Metalloid Clusters

DOI: 10.1002/anie.201204440

Low-Valent Ge_2 and Ge_4 Species Trapped by N-Heterocyclic Gallylene**

Adinarayana Doddi, Christian Gemel, Manuela Winter, Roland A Fischer, Catharina Goedecke, Henry S. Rzepa, and Gernot Frenking**

Much progress has been made in the field of low-valent main group 13–15 compounds. The disilicon molecule LSi=SiL (L = :C{N(2,6-*i*$Pr_2C_6H_3$)CH}$_2$)[1] and the closely related species E_2L_2 (i.e. "Ge_2",[2] "P_2",[3] "As_2")[4] were major discoveries in recent years.[5] Even the dicarbon congeners C_2L_2 should be accessible, as was deduced from quantum chemical studies.[6] N-heterocyclic carbenes (NHCs) turned out to be the key for opening the door to this new chemistry, and their heavier main group 13–14 analogs such as gallylenes (NHGa), silylenes (NHSi), germylenes (NHGe), expand this library of "multitalented" Lewis base ligands for stabilizing reactive species and unusual bonding situations.[7] In particular the NHGa compound Ga(DDP) (DDP = HC(CMeNC_6H_3-2,6-*i*Pr_2)$_2$)[8] behaves as a potent trapping ligand and a selective reducing agent as well. This unique combination of properties has been used for the synthesis of the metalloid tin clusters $Sn_7L'_2$, $Sn_{17}L'_4$[9] and the bismuthenes $Bi_2L'_2$ (L′ = (DDP)XGa; X = Cl, CF_3SO_3).[10]

Herein, we report about the reduction of $GeCl_2$ with Ga(DDP)/KC_8 and the properties of two interesting products (Figure 1), namely Ge_2[Ga(DPP)]$_2$ (**1**) and Ge_4[Ga(DPP)]$_2$ (**2**). Compound **1** reveals a planar, four-membered Ge_2Ga_2 ring with the two NHGa ligands in a bridging position much in contrast to the chain-structured congener LGe=GeL[3] with terminal NHC ligands L. The structure of **2** is derived from a Ge_4 tetrahedron by insertion of Ga(DDP) into two opposite Ge–Ge edges. This structural motif is unknown for ligand-stabilized metalloid Ge_nR_m clusters ($n > m$; R = bulky aryl, silylamide, etc.).[11]

The new compounds Ge_2[Ga(DPP)]$_2$ (**1**) and Ge_4[Ga(DPP)]$_2$ (**2**) were reproducibly isolated in low yields (**1**, about 7%; **2**, about 11%) upon treatment of $(PCy_3)\cdot GeCl_2$ with Ga(DDP)/KC_8 in THF (25 °C, 2 h) and (NHC)·$GeCl_2$ (NHC = :C{N(2,6-*i*$Pr_2C_6H_3$)CH}$_2$) with Ga(DDP) in fluorobenzene (25 °C, 8d), respectively (see Scheme S1 in the Supporting Information). In case of **2**, the anticipated by-product Cl_2Ga(DDP) was observed by ^{1}H NMR spectroscopy as well as single-crystal X-ray crystallography. Liquid injection field desorption ionization mass spectrometry (LIFDI-MS) studies of the reaction solution reveal that the formation of **1** (*m*/*z* 1120.3, $[M]^{+\bullet}$) and **2** (*m*/*z* 1264.08, $[M]^{+\bullet}$) proceeds very rapidly with both clusters being present after short reaction times (30 min). The ratio of the products changes in favor of **2** with longer reaction times. No other (larger) clusters are found by LIFDI-MS (see Figure S1 a and S1 b for details). Our attempts to optimize the conditions to achieve more selective reactions and increased isolated yields were unsuccessful. Nevertheless, **1** and **2** were characterized by solution NMR spectroscopy, matching isotope patterns (LIFDI-MS) (Figure S6 a and S6 b, Figure S7 a and S7 b), UV/VIS spectroscopy, single-crystal X-ray analysis (Figure 1), and elemental analysis. The absence of Ge–H moieties is confirmed by ^{1}H NMR as well as Raman and IR spectroscopy.[12] The experimental and complete analytical details are given in the Supporting Information.

