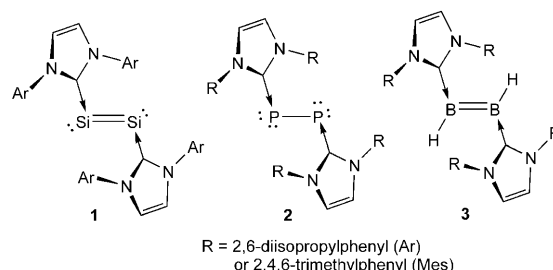


N-Heterocyclic Carbene Stabilized Digermanium(0)**

Anastas Sidiropoulos, Cameron Jones,* Andreas Stasch,* Susanne Klein, and Gernot Frenking*

The ability of very nucleophilic N-heterocyclic carbenes (NHCs) to stabilize transition metals in the zero oxidation state is extensively documented.^[1] Although the main-group coordination chemistry of these important ligands is also well-developed,^[2] it was not until recently that NHC complexes of p-block elements formally in the zero oxidation state were described.^[3] Arguably the most spectacular example of such a complex (**1**) was reported by Schleyer, Robinson, et al. to be formed by the KC_8 reduction of $[\text{SiCl}_4(\text{IPr})]$ ($\text{IPr} = \text{C}[\text{N}(\text{Ar})\text{CH}_2]_2$, $\text{Ar} = 2,6\text{-diisopropylphenyl}$).^[4] The complex can be considered as an NHC adduct of the singlet fragment $:\text{Si}=\text{Si}:$ and has been described as a base-stabilized, soluble “allotrope” of silicon.^[3b] This assignment has been supported by theoretical calculations.^[4,5] Closely related to **1** are the NHC-stabilized diphosphorus complexes **2**, also reported by Robinson et al.^[6] Similarly, Bertrand and co-workers have investigated the activation of P_4 with saturated NHCs, acyclic carbenes, and cyclic (alkyl)(amino) carbenes (CAACs). Their efforts have afforded an impressive array of neutral carbene complexes of P_2 , P_4 , and P_{12} units,^[7a-c] which has recently been extended to radical cationic and dicationic bis(carbene) adducts of the P_2 unit.^[7d] The same group has also published the synthesis of the extremely bent acyclic allene $(\text{R}_2\text{N})_2\text{C}=\text{C}=\text{C}(\text{NR}_2)_2$ ($\text{C}-\text{C}-\text{C}$ angle = $134.8(2)^\circ$, $(\text{NR}_2)_2 = 1,2\text{-}[\text{N}(\text{Me})]_2\text{C}_6\text{H}_4$), an alternative resonance form of which, $(\text{R}_2\text{N})_2\text{C} \rightarrow \text{C} \leftarrow \text{C}(\text{NR}_2)_2$, was described as an NHC complex of carbon(0), that is, a “carbodicarbene”.^[8,9] This interpretation has been given weight by theoretical studies on model compounds and on models of higher Group 14 homologues.^[10] It is worthy of note that attempts to prepare homoleptic NHC complexes of Group 13 elements in the zero oxidation state have been carried out. These have not yet been successful, and KC_8 reductions of NHC adducts of BBr_3 have instead led

to NHC complexes of the parent diborene **3**, amongst other products.^[11]



Given the remarkable thermal stability of **1** ($T_{\text{decomp}} = 209^\circ\text{C}$), it seemed to us that germanium analogues of this compound may be synthetically accessible. If so, they would not only be of much fundamental interest but would also have significant synthetic potential as soluble sources of elemental germanium. A further impetus to pursue such targets came from the preparation of the related molecule $(\text{OC})\text{Ge}=\text{Ge}(\text{CO})$ in a solid argon matrix.^[12] A combination of theoretical and spectroscopic investigations of this molecule showed it to have a trans-bent structure ($\text{C}-\text{Ge}-\text{Ge}$ angles of ca. 80°) and a singlet ground state (cf. **1**). Moreover, higher oxidation-state compounds containing $\text{Ge}-\text{Ge}$ multiple bonds, for example, trans-bent digermenes $(\text{R}_2\text{Ge}^{\text{II}}\text{Ge}^{\text{II}}\text{R}_2)$ ^[13] and digermynes $(\text{RGe}^{\text{I}}\text{Ge}^{\text{I}}\text{R})$,^[14] have been known for some time and can be very thermally stable. Herein, we report the synthesis, characterization, and theoretical analysis of an unprecedented NHC-stabilized germanium(0) dimer.

