Group 14 Compounds

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Stable N-Heterocyclic Carbene Complexes of Hypermetallyl Germanium(II) and Tin(II) Compounds**

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The chemistry of the heavier Group 14 element carbene analogues has received wide interest because of their special properties and reactivity.[1] Recently, an unexpected application of cyclopentadienyl, amido, or alkoxy germylenes and cyclic diazastannylene as precursors of nanomaterials has been described, thus opening a wide and promising field for investigation.[2] Germanium nanowires have also been obtained by decomposition of hexakis(trimethylsilyl)digermane,[3] highlighting the labile character of trimethylsilyl groups. Thus, the hypermetallyl germylenes or stannylenes, which contain both a low-coordinate Group 14 atom and a good leaving substituent, might be suitable candidates for nanomaterial alloys preparations.

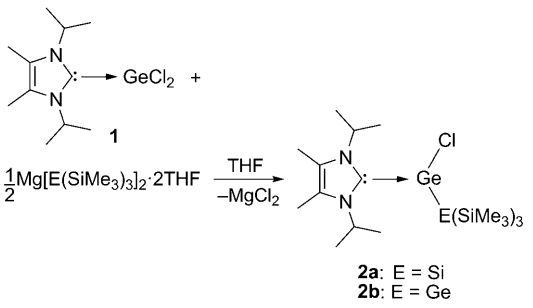
However, to the best of our knowledge, germylenes or stannylenes having electropositive silyl or germyl substituents have only been postulated as transient species; for example, in the reaction of Cl_2Ge•dioxane with $(Me_3Si)_3ELi$ (E = Si, Ge),[4] chloro(silyl)germylenes rapidly oligomerize with the formation of cyclotetragermanes $[(Me_3Si)_3EGeCl]_4$ or rearrange leading to cyclotrimetallanes $[(Me_3Si)_2E\{Ge(SiMe_3)_2\}E(SiMe_3)_2]$. To date, only one bis(hypersilyl)stannylene has been reported, but in its dimeric form in equilibrium with the monomeric form in solution and as a dimer in the solid state.[5] Recently, a thermally unstable bis(hypergermyl)stannylene was synthesized (requiring preparation and handling below −30 °C),[6] but like its hypersilyl substituted analogue, the X-ray structural analysis revealed the presence of dimers in the solid state. These results show the limitations of the steric shielding of the hypersilyl or hypergermyl ligands for the stabilization of low-coordinate species.

Among the stabilization strategies of germylenes or stannylenes, the intermolecular coordination has aroused a great interest in the last decades, particularly with the use of N-heterocyclic carbenes (NHC) as stabilizing co-ligand.[7] The first examples of carbene–germanium(II) adducts were described by Arduengo et al. ($(NHC)GeI_2$)[8] and then by Lappert et al. (NHC–heterocyclic germylene).[9] Later, NHCs were successfully employed for the stabilization of transient germanium(II) species.[10] In contrast, there are few examples of carbene–stannylene adducts.[11] In all of these cases, the carbene coordination is one of the key factors to obtain divalent species in their monomeric state.

Herein we describe the synthesis of hypermetallyl germylenes and stannylenes that are stabilized by complexation with carbene units. We investigated the reactivity of the carbene–germylene adduct **1**[10a] and of the carbene–stannylene adduct **3**,[12] which were obtained as previously reported from the known carbene $[:C\{N(iPr)C(Me)\}_2]$[13] and Cl_2Ge•dioxane or Cl_2Sn, respectively, towards various sources of hypermetallyl units.

All attempts to displace the chloride from germylenes with hypersilyl salts $(Me_3Si)_3SiLi$[14] or $(Me_3Si)_3SiK$[15] were unsuccessful and led to complex mixtures in which only some amounts of disilagermirane $[(Me_3Si)_2Si\{Ge(SiMe_3)_2\}Si(SiMe_3)_2]$ could be identified.[4a] The latter has been previously obtained by mixing $(Me_3Si)_3SiLi$ and Cl_2Ge•dioxane. By contrast, treatment of **1** with one half equivalent of $[(Me_3Si)_3Si]_2Mg$[16] in THF solution at room temperature gave the complex **2a** as the only product in a good yield (71%) (Scheme 1).