Compound **1** crystallizes in the monoclinic space group *C*2/*c* and compound **2** crystallizes in the trigonal space group $P3_121$ with half of the molecule as well as one disordered solvent molecule in the asymmetric unit.[13] Both molecules **1** and **2** reveal centers of symmetry in their solid-state structures. The planar, four-membered Ge_2Ga_2 rhombic ring of **1** exhibits two sets of equivalent Ga–Ge bonds of 2.3899(8) and 2.4113(8) Å which are shorter than in **2** (2.5059(6) and 2.4755(6) Å). The distance Ge(1)–Ge(1′) of 2.8714(11) Å of **1** is much longer than the four Ge–Ge bonds of **2**, which only slightly vary around the average value of 2.459 Å and match the value of elemental germanium (2.45 Å).[14] Larger metalloid Ge_nR_m clusters ($n > 4$; $m < n$) exhibit longer Ge–Ge contacts, that is, Ge_6R_2 (2.546(1)–2.886(2) Å; R = C_6H_3-2,6-$Dipp_2$; Dipp = C_6H_3-2,6-*i*Pr_2)[15a] and Ge_8R_6 (2.50 to 2.67 Å; R = N(SiMe_3)$_2$).[15b] The structure of **2** can be viewed as derived from an ideal Ge_4 tetrahedron with two opposite edges being opened by insertion of two carbenoid Ga(DDP) ligands in trans fashion which results in two long Ge–Ge distances of 2.952 Å. Compound **2** may be compared with P_4[Al(DDP)]$_2$.[16] The latter was described by an ionic bonding model as P_4^{4-} butterfly-shaped Zintl anion coordinated by two cationic $[Al(DDP)]^{2+}$ units. Thus, **2** may be regarded as a similar contact ion pair of a Ge_4^{4-} anion and two $[Ga(DDP)]^{2+}$ units. However, such a description suggests to view the very long Ge···Ge distances of 2.952 Å as Ge–Ge

[*] A. Doddi, Dr. C. Gemel, M. Winter, Dr. R. A. Fischer
Lehrstuhl für Anorganische Chemie II
Organometallics and Materials, Fakultät für Chemie und Biochemie
Ruhr-Universität Bochum, 44780 Bochum (Germany)
E-mail: roland.fischer@rub.de
C. Goedecke, Dr. G. Frenking
Fachbereich Chemie, Philipps-Universität Marburg
Hans-Meerwein-Straße, 35032 Marburg (Deutschland)
E-mail: frenking@chemie.uni-marburg.de
Dr. H. S. Rzepa
Department of Chemistry, Imperial College, London (UK)

[**] Support by the German Chemical Industry Fund is gratefully acknowledged.

Supporting information for this article (experimental, analytical, and computational details for compounds **1** and **2**) is available on the WWW under http://dx.doi.org/10.1002/anie.201204440.

