toluene lattice solvent molecules are omitted for clarity. Selected interatomic distances (\AA) and angles ($^{\circ}$): Ge1–C1 1.965(3), Ge1–C2 1.961(3), C1–N1 1.382(4), C1–N2 1.378(4), C2–N3 1.377(4), C2–N4 1.375(4), C1–Ge1–C2 86.5(1), Ge1–C1–N2 128.6(2), Ge1–C1–N1 128.1(2), N1–C1–C2 103.3(1), Ge1–C2–N3 127.7(2), Ge1–C2–N4 129.0(2), N3–C2–N4 102.9(2).

ray diffraction analysis reveals that the Ge atom in **3** is two-coordinate with a C–Ge–C angle of $86.6(1)^{\circ}$. This angle is only slightly smaller than the corresponding value for the precursor **2** ($85.2(1)^{\circ}$), but much more acute than the Ge–Ge–Ge bond angle of the trigermaylidone of type **B** (Scheme 1) reported by Kira and co-workers (122.6°).^{5b} In fact, compound **3** represents the most bent allene or ylidone hitherto structurally characterized ($117\text{--}156^{\circ}$).^{4–6,8} Similar to **2**, the six-membered $\text{C}_3\text{N}_2\text{Ge}$ ring in **3** is also puckered in a boat conformation, but exhibits a larger dihedral angle between

the plane defined by C3, N2, N3 and the plane defined by N2, N3, C1, C2 (46° in **3** vs 38.7° in **2**), and a smaller dihedral angle between the plane defined by Ge1, C1, C2 and the plane defined by C1, C2, N2, N3 (13° in **3** vs 18.4° in **2**). In addition, the sum of angles around each carbene carbon atom in **3** (359.95° and 359.59°), just as in **2**, indicates an almost ideal trigonal-planar coordination geometry. The Ge–C bond distances of 1.967(2) and 1.962(2) \AA in **3** are significantly shorter by about 0.10 \AA than those in the precursor **2** (2.058(3) and 2.057(3) \AA), and distinctly shorter by about 0.15 \AA than that in NHC-GeCl_2 (2.112(2) \AA).¹² The short Ge–C bond distances in **3** are comparable to the Ge– C_{sp^2} single bond in $\text{Ph}_3\text{GeC(F)=CF}_2$ (1.969(6) \AA)¹⁶ but slightly longer than the Ge– C_{sp^3} single bonds in 9,10-dihydro-10-germa-9-silaanthracene (1.903–1.913 \AA)¹⁷ and 2,3,5,6-tetrakis(trimethylgermyl)-1,4-benzoquinones (1.941(6)–1.965(7) \AA).¹⁸

In order to shed light on the electronic nature of compound **3**, DFT calculations [B3LYP/6-31G(d)] were performed. The optimized structure of **3** in the singlet ground state is in good agreement with the metric data observed by X-ray analysis. Furthermore, it was found through DFT calculation that the structure with the first triplet state is by $33.2\text{ kcal mol}^{-1}$ less stable than the singlet ground state. The HOMO of **3** consists of the π -type orbital at the Ge center, including Ge–C π bonding (Figure 4, left). This π interaction (back-bonding)

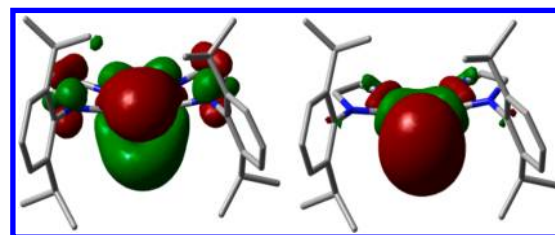


Figure 4. HOMO (left) and HOMO–1 (right) of cyclic germylidone **3**. Hydrogen atoms are omitted for clarity.

may explain the relatively short Ge–C bond lengths in **3**. On the other hand, the HOMO–1 represents a σ lone-pair orbital at Ge (Figure 4, right). In addition, the proton affinities (PA) of compound **3** were calculated to certificate the germylone character. The first and second values PA(1) PA(2) were estimated to be 279.6 and 175.0 kcal mol^{-1} , respectively. It follows from the relatively large value for PA(2) that compound **3** clearly possesses germylone character. These trends can also be observed in the acyclic silylone **D**,^{8a} and similar structural and electronic features of related species (carbene, silylone, germylone, etc.) have been theoretically predicted by Frenking and co-workers.³