Compound **2a** is the first example of a donor-stabilized hypersilyl(chloro)germylene that could be isolated by the combination of both steric hindrance of the hypersilyl ligand and strong Lewis base coordination. Similarly, the addition of a stoichiometric amount of digermylmagnesium $[(Me_3Si)_3Ge]_2Mg$[17] to **1** produces the hypergermyl-



Scheme 1. Syntheses of carbene-stabilized hypermetallyl-(chloro)germylenes.

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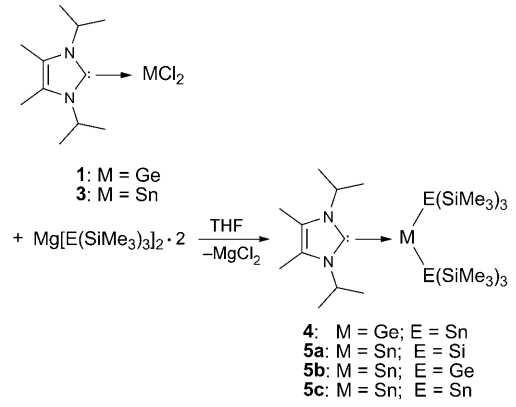
(chloro)germylene **2b** in a moderate yield (45%). In this case as well, the carbene coordination allows the sole formation of the chlorogermanium(II) species into its monomeric state by preventing its polycondensation in cyclic tetragermane.[4b] Thus, although the Ge and Si atoms exhibit some differences in their atomic radius (1.20 Å for Ge and 1.11 Å for Si)[18] and in their electronegativity (2.01 and 1.90), $(Me_3Si)_3Si$ and $(Me_3Si)_3Ge$ groups appear to induce similar substituent effects.[4b] In contrast, using the same experimental process did not afford the corresponding hyperstannyl-(chloro)germylene: we have only been able to isolate the bis(hyperstannyl)germylene **4** in a moderate yield (30%). However, the later was prepared nearly quantitatively using one equivalent of distannylmagnesium[19] (Scheme 2).



Scheme 2. Syntheses of carbene-stabilized hypermetallyl germylene and stannylenes.

For the carbene-stabilized stannylene analogue **3**,[12] we observed the exclusive formation of bis(hypermetallyl)tin(II) derivatives **5** in all cases (Scheme 2). This great difference with the corresponding germylene analogue is probably due to the larger covalent radius of the tin atom (1.39 Å)[18] compared to that of germanium.

All of the compounds **2**, **4**, and **5** are stable in the solid state at room temperature for a few days, with the exception of the stannylenes **5b–c**, which slowly decompose after 24 h. They can be stored at low temperatures (−24 °C) under an inert atmosphere for months. In solution, their stability decreases when going from hypersilyl to hyperstannyl substituents, in agreement with their decreasing steric hindrance.

The products were characterized by multinuclear NMR spectroscopy. The ^{1}H NMR spectra reveal very similar chemical shifts for the Me_3Si groups and either a 1/1 ratio between the carbene and the $(Me_3Si)_3E$ fragment for compounds **2** or a 1/2 ratio for **4** and **5**. The carbene signals (Me on the C=C double bond and *i*Pr groups) are non equivalent in the disubstituted derivatives **4** and **5** owing to a slow rotation around the $M–C_{carbene}$ bond on the NMR timescale. The ^{13}C NMR spectra exhibit significantly upfield-shifted resonances for the carbenic carbons ($\delta = 170$–175 ppm) in comparison to that of the free carbene[13] ($\delta = 206$ ppm), in agreement with a carbene coordination.[20] The hypersilyl derivatives **2a** and **5a** display characteristic ^{29}Si NMR signals at $\delta = -7.57$ and $\delta = -7.16$ ppm, which were assigned to the Me_3Si groups and at $\delta = -119.12$ and $\delta = -131.62$ ppm corresponding to the silicon of the $Si(SiMe_3)_3$ ligand. For **5a**, additional $^{117/119}$Sn satellites with a $^2J_{Si–Sn}$ coupling of 47.6 Hz were observed. The ^{119}Sn NMR spectra of tin(II) complexes **5a–c** displayed singlet resonances at $\delta = -196.8$, -115.0, and -138.3 ppm, respectively, in agreement with the electronegativity of E; they are upfield relative to the range (from $\delta = -240$ to -350 ppm) of three-coordinate triamidotin.[21]