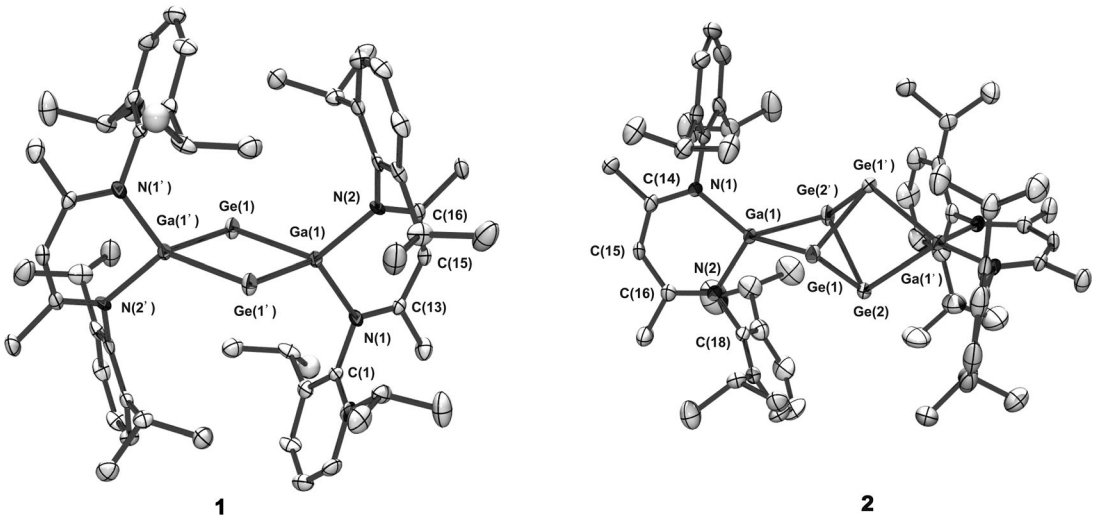

Figure 1. Molecular structures of $Ge_2[Ga(DDP)]_2$ (**1**) and $Ge_4[Ga(DDP)]_2$ (**2**). Anisotropic displacement parameters are depicted at 50% probability level. Hydrogen atoms have been removed for clarity. Interatomic distances (Å) and angles (°) of the Ge_2Ga_2 core of **1**: Ge(1)-Ge(1′), 2.8714(11) [2.911]; Ga(1)-Ge(1) = 2.4113(8) [2.467]; Ga(1)-Ge(1′) = 2.3899(8) [2.443] and Ga(1)-Ga(1′) = 3.848 [3.954]; Ge(1)-Ga(1)-Ge(1′) = 73.46(3) [72.7]; Ga(1)-Ge(1)-Ga(1′) = 106.54(3) [107.3] (The respective computational values for **1** at the BP86/SVP level of DFT theory are given in brackets). Selected interatomic distances (Å) of the Ge_4Ga_2 core of **2**: Ge(1)-Ge(1′) = 2.4545(9), Ge(1)-Ge(2) = 2.4637(6), Ge(2)-Ge(2′) = 2.4609(9), Ga(1)-Ge(1) = 2.5062(6), Ga(1′)-Ge(2) = 2.4750(6) Å. Further details on the molecular structure determination and bonding parameters of **1** and **2** are given in the Supporting Information (Table S1).

bonding (note: the electron precise Ge_4^{4-} Zintl ion is tetrahedral).

We carried out quantum chemical calculations[17a] of compounds **1** and **2** to analyze the electronic structure and the bonding situation in both molecules. Herein we will focus on compound **1**, which reveals an unusual bonding situation. A detailed account of the bonding aspects of both molecules will be given in a forthcoming full paper.[17b] We optimized the model structure **1M** at the BP86/SVP level of theory (**1M** contains CH_3 groups at the N atoms instead of the bulky aryl substituents in **1**). A comparison of the most important calculated bond lengths and bond angles (see the Figure 1 and Table S2) of **1M** shows a good agreement with the experimental results of **1**. The calculated Ga–Ge and Ga–N distances are slightly longer than the experimental values. Intermolecular forces usually lead to shorter bond lengths, which holds particularly for long and weak bonds.[18] The calculated transannular Ge–Ge distance (2.911 Å) is also a bit longer than the measured data (2.871 Å).