To prepare a suitable precursor for germanium(0) compounds, a diethylether suspension of GeCl_2 -dioxane was treated with one equivalent of the N-heterocyclic carbene IPr. This procedure afforded a high yield of the adduct complex $[\text{GeCl}_2(\text{IPr})]$ (**4**).^[15] The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopic data for the compound are consistent with its formulation and are similar to those reported for the silicon(II) analogues $[\text{SiX}_2(\text{IPr})]$ ($\text{X} = \text{Cl}$ ^[16] or Br ^[17]). An X-ray crystallographic study of **4** (Figure 1) revealed it to be monomeric in the solid state and broadly isostructural with $[\text{SiX}_2(\text{IPr})]$. Its carbene center (C1) has an almost planar geometry, whilst the pyramidalization of the germanium atom (sum of angles about $\text{Ge}1$ 284.7°) suggests that it possesses a stereochemically active lone pair. Both the $\text{Ge}-\text{Cl}$ bond lengths and the $\text{Ge}-\text{C}$ separation are comparable to those in the only other crystallographically characterized NHC- GeCl_2 adduct $[\text{GeCl}_2\{\text{C}[\text{N}(\text{iPr})\text{C}(\text{Me})]_2\}]$, $2.294 \text{ \AA}$ (mean) and $2.106(3) \text{ \AA}$, respectively.^[18]

We are currently exploring the facility of soluble β -diketiminato stabilized magnesium(I) reagents

[*] A. Sidiropoulos, Prof. C. Jones, Dr. A. Stasch
School of Chemistry, Monash University
PO Box 23, Melbourne, VIC, 3800 (Australia)
Fax: (+61) 3-9905-4597
E-mail: cameron.jones@sci.monash.edu.au
andreas.stasch@sci.monash.edu.au

S. Klein, Prof. Dr. G. Frenking
Fachbereich Chemie, Philipps-Universität Marburg
35032 Marburg (Germany)
Fax: (+49) 6421-282-5566
E-mail: frenking@chemie.uni-marburg.de

[**] We thank the Australian Research Council (fellowships for C.J. and A.S.) and the Deutsche Forschungsgemeinschaft (grant FR641/25-1 to G.F.). The EPSRC is also thanked for access to the UK National Mass Spectrometry Facility.

Supporting information for this article, including full synthetic, spectroscopic, and crystallographic details as well as details and references for the DFT calculations, is available on the WWW under <http://dx.doi.org/10.1002/ange.200905495>.

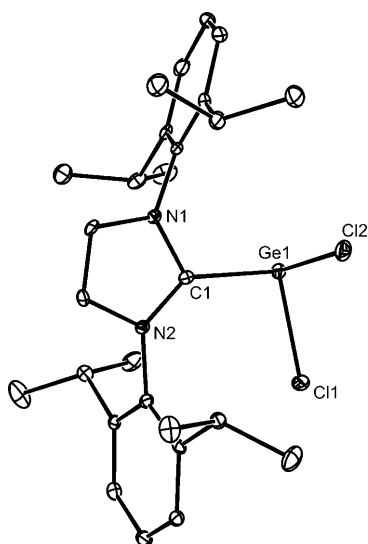
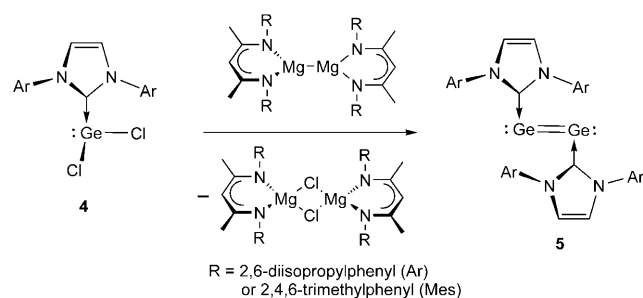


Figure 1. Molecular structure of compound **4** (25% ellipsoids; hydrogen atoms omitted). Relevant bond lengths [Å] and angles [°]: Ge1–C1 2.110(4), Ge1–Cl1 2.2651(12), Ge1–Cl2 2.2855(13), N1–C1 1.365(5), C1–N2 1.353(5); C1–Ge1–Cl1 97.55(11), C1–Ge1–Cl2 91.30(11), Cl1–Ge1–Cl2 95.85(5), N2–C1–N1 104.1(4).