The molecular structures of **2a** (Figure 1), **4** (Figure 2), and **5a** and **5c** (Figure 3) were unambiguously determined by single-crystal X-ray diffraction studies. These analyses showed similar features in the solid state, consisting of an almost planar environment around the carbenic carbon atom

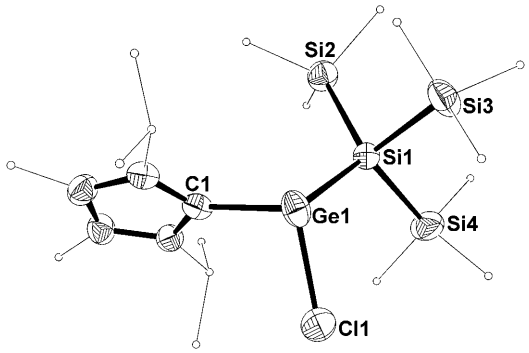


Figure 1. Molecular structure of compound **2a** in the solid state (ellipsoids set at 50% probability). For clarity, hydrogen atoms and crystallization solvent (toluene) have been omitted and methyl/isopropyl groups are simplified. Selected bond distances [Å] and bond angles [°]: Ge1–C1 2.093(3), Ge1–Si1 2.510(1), Ge1–Cl1 2.325(1), Si1–Si2 2.361(2), Si1–Si3 2.353(2), Si1–Si4 2.359(2); C1-Ge1-Cl1 97.21(8), C1-Ge1-Si1 104.92(8), Si1-Ge1-Cl1 99.87(3).

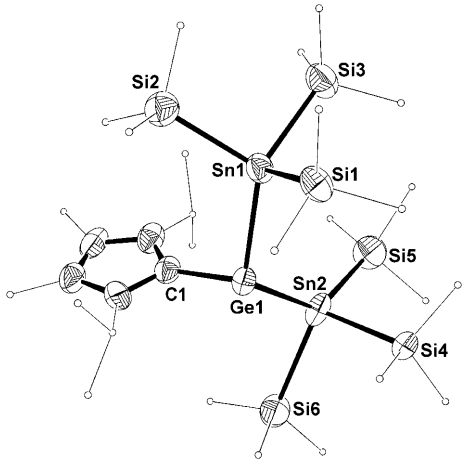


Figure 2. Molecular structure of compound **4** in the solid state (ellipsoids set at 50% probability). For clarity, hydrogen atoms and disorder are omitted and methyl/isopropyl groups are simplified. Selected bond distances [Å] and bond angles [°]: Ge1–C1 2.082(4), Ge1–Sn1 2.703(1), Ge1–Sn2 2.686(1), Sn1–Si1 2.606(9), Sn1–Si2 2.569(4), Sn1–Si3 2.562(5), Sn2–Si4 2.573(2), Sn2–Si5 2.674(4), Sn2–Si6 2.730(5); C1-Ge1-Sn1 99.51(12), C1-Ge1-Sn2 104.26(12), Sn1-Ge1-Sn2 113.13(2).

