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Main-Group Chemistry

# N-Heterocyclic Carbene Stabilized Digermanium(0)**

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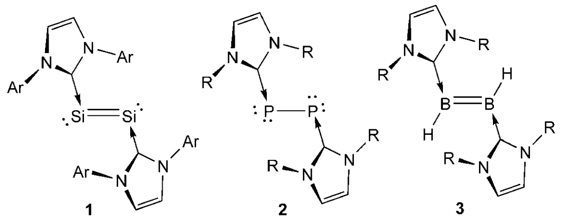
The ability of very nucleophilic N-heterocyclic carbenes (NHCs) to stabilize transition metals in the zero oxidation state is extensively documented.[1] Although the main-group coordination chemistry of these important ligands is also well-developed,[2] it was not until recently that NHC complexes of 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 $[SiCl_4(IPr)]$ (IPr = $:C\{N(Ar)CH\}_2$, Ar = 2,6-diisopropylphenyl).[4] The complex can be considered as an NHC adduct of the singlet fragment $:Si{=}Si:$ 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 $(R_2N)_2C{=}C{=}C(NR_2)_2$ (C-C-C angle = 134.8(2)°, $(NR_2)_2 = 1,2\text{-}\{N(Me)\}_2C_6H_4$), an alternative resonance form of which, $(R_2N)_2C{\rightarrow}:C:{\leftarrow}C(NR_2)_2$, 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]



**1** **2** **3**

R = 2,6-diisopropylphenyl (Ar)
or 2,4,6-trimethylphenyl (Mes)

Given the remarkable thermal stability of **1** ($T_{decomp}$ = 209 °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 $(OC)Ge{=}Ge(CO)$ in a solid argon matrix.[12] A combination of theoretical and spectroscopic investigations of this molecule showed it to have a trans-bent structure (C-Ge-Ge angles of ca. 80°) and a singlet ground state (cf. **1**). Moreover, higher oxidation-state compounds containing Ge–Ge multiple bonds, for example, trans-bent digermenes $(R_2Ge^{II}Ge^{II}R_2)$[13] and digermynes $(RGe^{I}Ge^{I}R)$,[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 $GeCl_2{\cdot}$dioxane was treated with one equivalent of the N-heterocyclic carbene IPr. This procedure afforded a high yield of the adduct complex $[GeCl_2(IPr)]$ (**4**).[15] The $^1H$ and $^{13}C\{^1H\}$ NMR spectroscopic data for the compound are consistent with its formulation and are similar to those reported for the silicon(II) analogues $[SiX_2(IPr)]$ (X = 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 $[SiX_2(IPr)]$. Its carbene center (C1) has an almost planar geometry, whilst the pyramidilization of the germanium atom (sum of angles about Ge1 284.7°) suggests that it possesses a stereochemically active lone pair. Both the Ge–Cl bond lengths and the Ge–C separation are comparable to those in the only other crystallographically characterized NHC–$GeCl_2$ adduct $[GeCl_2\{C[N(iPr)C(Me)]_2\}]$, 2.294 Å (mean) and 2.106(3) Å, respectively.[18]

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

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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/anie.200905495.

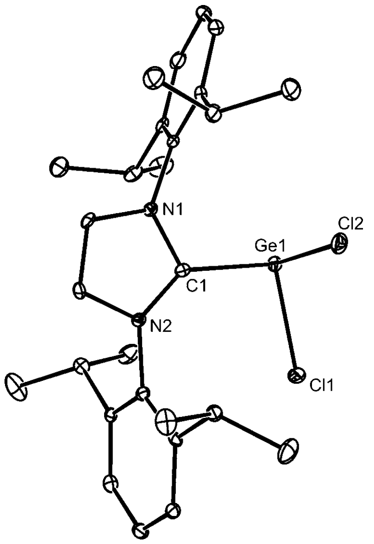
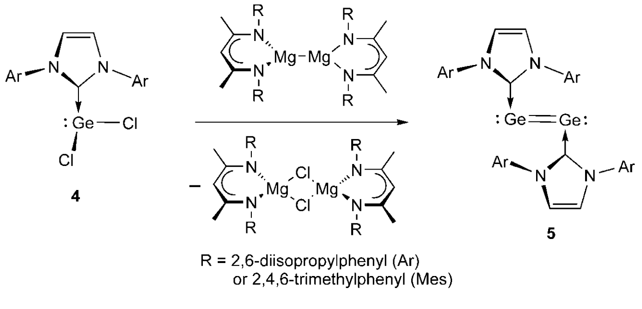


**Figure 1.** Molecular structure of compound **4** (25% ellipsoids; hydrogen atoms omitted). Relevant bond lengths [Å] and angles [°]: Ge1–C1 2.110(4), Ge1–Cl1 2.2651(12), Ge1–Cl2 2.2855(13), N1–C1 1.365(5), C1–N2 1.353(5); C1-Ge1-Cl1 97.55(11), C1-Ge1-Cl2 91.30(11), Cl1-Ge1-Cl2 95.85(5), N2-C1-N1 104.1(4).