$[\text{Mg}\{\text{N}(\text{R})\text{CMe}_2\text{CH}\}_2]$ (R = Ar or Mes) to act as two-center, two-electron reductants towards a variety of organic substrates.^[19–21] It seemed reasonable that they should also be effective as reducing agents in organometallic synthesis. Accordingly, compound **4** was treated with one equivalent of $[\text{Mg}\{\text{N}(\text{Mes})\text{CMe}_2\text{CH}\}_2]$ ^[21] to give rapidly a deep red solution from which a 20% yield of the dimeric germanium(0) complex **5** was isolated as a red crystalline solid (Scheme 1). A



Scheme 1. Synthesis of the digermanium(0) compound **5**.

much lower yield of **5** (less than 5%) was obtained from the reduction of **4** with the bulkier magnesium(I) dimer $[\text{Mg}\{\text{N}(\text{Ar})\text{CMe}_2\text{CH}\}_2]$.^[19] We have to date had no success in isolating the related germanium(I) compound $[(\text{IPr})\text{Ge}(\text{Cl})\text{Ge}(\text{Cl})(\text{IPr})]$ (cf. the known silicon(I) species $[(\text{IPr})\text{Si}(\text{Cl})\text{Si}(\text{Cl})(\text{IPr})]$ ^[4]) from either the reaction of **4** with half an equivalent of magnesium(I) dimer or from the 2:1 reaction of **4** and **5**. Moreover, attempts to prepare either **5** or $[(\text{IPr})\text{Ge}(\text{Cl})\text{Ge}(\text{Cl})(\text{IPr})]$ by reducing the germanium dichloride complex **4** with sodium metal or KC_8 in diethyl-ether have not been successful, and the only product isolated from these reactions was free IPr.

Compound **5** is thermally stable ($T_{\text{decomp}} = 162\text{--}165^\circ\text{C}$, cf. **1** $T_{\text{decomp}} = 209^\circ\text{C}$) but extremely oxygen- and moisture-sensitive. As was the case with **1**, its ^1H NMR spectrum displays two doublet methyl resonances and one methine septet signal. This observation indicates rapid fluxional behavior, as twice the number of these resonances would be expected if the molecule displayed time-averaged C_{2h} symmetry in solution. Cooling solutions of **5** did not lead to a resolution of its spectrum. A signal for the carbenic carbon atom of **5** was observed at $\delta = 203.3$ ppm in its $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum. This resonance is close to the signal in the spectrum of **1** ($\delta = 196.3$ ppm) but is significantly downfield from the related resonance in the spectrum of **4** ($\delta = 175.3$ ppm; cf. $\delta = 220.6$ ppm for free IPr^[22]).

The X-ray crystal structure of **5** was determined and found to be isomorphous with that of **1**. The molecular structure of the compound (Figure 2) shows it to be dimeric with a Ge–Ge

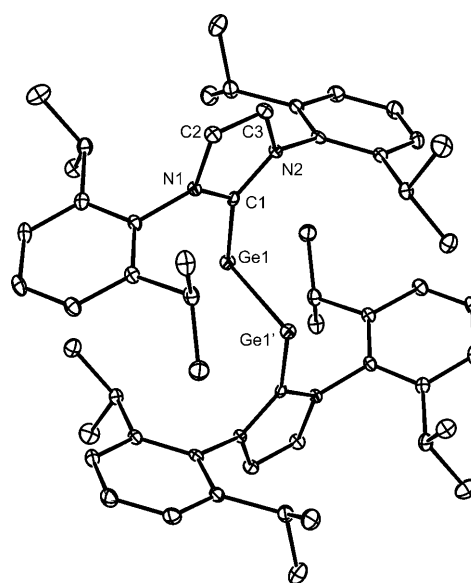


Figure 2. Molecular structure of compound **5** (25% ellipsoids; hydrogen atoms omitted). Relevant bond lengths [Å] and angles [°]: Ge1–C1 2.030(3), Ge1–Ge1' 2.3490(8), N1–C1 1.365(3), C1–N2 1.369(3), N1–C2 1.384(3), N2–C3 1.387(4), C2–C3 1.341(4); C1–Ge1–Ge1' 89.87(8), N1–C1–N2 103.6(2), N1–C1–Ge1 129.5(2), N2–C1–Ge1 126.7(2). Symmetry operation: $' -x, -y+1, -z$.