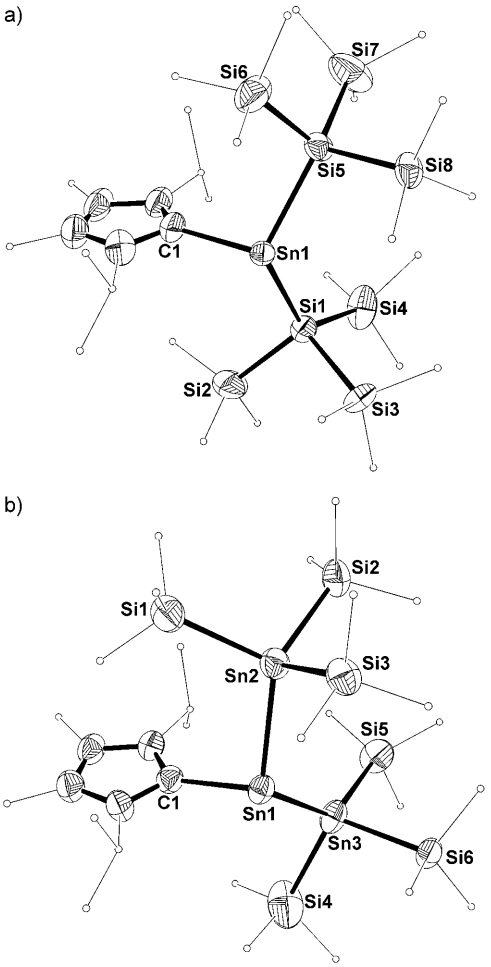


Figure 3. Molecular structure of compounds a) **5a** and b) **5c** in the solid state (ellipsoids set at 50% probability). For clarity, hydrogen atoms and disorder are omitted and methyl/isopropyl groups are simplified. Selected bond distances [Å] and bond angles [°]: **5a**: Sn1–C1 2.328(5), Sn1–Si1 2.713(4), Sn1–Si5 2.665(3), Si1–Si2 2.349(4), Si1–Si3 2.369(4), Si1–Si4 2.349(4), Si5–Si6 2.382(4), Si5–Si7 2.342(4), Si5–Si8 2.369(4); C1-Sn1-Si1 101.1(2), C1-Sn1-Si5 102.9(2), Si1-Sn1-Si5 118.09(10). **5c**: Sn1–C1 2.309(4), Sn1–Sn2 2.883(1), Sn1–Sn3 2.864(1), Sn2–Si1 2.626(12), Sn2–Si2 2.554(4), Sn2–Si3 2.578(10), Sn3–Si4 2.574(9), Sn3–Si5 2.640(5), Sn3–Si6 2.642(16); C1-Sn1-Sn2 97.71(10), C1-Sn1-Sn3 102.50(10), Sn2-Sn1-Sn3 113.22(2).

(sum of angles ca. 359°) and a flattened pyramidal geometry at the three-coordinated Group 14 atom (Ge, Sn). The Ge–$C_{carbene}$ bonds of **2a** and **4** (2.093(3) and 2.082(4) Å, respectively) compare well with those of (NHC)$GeMes_2$ (2.078(3) Å)[20] and of (NHC)$GeCl_2$ (2.106(3) Å).[10a] The Sn–$C_{carbene}$ bond distances in **5a** and **5c** (2.328(5) Å and 2.309(4) Å, respectively) are close to that reported for **3** (2.290(5) Å),[12] but are slightly shorter than the Sn–C distance (2.379(5) Å) in (NHC)SnR_2 (R = 2,4,6-*i*$Pr_3C_6H_2$).[11a]

Thus, the replacement of a chlorine atom by a $E(SiMe_3)_3$ group (E = Si, Ge, Sn) has almost no influence on the E–C bond lengths, despite a very different electronic effect. Our results are in good agreement with the work performed by Baines et al. on the lack of a substituent effect on the carbenic carbon–germanium bond length.[10g]

In summary, the first stable hypermetallyl germanium(II) and tin(II) compounds have been prepared by a convenient route using dimetallyl magnesium reagents. Depending on the Group 14 element, mono- and disubstituted divalent species coordinated to a nucleophilic carbene have been isolated and fully characterized, including X-ray diffraction analysis. We are currently investigating the reactivity of these complexes and their ability to produce nanomaterials by controlled thermolysis.

Experimental Section

All manipulations with air-sensitive materials were performed in a dry and oxygen-free atmosphere of argon by using standard Schlenk and glove-box techniques. NMR spectra were recorded with a Bruker Avance II 300: ^{1}H (300.13 MHz), ^{13}C (74.48 MHz), ^{29}Si (59.63 MHz), ^{119}Sn (111.92 MHz) at 298 K.