In summary, we report here for the first time the bis-carbene-stabilized chlorogermylumylidene cation **2** which could be successfully dehalogenated by sodium naphthalenide to give the unique isolable cyclic germadicarbene (germylone) **3**. The latter contains a single Ge atom in the formal oxidation state zero which is coordinated by the bis-carbene chelate ligand **1**.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details for the synthesis, and spectroscopic and crystallographic (CIF) data for **2** and **3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Wang, Y.; Xie, Y.; Wie, P.; King, R. B.; Schaefer, H. F.; Schleyer, P. v. R.; Robinson, G. H. *Science* **2008**, *321*, 1069.
- (2) Sidiropoulos, A.; Jones, C.; Stasch, A.; Klein, S.; Preking, G. *Angew. Chem., Int. Ed.* **2009**, *48*, 9701.
- (3) (a) Tonner, R.; Frenking, G. *Angew. Chem., Int. Ed.* **2007**, *46*, 8695. (b) Tonner, R.; Frenking, G. *Chem.—Eur. J.* **2008**, *14*, 3260. (c) Tonner, R.; Frenking, G. *Chem.—Eur. J.* **2008**, *14*, 3273. (d) Tonner, R.; Frenking, G. *Pure Appl. Chem.* **2009**, *81*, 597. (e) Takagi, N.; Shimizu, T.; Frenking, G. *Chem.—Eur. J.* **2009**, *15*, 3448. (f) Takagi, N.; Shimizu, T.; Frenking, G. *Chem.—Eur. J.* **2009**, *15*, 8593. (g) Takagi, N.; Tonner, R.; Frenking, G. *Chem.—Eur. J.* **2012**, *18*, 1772. (h) Kosa, M.; Karni, M.; Apeloig, Y. *J. Chem. Theory Comput.* **2006**, *2*, 956.
- (4) (a) Dyker, C. A.; Lavallo, V.; Donnadieu, B.; Bertrand, G. *Angew. Chem., Int. Ed.* **2008**, *47*, 3206. (b) Hofmann, M. A.; Bergstrasser, U.; Reiss, G. J.; Nyulaszi, L.; Regitz, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 1261. (c) Fürstner, A.; Alcarazo, M.; Goddard, R.; Lehmann, C. W. *Angew. Chem., Int. Ed.* **2008**, *47*, 3210. (d) Alcarazo, M.; Lehmann, C. W.; Anoop, A.; Thiel, W.; Fürstner, A. *Nat. Chem.* **2009**, *1*, 295.
- (5) (a) Ishida, S.; Iwamoto, T.; Kabuto, C.; Kira, M. *Nature* **2003**, *421*, 725. (b) Kira, M. *Chem. Commun.* **2010**, *46*, 2893. (c) Iwamoto, T.; Masuda, H.; Kabuto, C.; Kira, M. *Organometallics* **2005**, *24*, 197. (d) Kira, M.; Iwamoto, T.; Ishida, S.; Masuda, H.; Abe, T.; Kabuto, C. *J. Am. Chem. Soc.* **2009**, *131*, 17135. (e) Tanaka, H.; Inoue, S.; Ichinohe, M.; Driess, M.; Sekiguchi, A. *Organometallics* **2011**, *30*, 3475.
- (6) Wiberg, N.; Lerner, H.-W.; Vasisht, S.-K.; Wagner, S.; Karaghiosoff, K.; Nöth, H.; Ponikvar, W. *Eur. J. Inorg. Chem.* **1999**, 1211.
- (7) Ramirez, F.; Desai, N. B.; Hansen, B.; McKelvie, N. *J. Am. Chem. Soc.* **1961**, *83*, 3539.
- (8) (a) Mondal, K. C.; Roesky, H. W.; Schwarzer, M. C.; Frenking, G.; Niepötter, B.; Wolf, H.; Herbst-Irmer, R.; Stalke, D. *Angew. Chem., Int. Ed.* **2013**, *52*, 2963. (b) Mondal, K. C.; Roesky, H. W.; Schwarzer, M. C.; Frenking, G.; Tkach, I.; Wolf, H.; Kratzert, D.; Herbst-Irmer, R.; Diepötter, B.; Stalke, D. *Angew. Chem., Int. Ed.* **2013**, *52*, 1801.
- (9) (a) Johnson, R. P. *Chem. Rev.* **1989**, *89*, 1111. (b) Christl, M. In *Modern Allene Chemistry*; Krause, N.; Hashmi, A. S. K., Eds.; Wiley-VCH: Weinheim, 2004; pp 243–357.
- (10) (a) Xiong, Y.; Yao, S.; Inoue, S.; Irran, E.; Driess, M. *Angew. Chem., Int. Ed.* **2012**, *51*, 10074. (b) Xiong, Y.; Yao, S.; Inoue, S.; Berkefeld, A.; Driess, D. *Chem. Commun.* **2012**, *48*, 12198.
- (11) Kreisel, K. A.; Yap, G. P. A.; Theopold, K. H. *Organometallics* **2006**, *25*, 4670.
- (12) (a) Zlatogorsky, S.; Muryn, C. A.; Tuna, F.; Evans, D. J.; Ingleson, M. J. *Organometallics* **2011**, *30*, 4974. (b) Zlatogorsky, S.; Ingleson, M. J. *Dalton Trans.* **2012**, *41*, 2685.
- (13) Thimer, K. C.; Al-Rafia, S. M. I.; Ferguson, M. J.; McDonald, R.; Rivard, E. *Chem. Commun.* **2009**, 7119.
- (14) Singh, A. P.; Roesky, H. W.; Carl, E.; Stalke, D.; Demers, J.-P.; Lange, A. *J. Am. Chem. Soc.* **2012**, *134*, 4998.
- (15) Cheng, F.; Dyke, J. D.; Ferrante, F.; Hector, A. L.; Levason, W.; Reid, G.; Webster, M.; Zhang, W. *Dalton Trans.* **2010**, *39*, 847.
- (16) Brisdon, A. K.; Crossley, I. R.; Pritchard, R. G.; Warren, J. E. *Inorg. Chem.* **2002**, *41*, 4748.

(17) McCarthy, W. Z.; Corey, J. Y.; Corey, E. R. *Organometallics* **1984**, *3*, 255.

(18) Tsutsui, S.; Sakamoto, K.; Yoshida, H.; Kunai, A. *Organometallics* **2004**, *23*, 1554.