Figure 2 shows the Laplacian distribution $\nabla^2\rho(\mathbf{r})$ of the electron density in the plane of the Ge_2Ga_2 ring of **1M**. The contour line diagram shows four Ge–Ga bond paths and one ring critical point but there is no Ge–Ge bond path. There are four small areas of charge concentration ($\nabla^2\rho(\mathbf{r}) < 0$, solid lines) along the Ga–Ge bond paths which are on the Ge side of the bond critical points. This is in agreement with the higher electronegativity of Ge (2.0) compared to Ga (1.8). A striking aspect of the Laplacian distribution $\nabla^2\rho(\mathbf{r})$ is the absence of electron density at the Ge atoms which would come from σ lone-pair orbitals at Ge. The latter were found in the Laplacian distribution $\nabla^2\rho(\mathbf{r})$ of the electron density at the Si atoms in the four-membered ring of $Si_2(NAr)_2$ which was recently synthesized where two N atoms instead of Ga are bonded to Si.[19] We want to point out that the silicon atoms in the four-membered ring of the former compound are bonded to nitrogen atoms which have lone-pair π orbitals that can donate electronic charge into the formally empty p(π) AOs of Si. The gallium atoms in **1M** do not possess lone-pair π orbitals which leads to a bonding situation at the dicoordinated Ge atoms that is quite different from that of the

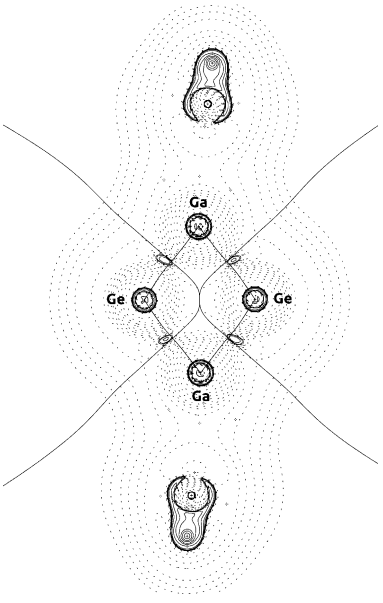

Figure 2. Contour line diagram of the Laplacian distribution $\nabla^2\rho(r)$ of **1M** in the plane of the four-membered ring. Solid lines indicate areas of charge concentration ($\nabla^2\rho(r) < 0$) while dotted lines show areas of charge depletion ($\nabla^2\rho(r) > 0$). The thick solid lines connecting the atomic nuclei are the bond paths. The thick solid lines separating the atomic basins indicate the zero-flux surfaces crossing the molecular plane.

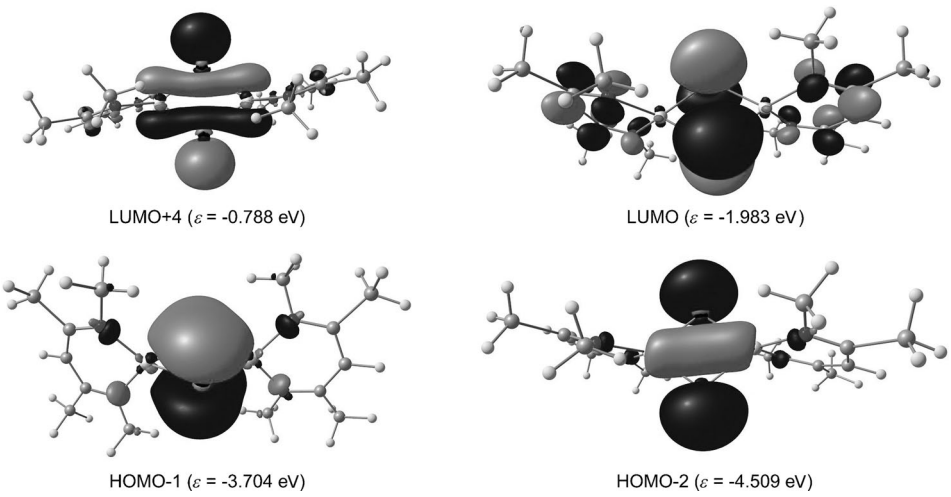

Figure 3. Shapes and eigenvalues ε of important vacant and occupied orbitals of **1M** which are relevant for the bonding situation.

dicoordinated Si atoms in $Si_2(NAr)_2$. This difference comes clearly to the fore when the relevant occupied and vacant valence orbitals in the two compounds are compared with each other.