distance (2.3490(8) Å) that is close to the mean for all crystallographically characterized digermenes (2.344 Å)^[23] but outside the reported range for digermynes (2.206–2.285 Å).^[23] It is also of note that the Ge–Ge separation in **5** is shorter than those calculated for both $(\text{OC})\text{Ge}=\text{Ge}(\text{CO})$ (2.456 Å)^[12] and the triplet ground state ($^3\Sigma_g^-$) of Ge_2 (2.422 Å).^[24] The C–Ge separations in **5** (2.030(3) Å), although slightly shorter than that in **4**, are well within the $\text{C}-\text{Ge}_{(\text{two-coordinate})}$ single-bond range (1.917–2.081 Å).^[23] These structural features, combined with the almost orthogonal coordination of the IPr ligands to the Ge_2 fragment (C–Ge–Ge 89.87(8)° cf. C–Si–Si 93.37(5)° in **1**), allow the compound to be tentatively described as an NHC adduct of a singlet, doubly

bonded $\text{:Ge}^0=\text{Ge}^0\text{:}$ fragment, in much the same way as the bonding in **1** has been portrayed.

To shed light on the validity of this bonding description, we carried out quantum chemical calculations of the model compound $[\text{Ge}[\text{N}(\text{Me})\text{C}(\text{H})_2]_2]$ (**5M**), in which the aryl substituents at nitrogen are replaced by methyl groups. The calculations were performed using density functional theory at the BP86/TZ2P level (see the Supporting Information for full details). Figure S2 in the Supporting Information shows the optimized geometry of **5M**, which is similar to that of **5** and has C_{2h} symmetry. The calculated lengths for the Ge–Ge (2.407 Å) and Ge–C (2.064 Å) bonds are slightly larger than the experimental values for **5**, which may be due to the different nitrogen substituents, solid-state effects which tend to shorten bonds,^[25] and the level of theory. The general agreement between the experimental geometry of **5** and the theoretical structure of **5M** is, however, acceptable. The NHC rings in both compounds are orthogonal to their C–Ge–Ge'–C' planes, and their C–Ge–Ge' bond angles are close to 90° (for **5M**, C–Ge–Ge' 87.6°). The preference for the trans-bent geometry can be explained in terms of the orbital interactions between the Ge_2 fragment and the NHC ligands. The electronic ground state of Ge_2 is the $X^3\Sigma_g^-$ state (Figure 3 a).

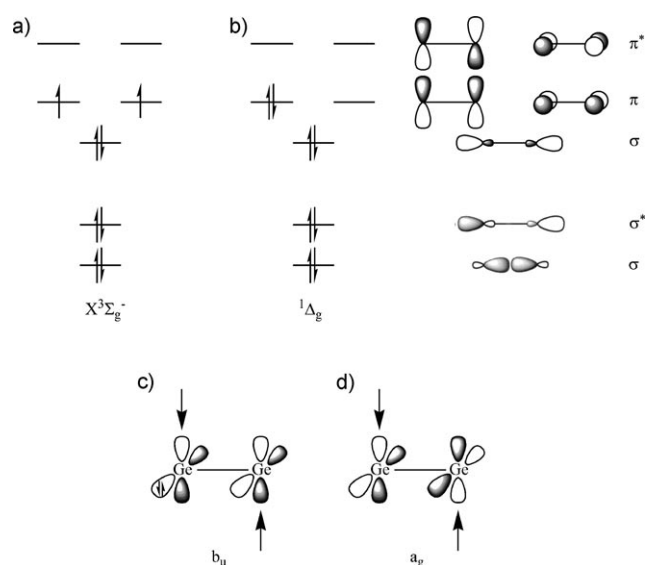


Figure 3. Schematic representation of a) the $X^3\Sigma_g^-$ ground state b) the $^1\Delta_g$ excited state of Ge_2 and a pictorial description of the electron donation from the carbon σ lone pair orbitals of the NHC ligands into the vacant orbitals of ($^1\Delta_g$) Ge_2 . c) Donation of the lone pairs into the in-plane vacant π MO and d) donation of the minus combination of the lone pairs into the in-plane vacant π^* MO.