2a: A solution of (NHC)$GeCl_2$ (0.50 g, 1.54 mmol) in THF (6 mL) was added dropwise to a solution of $Mg[Si(SiMe_3)_3]_2$·2THF (0.58 g, 0.88 mmol) in THF (10 mL). The solution was stirred for 2 days at room temperature. Volatile components were removed under reduced pressure and the red residue was washed with pentane. After filtration, the yellow solid was dried under vacuum to give **2a** (0.59 g, 71%). Crystallization from toluene at 4°C gave yellow crystals suitable for an X-ray study. M.p.: 95°C (dec). ^{1}H NMR (C_6D_6): $\delta = 0.51$ (s, $^2J_{H-Si} = 6.3$ Hz, 27H, $SiMe_3$), 1.15 (d, $^3J_{H-H} = 7.0$ Hz, 6H, CH*Me*Me′); 1.30 (d, $^3J_{H-H} = 7.0$ Hz, 6H, CHMe*Me*′), 1.49 (s, 6H, Me), 5.48 ppm (sept, $^3J_{H-H} = 7.0$ Hz, 2H, C*H*MeMe′). ^{13}C NMR (C_6D_6): $\delta = 3.63$ ($^1J_{C-Si} = 43.4$ Hz, $SiMe_3$); 9.69 (Me); 21.70 and 21.80 (CH*Me*Me′); 52.44 (*C*HMeMe′); 126.71 (Me*C*=*C*Me); 173.11 ppm (N-C-N). ^{29}Si NMR (C_6D_6): $\delta = -119.12$ (GeSi); −7.57 ppm ($SiMe_3$).

2b: Red-orange powder (45%), M.p.: 107°C (dec). ^{29}Si NMR (C_6D_6): $\delta = -2.76$ ppm.

5a: A solution of (NHC)$SnCl_2$ (0.40 g, 1.08 mmol) in THF (12 mL) was added to a solution of $Mg[Si(SiMe_3)_3]_2$·2THF (0.72 g, 1.09 mmol) in THF (6 mL) at −60°C. After 40 min, the mixture was warmed to room temperature and stirred overnight. The volatiles were removed under reduced pressure, and the residue was extracted with pentane. The filtrate was concentrated under vacuum to give **5a** (0.49 g, 57%). Yellow crystals were obtained from a saturated pentane solution at −24°C. M.p.: 151°C. ^{1}H NMR (C_6D_6): $\delta = 0.45$ (s, $^2J_{H-Si} = 6.2$ Hz, 54H, $SiMe_3$); 1.12 (d, $^3J_{H-H} = 7.1$ Hz, 6H, $CHMe_2$); 1.35 (d, $^3J_{H-H} = 7.1$ Hz, 6H, $CHMe_2$); 1.54 (s, 3H, Me); 1.60 (s, 3H, Me); 5.31 (sept, $^3J_{H-H} = 7.1$ Hz, 1H, C*H*Me_2); 6.22 ppm (sept, $^3J_{H-H} = 7.1$ Hz, 1H, C*H*Me_2). ^{13}C NMR (C_6D_6): $\delta = 4.70$ ($SiMe_3$); 9.87 and 10.24 (Me); 21.49 and 23.09 ($CHMe_2$); 53.84 and 56.97 (*C*HMe_2); 126.29 (Me*C*=*C*Me); 170.10 ppm (N-C-N). ^{29}Si NMR (C_6D_6): $\delta = -131.62$ (SnSi); −7.16 ($^2J_{Si-Sn} = 47.6$ Hz, $SiMe_3$). ^{119}Sn NMR (C_6D_6): $\delta = -196.8$.

4, **5b**, and **5c** were obtained according to the same experimental procedure. **4**: Orange powder (93%), M.p.: 69°C (dec). ^{29}Si NMR (C_6D_6): $\delta = -9.96$ ppmn ($^1J(^{29}Si-^{117/119}Sn) = 203.7/213.2$ Hz, SnSi). ^{119}Sn NMR (C_6D_6): $\delta = -589.76$ ppm. **5b**: Red-orange powder (58%), M.p.: 117°C (dec). ^{29}Si NMR (C_6D_6): $\delta = -2.82$ ppm ($^2J_{Si-Sn} = 27.4$ Hz). ^{119}Sn NMR (C_6D_6): $\delta = -115.0$ ppm. **5c**: Brown powder (69%), M.p.: 95°C (dec.). ^{29}Si NMR (C_6D_6): $\delta = -9.19$ ($^1J(^{29}Si-^{117/119}Sn) = 191.6/201.2$ Hz, $^2J(^{29}Si-^{117/119}Sn) = 26.5/27.6$ Hz, $^3J(^{29}Si-^{117/119}Sn) = 19.9/20.7$ Hz). ^{119}Sn NMR (C_6D_6): $\delta = -655.5$ (*Sn*Sn), −138.3 ppm (*Sn*Si).