Figure 3 shows the shape of two occupied and two vacant orbitals of **1M** which are crucial for the discussion of the bonding situation. The complete set of occupied valence orbitals is shown in the Supporting Information (Figure S20). The HOMO−1 and the LUMO of **1M** are the plus and minus combination of the out-of-plane p($\pi_\perp$) AOs of Ge where the former orbital has a small contribution from Ga. The shape of the HOMO−1 clearly identifies it as transannular Ge–Ge π-bonding MO. The HOMO−2 and the LUMO + 4 of **1M** are the plus and minus combination of the σ lone-pair orbitals at the Ge atoms.

There is a striking difference to the bonding situation in $Si_2(NAr)_2$, where the orbital analogs to the LUMO + 4 of **1** is occupied while the HOMO−1 is vacant.[19] The Ge_2Ga_2 ring in **1M** has only one occupied σ lone-pair MO which is the HOMO−2 while there are two occupied σ lone-pair MOs at Si in $Si_2(NAr)_2$. This explains the emergence of charge concentration at Si in the Laplacian distribution which comes from the σ lone-pair orbitals. There is no such charge concentration at the Ge atoms which have only one-half lone-pair MO each. Instead of a second occupied σ lone-pair MO there is the occupied Ge–Ge out-of-plane $\pi_\perp$ HOMO-1 (Figure 3). Note that **1M** may be regarded as hypoelectronic (12 valence electrons for the Ge_2Ga_2 ring) with respect to the $Si_2(NAr)_2$ reference compound (16 valence electrons for the Si_2N_2 ring). In spite of the difference between the occupation of the valence orbitals, both compounds $Si_2(NAr)_2$ and **1M** have electronic singlet ground states. Calculation of **1M** in the triplet state gave a structure which is 19.1 kcal mol^{-1} higher in energy than the singlet.[20]

The unusual bonding situation in **1M** in terms of Ge–Ge π-bonding but no σ-bonding is supported by the NBO analysis and by the ELF (electron localization function) calculations.[21] Two trisynaptic areas are found which connect the germanium atoms with gallium (Figure S21). They represent the Ge–Ga σ bonds of the Ge_2Ga_2 ring. The most important result is the finding of two disynaptic basins above and below the four-membered ring which feature the Ge-Ge π bond. In contrast, there is no disynaptic basin in the plane which would indicate a Ge–Ge σ bond. Thus, the ELF calculations also suggest that **1M** exhibits a Ge–Ge π bond but no genuine Ge–Ge σ bond! This unusual bonding situation of **1M** which is suggested by the AIM investigation, the shape analysis of the MOs, and the ELF results is further supported by the results of NBO calculations. Table 1 gives the bonding orbitals and their occupation as well as the Wiberg bond indices (WBI). The NBO results give four Ga–Ge σ bonds and four Ga-N σ bonds. The occupation of the natural orbitals is close to a value of two, which is a normal value for a two-electron bond. Furthermore, there is a Ge–Ge π bond which has also a rather high occupation of 1.795. Note that the WBI value for the nonpolar Ge−Ge bond is very high while the WBI value for the very polar Ga–N bonds is much smaller. The calculated value of 1.203 for the bond order indicates that the Ge–Ge π bond is supported by some weak Ge–Ge σ bonding which comes from the small backside lobes of the orbitals in the HOMO−2. The NBO analysis also gives one lone-pair orbital for each germanium atom which, however, is occupied by only about 0.8 electrons. There is no genuine Ge–Ge σ orbital in the NBO calculation. The best description of this bonding situation in terms of the Lewis formula concept features equivalent mesomeric structures (Figure 4). Alternatively, the situation may be described by two unpaired electrons at the germanium atoms possessing opposite spins which are weakly coupled.

Table 1: Natural orbital occupations for the bonds in the four-membered ring of **1M** and Wiberg bond indices WBI.