The electronic reference state for the diamagnetic complex is the $^1\Delta_g$ excited state (Figure 3 b), which is only 9.5 kcal mol^{−1} higher in energy.^[26] The orbital occupation of the latter state is perfectly suited for donor–acceptor interactions with two NHC ligands. Figure 3 c shows that the vacant π -bonding orbital of the $^1\Delta_g$ state of Ge_2 can serve as an acceptor orbital for donation from the minus combination of the carbon lone-pair orbitals of the NHC ligands (b_u symmetry in C_{2h}), while the associated π^* antibonding MO (Figure 3 d) is available as

an acceptor orbital for electron donation from the plus combination of the NHC donor orbitals (a_g symmetry).

To quantify the strength of the orbital interactions in **5M** we analyzed the nature of the bonding in the complex using the EDA^[27] (energy decomposition analysis) technique developed by Morokuma^[28] and Ziegler and Rauk.^[29] Details of the method are given in the Supporting Information, while Table 1 gives a summary of the numerical results.

Table 1: Results of the EDA calculations of the $\text{Ge}_2(\text{NHC})_2$ complex **5M** using ($^1\Delta_g$) Ge_2 and $(\text{NHC})_2$ as interacting fragments. The energy values are given in kcal mol^{−1}.

ΔE_{int}	−100.6	
ΔE_{Pauli}	313.3	
$\Delta E_{\text{elstat}}^{[a]}$	−244.9	(59.2%)
$\Delta E_{\text{orb}}^{[a]}$	−169.0	(40.8%)
$\Delta E(a_g)^{[b]}$	−78.5	(46.5%)
$\Delta E(b_g)^{[b]}$	−1.8	(1.0%)
$\Delta E(a_u)^{[b]}$	−10.5	(6.2%)
$\Delta E(b_u)^{[b]}$	−78.2	(46.3%)
ΔE_{prep}	25.0	
$\Delta E = -D_e$	−75.6	

[a] The percentage values in parentheses give the contribution to the total attractive interactions $\Delta E_{\text{elstat}} + \Delta E_{\text{orb}}$. [b] The percentage values in parentheses give the contribution to the orbital interactions ΔE_{orb} .

The total interaction energy ΔE_{int} between ($^1\Delta_g$) Ge_2 and the $(\text{NHC})_2$ ligands using the frozen geometries of the fragments amounts to −100.6 kcal mol^{−1}. This result gives a bond dissociation energy (BDE) of $D_e = 75.6$ kcal mol^{−1} for both ligands after geometrical and electronic relaxation yielding two NHC molecules and Ge_2 in its $X^3\Sigma_g^-$ ground state.^[30] The average BDE for the $(\text{Ge}_2)-(\text{NHC})_2$ donor–acceptor bonds is thus predicted as $D_e = 37.8$ kcal mol^{−1}, which is quite high in comparison with other donor–acceptor complexes.^[25] The breakdown of the total interaction into its main components shows (Table 1) that the $(\text{Ge}_2)-(\text{NHC})_2$ bonds are more electrostatic ($\Delta E_{\text{elstat}} = 59.2\%$) than covalent ($\Delta E_{\text{orb}} = 40.8\%$). Because **5M** has C_{2h} symmetry it is possible to estimate the strength of the different orbital contributions to the ΔE_{orb} term. Table 1 shows that the contributions of the orbitals which have a_g symmetry (46.5%) and b_u symmetry (46.3%) have essentially the same size. The orbital interactions which yield $(\text{Ge}_2)-(\text{NHC})_2$ covalent bonding thus come mainly from the plus and minus combinations of the lone pairs of the NHC ligands into the vacant in-plane π and π^* orbitals of Ge_2 , while the out-of-plane π interactions are very weak. The donation from the occupied π MO of Ge_2 into the $p(\pi)$ orbitals of the carbene carbon atoms (a_u symmetry) provides only 6.2% of ΔE_{orb} , and the π donation of the NHC ligands into the out-of-plane π^* orbital of Ge_2 (b_g symmetry) is negligibly small. The above EDA results give a comprehensive picture of the nature and the strength of the $(\text{Ge}_2)-(\text{NHC})_2$ bonding in **5M**, and by implication, **5**.