[{Mg{[N(R)CMe]$_2$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 [{Mg{[N(Mes)CMe]$_2$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 much lower yield of **5** (less than 5%) was obtained from the reduction of **4** with the bulkier magnesium(I) dimer [{Mg{[N(Ar)CMe]$_2$CH}}$_2$].[19] We have to date had no success in isolating the related germanium(I) compound [(IPr)Ge(Cl)Ge(Cl)(IPr)] (cf. the known silicon(I) species [(IPr)Si(Cl)Si(Cl)(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 [(IPr)Ge(Cl)Ge(Cl)(IPr)] by reducing the germanium dichloride complex **4** with sodium metal or KC$_8$ in diethylether have not been successful, and the only product isolated from these reactions was free IPr.



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

Compound **5** is thermally stable ($T_{\text{decomp}} = 162$–$165\,^{\circ}$C, cf. **1** $T_{\text{decomp}} = 209\,^{\circ}$C) but extremely oxygen- and moisture-sensitive. As was the case with **1**, its $^1$H 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 $^{13}$C{$^1$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 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 (OC)Ge=Ge(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 C–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

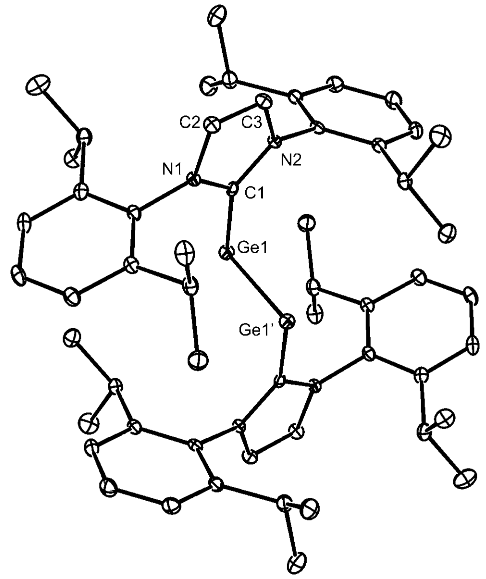


**Figure 2.** Molecular structure of compound **5** (25% ellipsoids; hydrogen atoms omitted). Relevant bond lengths [Å] and angles [°]: Ge1–C1 2.030(3), Ge1–Ge1′ 2.3490(8), N1–C1 1.365(3), C1–N2 1.369(3), N1–C2 1.384(3), N2–C3 1.387(4), C2–C3 1.341(4); C1-Ge1-Ge1′ 89.87(8), N1-C1-N2 103.6(2), N1-C1-Ge1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

bonded :Ge$^0$=Ge$^0$: 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 [{Ge[N(Me)C(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). 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).

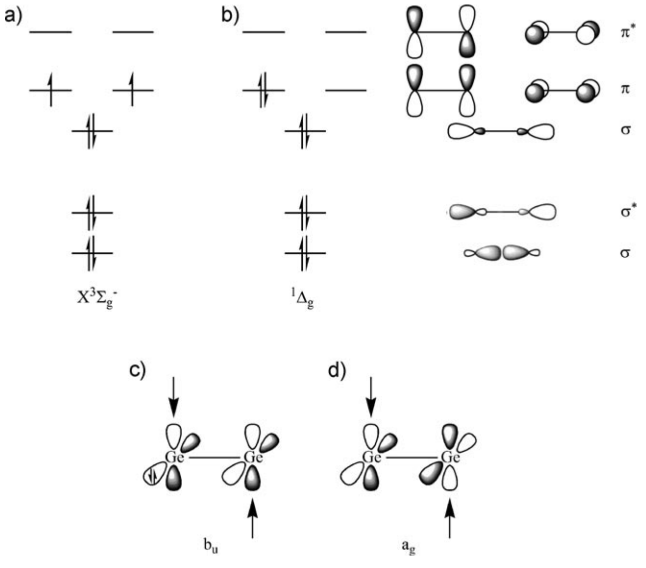


***Figure 3.*** Schematic representation of a) the X$^3\Sigma_g^-$ ground state b) the $^1\Delta_g$ excited state of Ge$_2$ and a pictorial description of the electron donation from the carbon σ lone pair orbitals of the NHC ligands into the vacant orbitals of ($^1\Delta_g$)Ge$_2$. c) Donation of the plus combination 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.

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 Ge$_2$(NHC)$_2$ complex **5M** using ($^1\Delta_g$) Ge$_2$ and (NHC)$_2$ as interacting fragments. The energy values are given in kcal mol$^{-1}$.

| | | |
|---|---|---|
| $\Delta E_{\text{int}}$ | −100.6 | |
| $\Delta E_{\text{Pauli}}$ | 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 %) |
| $\Delta E_{\text{prep}}$ | 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 $\Delta E_{\text{orb}}$.

The total interaction energy $\Delta E_{\text{int}}$ between ($^1\Delta_g$) Ge$_2$ and the (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 (Ge$_2$)–(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 (Ge$_2$)–(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 $\Delta E_{\text{orb}}$ 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 (Ge$_2$)–(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(π) orbitals of the carbene carbon atoms (a$_u$ symmetry) provides only 6.2 % of $\Delta E_{\text{orb}}$, 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 (Ge$_2$)–(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]

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

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[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.