Type	Atom(s)	Occ.	WBI
σ bond	Ga1-Ge1	1.836	0.951
σ bond	Ga1-Ge2	1.843	0.983
σ bond	Ga2-Ge1	1.843	0.983
σ bond	Ga2-Ge2	1.836	0.951
σ bond	Ga1-N1	1.943	0.405
σ bond	Ga2-N2	1.943	0.405
σ bond	Ga2-N3	1.943	0.405
σ bond	Ga2-N4	1.943	0.405
π bond	Ge1-Ge2	1.761	1.203
lone pair	Ge1	0.774	–
lone pair	Ge2	0.774	–

In summary, the bonding analysis of **1M** clearly rules out an ionic description of $Ge_2[Ga(DPP)]_2$ (**1**) and provides

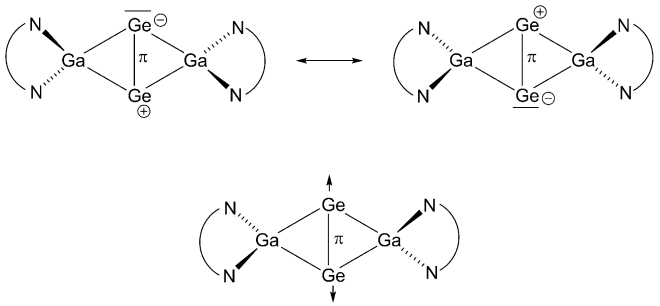

Figure 4. Schematic description of the bonding situation in the four-membered ring of **1** using two equivalent Lewis structures (above) or spin-coupled lone-electrons (below). The formal negative charge at Ga which cancels with a positive charge at N has been omitted because this is not relevant for the discussion.

evidence for covalent Ge–Ga bonding. The striking feature is the important transannular π(Ge–Ge) single bond interaction. The main difference in the bonding situation of the four-membered cyclic moieties between **1M** and $Si_2(NAr)_2$[19] is the absence of π lone-pair donation into the group 14 atoms of the former molecule.[20] Thus, compound **1** represents an unusual example of a bonding situation where two (heavier) main group atoms are bonded in π fashion without an additional σ bond between them. We are not aware of a previous example where a molecule exhibits a π bond between two atoms without a σ bond.[22–24]

Received: June 7, 2012
Revised: August 15, 2012
Published online: November 21, 2012

Keywords: bonding analysis · density functional calculations · gallium · germanium · metalloid clusters