In summary, the reductions of an NHC adduct of GeCl_2 with magnesium(I) dimers have given a dimeric compound, the spectroscopic, structural, and theoretical analyses of which suggest is best formulated as a singlet germanium(0) dimer :Ge=Ge: datively coordinated by two NHC ligands. We

continue to explore the use of magnesium(I) dimers as hydrocarbon-soluble, selective, stoichiometric reducing agents in organometallic synthesis.^[31]

Received: September 30, 2009

Published online: November 17, 2009

Keywords: carbene ligands · density functional calculations · germanium · magnesium · metal–metal interactions

- [1] See for example a) P. de Frémont, N. Marion, S. P. Nolan, *Coord. Chem. Rev.* **2009**, 253, 862–892; b) F. E. Hahn, M. C. Jahnke, *Angew. Chem.* **2008**, 120, 3166–3216; *Angew. Chem. Int. Ed.* **2008**, 47, 3122–3172; c) W. A. Herrmann, *Angew. Chem.* **2002**, 114, 1342–1363; *Angew. Chem. Int. Ed.* **2002**, 41, 1290–1309; d) D. Bourissou, O. Guerret, F. P. Gabbaï, G. Bertrand, *Chem. Rev.* **2000**, 100, 39–91, and references therein.
- [2] See for example a) N. Kuhn, A. Al-Sheikh, *Coord. Chem. Rev.* **2005**, 249, 829–857; b) C. J. Carmalt, A. H. Cowley, *Adv. Inorg. Chem.* **2000**, 50, 1–32, and references therein.
- [3] a) Y. Wang, G. H. Robinson, *Chem. Commun.* **2009**, 5201–5213; b) C. A. Dyker, G. Bertrand, *Science* **2008**, 321, 1050–1051.
- [4] Y. Wang, Y. Xie, P. Wei, R. B. King, H. F. Schaefer III, P. von R. Schleyer, G. H. Robinson, *Science* **2008**, 321, 1069–1071.
- [5] Z. Liu, *J. Phys. Chem. A* **2009**, 113, 6410–6414.
- [6] Y. Wang, Y. Xie, P. Wei, R. B. King, H. F. Schaefer III, P. von R. Schleyer, G. H. Robinson, *J. Am. Chem. Soc.* **2008**, 130, 14970–14971.
- [7] a) O. Back, G. Kuchenbeiser, B. Donnadieu, G. Bertrand, *Angew. Chem.* **2009**, 121, 5638–5641; *Angew. Chem. Int. Ed.* **2009**, 48, 5530–5533; b) J. Masuda, W. W. Schoeller, B. Donnadieu, G. Bertrand, *J. Am. Chem. Soc.* **2007**, 129, 14180–14181; c) J. Masuda, W. W. Schoeller, B. Donnadieu, G. Bertrand, *Angew. Chem.* **2007**, 119, 7182–71851; *Angew. Chem. Int. Ed.* **2007**, 46, 7052–7055; d) O. Back, B. Donnadieu, P. Parameswaram, G. Frenking, G. Bertrand, *Nature*, in press.
- [8] C. A. Dyker, V. Lavallo, B. Donnadieu, G. Bertrand, *Angew. Chem.* **2008**, 120, 3250–3253; *Angew. Chem. Int. Ed.* **2008**, 47, 3206–3209.
- [9] A related acyclic “carbodicarbene” complex was simultaneously reported. A. Fürstner, M. Alcarazo, R. Goddard, C. W. Lehmann, *Angew. Chem.* **2008**, 120, 3254–3258; *Angew. Chem. Int. Ed.* **2008**, 47, 3210–3214.
- [10] a) R. Tonner, G. Frenking, *Angew. Chem.* **2007**, 119, 8850–8853; *Angew. Chem. Int. Ed.* **2007**, 46, 8695–8698; b) N. Takagi, T. Shimizu, G. Frenking, *Chem. Eur. J.* **2009**, 15, 8593–8604.
- [11] a) Y. Wang, B. Quillian, P. Wei, Y. Xie, C. S. Wannere, R. B. King, H. F. Schaefer III, P. von R. Schleyer, G. H. Robinson, *J. Am. Chem. Soc.* **2008**, 130, 3298–3299; b) Y. Wang, B. Quillian, P. Wei, C. S. Wannere, Y. Xie, R. B. King, H. F. Schaefer III, P. von R. Schleyer, G. H. Robinson, *J. Am. Chem. Soc.* **2007**, 129, 12412–12413.