CCDC 809284 (**2a**), CCDC 809285 (**4**), CCDC 809286 (**5a**), and CCDC 809287 (**5c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] a) M. Driess, H. Grützmacher, *Angew. Chem.* **1996**, *108*, 900 – 929; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 828 – 856; b) M. Weidenbruch, *Eur. J. Inorg. Chem.* **1999**, 373 – 381; c) N. Tokitoh, R. Okazaki, *Coord. Chem. Rev.* **2000**, *210*, 251 – 277; d) N. J. Hill, R. West, *J. Organomet. Chem.* **2004**, *689*, 4165 – 4183; e) O. Kühl, *Coord. Chem. Rev.* **2004**, *248*, 411 – 427; f) H. Ottosson, P. G. Steel, *Chem. Eur. J.* **2006**, *12*, 1576 – 1585; g) M. Driess, S. Yao, M. Brym, C. van Wüllen, D. Lentz, *J. Am. Chem. Soc.* **2006**, *128*, 9628 – 9629; h) W.-P. Leung, K.-W. Kan, K.-H. Chong, *Coord. Chem. Rev.* **2007**, *251*, 2253 – 2265; i) S. Yao, M. Brym, C. van Wüllen, M. Driess, *Angew. Chem.* **2007**, *119*, 4237 – 4240; *Angew. Chem. Int. Ed.* **2007**, *46*, 4159 – 4162; j) S. Nagendran, H. W. Roesky, *Organometallics* **2008**, *27*, 457 – 492; k) A. V. Zabula, F. E. Hahn, *Eur. J. Inorg. Chem.* **2008**, 5165 – 5179; l) Y. Mizuhata, T. Sasamori, N. Tokitoh, *Chem. Rev.* **2009**, *109*, 3479 – 3511; m) S. Yao, Y. Xiong, M. Driess, *Chem. Commun.* **2009**, 6466 – 6468; n) Y. Xiong, S. Yao, M. Driess, *J. Am. Chem. Soc.* **2009**, *131*, 7562 – 7563; o) J. V. Dickschat, S. Urban, T. Pape, F. Glorius, F. E. Hahn, *Dalton Trans.* **2010**, *39*, 11519 – 11521; p) M. Asay, C. Jones, M. Driess, *Chem. Rev.* **2011**, *111*, 354 – 396.

[2] a) S. Mathur, H. Shen, V. Sivakov, U. Werner, *Chem. Mater.* **2004**, *16*, 2449 – 2456; b) H. Gerung, S. D. Bunge, T. J. Boyle, C. J. Brinker, S. M. Han, *Chem. Commun.* **2005**, 1914 – 1916; c) M. Veith, J. Frères, P. König, O. Schütt, V. Huch, J. Blin, *Eur. J. Inorg. Chem.* **2005**, 3699 – 3710; d) H. Gerung, T. J. Boyle, L. J. Tribby, S. D. Bunge, C. J. Brinker, S. M. Han, *J. Am. Chem. Soc.* **2006**, *128*, 5244 – 5250; e) T. J. Boyle, L. J. Tribby, L. A. M. Ottley, S. M. Han, *Eur. J. Inorg. Chem.* **2009**, 5550 – 5560; f) D. C. Lee, J. M. Pietryga, I. Robel, D. J. Werder, R. D. Schaller, V. I. Klimov, *J. Am. Chem. Soc.* **2009**, *131*, 3436 – 3437.

[3] R. G. Hobbs, S. Barth, N. Petkov, M. Zirngast, C. Marschner, M. A. Morris, J. D. Holmes, *J. Am. Chem. Soc.* **2010**, *132*, 13742 – 13749.

[4] a) A. Heine, D. Stalke, *Angew. Chem.* **1994**, *106*, 121 – 123; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 113 – 115; b) S. P. Mallela, S. Hill, R A. Geanangel, *Inorg. Chem.* **1997**, *36*, 6247 – 6250.

[5] a) K. W. Klinkhammer, W. Schwarz, *Angew. Chem.* **1995**, *107*, 1448 – 1451; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1334 – 1336; b) K. W. Klinkhammer, *Polyhedron* **2002**, *21*, 587 – 598.

[6] D. Kurzbach, S. Yao, D. Hinderberger, K. W. Klinkhammer, *Dalton Trans.* **2010**, *39*, 6449 – 6459.