- [12] M. Zhou, L. Jiang, Q. Xu, *J. Phys. Chem. A* **2005**, 109, 3325–3330.
- [13] P. P. Power, *ACS Symp. Ser.* **2006**, 917, 179–190, and references therein.
- [14] P. P. Power, *Organometallics* **2007**, 26, 4362–4372, and references therein.
- [15] In one attempted preparation of **4** in THF, a small amount of [IPrH(THF)][GeCl₃] was isolated. See the Supporting Information for crystallographic details of this compound.
- [16] R. S. Ghadwal, H. W. Roesky, S. Merkel, J. Henn, D. Stalke, *Angew. Chem.* **2009**, 121, 5793–5796; *Angew. Chem. Int. Ed.* **2009**, 48, 5683–5686.
- [17] A. C. Filippou, O. Chernov, G. Schnakenburg, *Angew. Chem.* **2009**, 121, 5797–5800; *Angew. Chem. Int. Ed.* **2009**, 48, 5687–5690.
- [18] P. A. Rupar, V. N. Staroverov, P. J. Ragnogna, K. M. Baines, *J. Am. Chem. Soc.* **2007**, 129, 15138–15139. NHC adducts of GeBr₂ and GeI₂ have also been reported. See A. J. Arduengo III, H. V. Rasika Dias, J. C. Calabrese, F. Davidson, *Inorg. Chem.* **1993**, 32, 1541–1542; P. A. Rupar, M. C. Jennings, K. M. Baines, *Organometallics* **2008**, 27, 5043–5051.
- [19] S. P. Green, C. Jones, A. Stasch, *Science* **2007**, 318, 1754–1757.
- [20] S. J. Bonyhady, S. P. Green, C. Jones, S. Nembenna, A. Stasch, *Angew. Chem.* **2009**, 121, 3017–3021; *Angew. Chem. Int. Ed.* **2009**, 48, 2973–2977.
- [21] S. J. Bonyhady, C. Jones, S. Nembenna, A. Stasch, A. J. Edwards, G. J. McIntyre, *Chem. Eur. J.*, in press.
- [22] A. J. Arduengo III, R. Krafczyk, R. Schmutzler, H. A. Craig, J. R. Goerlich, W. J. Marshall, M. Unverzagt, *Tetrahedron* **1999**, 55, 14523–14534.
- [23] As determined from a survey of the Cambridge Crystallographic Database, September, **2009**.
- [24] I. Shim, M. S. Baba, K. A. Gingerich, *Chem. Phys.* **2002**, 277, 9–20.
- [25] V. Jonas, G. Frenking, M. T. Reetz, *J. Am. Chem. Soc.* **1994**, 116, 8741–8753.
- [26] C. C. Arnold, C. Xu, G. R. Burton, D. M. Neumark, *J. Chem. Phys.* **1995**, 102, 6982–6989.
- [27] a) F. M. Bickelhaupt, E. J. Baerends, *Rev. Comput. Chem.* **2000**, 15, 1–86; b) G. Frenking, K. Wichmann, N. Fröhlich, C. Loschen, M. Lein, J. Frunzke, J. V. M. Rayón, *Coord. Chem. Rev.* **2003**, 238–239, 55–82; c) M. Lein, G. Frenking in *Theory and Applications of Computational Chemistry: The First 40 Years* (Eds.: C. E. Dykstra, G. Frenking, K. S. Kim, G. E. Scuseria), Elsevier, Amsterdam, **2005**, p. 367.
- [28] K. Morokuma, *J. Chem. Phys.* **1971**, 55, 1236–1244.
- [29] a) T. Ziegler, A. Rauk, *Inorg. Chem.* **1979**, 18, 1755–1759; b) T. Ziegler, A. Rauk, *Inorg. Chem.* **1979**, 18, 1558–1565.
- [30] The calculated excitation energy $X^3\Sigma_g^- \rightarrow ^1\Delta_g$ for Ge₂ at BP86/TZ2P is 18.0 kcal mol^{−1}, which is somewhat higher than the experimental value of 9.5 kcal mol^{−1}.^[26] The difference between the calculated and experimental values is not relevant for the bonding analysis.
- [31] **Note added in proof** (10.11.2009): The preparation and structural characterization of compound **4** was reported independently after the submission of this manuscript, see: K. C. Thimer, S. M. I. Al-Rafia, M. J. Ferguson, R. McDonald, E. Rivard, *Chem. Commun.* **2009**, DOI:10.1039/b915950a.