[7] a) N. Kuhn, A. Al-Sheikh, *Coord. Chem. Rev.* **2005**, *249*, 829 – 857; b) P. de Frémont, N. Marion, S. P. Nolan, *Coord. Chem. Rev.* **2009**, *253*, 862 – 892.

[8] A. J. Arduengo, H. V. R. Dias, J. C. Calabrese, F. Davidson, *Inorg. Chem.* **1993**, *32*, 1541 – 1542.

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

[10] a) P. A. Rupar, V. N. Staroverov, P. J. Ragogna, K. M. Baines, *J. Am. Chem. Soc.* **2007**, *129*, 15138 – 15139; b) P. A. Rupar, M. C. Jennings, K. M. Baines, *Organometallics* **2008**, *27*, 5043 – 5051; c) P. A. Rupar, V. N. Staroverov, K. M. Baines, *Science* **2008**, *322*, 1360 – 1363; d) A. Sidiropoulos, C. Jones, A. Stasch, S. Klein, G. Frenking, *Angew. Chem.* **2009**, *121*, 9881 – 9884; *Angew. Chem. Int. Ed.* **2009**, *48*, 9701 – 9704; e) K. C. Thimer, S. M. I. Al-Rafia, M. J. Ferguson, R. McDonald, E. Rivard, *Chem. Commun.* **2009**, 7119 – 7121; f) A. C. Filippou, O. Chernov, B. Blom, K. W. Stumpf, G. Schnakenburg, *Chem. Eur. J.* **2010**, *16*, 2866 – 2872; g) A. J. Ruddy, P. A. Rupar, K. J. Bladek, C. J. Allan, J. C. Avery, K. M. Baines, *Organometallics* **2010**, *29*, 1362 – 1367; h) S. M. I. Al-Rafia, A. C. Malcolm, S. K. Liew, M. J. Ferguson, E. Rivard, *J. Am. Chem. Soc.* **2011**, *133*, 777 – 779.

[11] a) A. Schäfer, M. Weidenbruch, W. Saak, S. Pohl, *J. Chem. Soc. Chem. Commun.* **1995**, 1157 – 1158; b) F. E. Hahn, L. Wittenbecher, M. Kühn, T. Lügger, R. Fröhlich, *J. Organomet. Chem.* **2001**, *617–618*, 629 – 634.

[12] N. Kuhn, T. Kratz, D. Blaser, R. Boese, *Chem. Ber.* **1995**, *128*, 245 – 250.

[13] N. Kuhn, T. Kratz, *Synthesis* **1993**, 561 – 562.

[14] a) H. Gilman, C. L. Smith, *J. Organomet. Chem.* **1968**, *14*, 91 – 101; b) G. Gutekunst, A. G. Brook, *J. Organomet. Chem.* **1982**, *225*, 1 – 3.

[15] a) K. W. Klinkhammer, W. Schwarz, *Z. Anorg. Allg. Chem.* **1993**, *619*, 1777 – 1789; b) C. Marschner, *Eur. J. Inorg. Chem.* **1998**, 221 – 226.

[16] a) J. D. Farwell, M. F. Lappert, C. Marschner, C. Strissel, T. D. Tilley, *J. Organomet. Chem.* **2000**, *603*, 185 – 188; b) W. Gaderbauer, M. Zirngast, J. Baumgartner, C. Marschner, T. D. Tilley, *Organometallics* **2006**, *25*, 2599 – 2606.

[17] D. Matioszek, N. Katir, S. Ladeira, A. Castel, *Organometallics*, DOI: 10.1021/om200024d.

[18] B. Cordero, V. Gomez, A. E. Platero-Prats, M. Reves, J. Echeverria, E. Cremades, F. Barragan, S. Alvarez, *Dalton Trans.* **2008**, 2832 – 2838.

[19] R. Fischer, J. Baumgartner, C. Marschner, F. Uhlig, *Inorg. Chim. Acta* **2005**, *358*, 3174 – 3182.

[20] P. A. Rupar, M. C. Jennings, P. J. Ragogna, K. M. Baines, *Organometallics* **2007**, *26*, 4109 – 4111.

[21] Y. Ding, H. W. Roesky, M. Noltemeyer, H.-G. Schmidt, P. P. Power, *Organometallics* **2001**, *20*, 1190 – 1194.