[1] Y. Wang, Y. Xie, P. Wei, R. B. King, H. F. Schaefer, P. von R. Schleyer, G. H. Robinson, *Science* **2008**, *321*, 1069 – 1071.
[2] A. Sidiropoulos, C. Jones, A. Stasch, S. Klein, G. Frenking, *Angew. Chem.* **2009**, *121*, 9881 – 9884; *Angew. Chem. Int. Ed.* **2009**, *48*, 9701 – 9704.
[3] Y. Wang, Y. Xie, P. Wei, R. B. King, H. F. Schaefer, P. von R. Schleyer, G. H. Robinson, *J. Am. Chem. Soc.* **2008**, *130*, 14970 – 14971.
[4] M. Y. Abraham, Y. Wang, Y. Xie, P. Wei, H. F. Schaefer, P. von R. Schleyer, G. H. Robinson, *Chem. Eur. J.* **2010**, *16*, 432 – 435.
[5] a) Y. Wang, G. H. Robinson, *Dalton Trans.* **2012**, *41*, 337 – 345; b) Y. Wang, G. H. Robinson, *Chem. Commun.* **2009**, 5201 – 5213.
[6] J. L. Dutton, D. J. D. Wilson, *Angew. Chem.* **2012**, *124*, 1506 – 1509; *Angew. Chem. Int. Ed.* **2012**, *51*, 1477 – 1480.
[7] M. Asay, C. Jones, M. Driess, *Chem. Rev.* **2011**, *111*, 354 – 396.
[8] N. J. Hardman, B. E. Eichler, P. P. Power, *Chem. Commun.* **2000**, 1991 – 1992.
[9] G. Prabusankar, A. Kempter, C. Gemel, M. K. Schröter, R. A. Fischer, *Angew. Chem.* **2008**, *120*, 7344 – 7347; *Angew. Chem. Int. Ed.* **2008**, *47*, 7234 – 7237.
[10] G. Prabusankar, C. Gemel, P. Parameswaran, C. Flener, G. Frenking, R. A. Fischer, *Angew. Chem.* **2009**, *121*, 5634 – 5637; *Angew. Chem. Int. Ed.* **2009**, *48*, 5526 – 5529.
[11] a) A. Schnepf, *Eur. J. Inorg. Chem.* **2008**, 1007 – 1018; b) A. Schnepf, *Chem. Soc. Rev.* **2007**, *36*, 745 – 758; c) A. Schnepf, *Coord. Chem. Rev.* **2006**, *250*, 2758 – 2770.
[12] All signals observed in the ^{1}H NMR spectrum of **1** are assigned and there are no signals in the typical region of Ge-H groups (about 3.92 and 8.0 ppm) also the IR and Raman spectra does not provide any indications for the presence of terminal Ge-H moieties: a) K. C. Thimer, S. M. I. Al-Rafia, M. J. Ferguson, R. McDonald, E. Rivard, *Chem. Commun.* **2009**, 7119 – 7121; b) S. L. Choong, W. D. Woodul, C. Schenk, A. Stasch, A. F. Richards, C. Jones, *Organometallics* **2011**, *30*, 5543 – 5550.
[13] Crystal Structure analyses (Oxford Excalibur 2 diffractometer): The structural solution and refinement was performed using the programs SHELXS-86 and SHELXL-97: G. M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structures, Universität Göttingen, **1997**; G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, Universität Göttingen, **1997**; a) X-ray crystal structure analysis of **1**: $C_{58}H_{82}Ga_2Ge_2N_4$, $M = 1119.90$, monoclinic, space group $C2/c$, $a = 24.2323(10)$ Å, $b = 15.2254(8)$ Å, $c = 15.0722(8)$ Å, $\beta = 94.492(4)°$, $V = 5543.8(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.342$ g cm^{-3}, $T = 110(2)$ K, $F(000) = 2336$, $\mu(Mo_{K\alpha}) = 2.075$ mm^{-1}, prismatic crystal, 30770 reflections measured, 4869 unique ($R_{int} = 0.1312$), 303 parameters, $R_1 = 0.0564$ ($I > 2\sigma(I)$), $wR_2 = 0.1024$ ($I > 2\sigma(I)$), $GOF = 1.026$. The overall data quality is limited, as revealed by the R(int)value of 0.1312, because the crystal was small and only weakly diffracting. No time dependency of the quality within the measurement has been observed. Attempts to obtain better crystals have not been successful; b) X-ray crystal structure analysis of **2**: $C_{64}H_{87}FGa_2Ge_4N_4$, $M = 1361.18$, Trigonal, space group $P3_121$, $a = 19.5740(3)$ Å, $c = 15.2771(3)$ Å, $V = 5069.10(15)$ Å^3, $Z = 3$, $\rho_{calcd} = 1.338$ g cm^{-3}, $T = 110(2)$ K, $F(000) = 2094$, $\mu(Mo_{K\alpha}) = 2.583$ mm^{-1}, prismatic crystal, 10993 reflections measured, 6540 unique ($R_{int} = 0.0203$), 307 parameters, $R_1 = 0.0295$ ($I > 2\sigma(I)$), $wR_2 = 0.0812$ ($I > 2\sigma(I)$), $GOF = 1.034$. The disordered solvent molecule in **2** was squeezed out with the program Platon 1.13: A. L. Spek, *Acta Crystallogr. Sect. A* **1990**, *46*, C34. The fluorobenzene molecule is included in the empirical formula. CCDC 833302 (**1**) and CCDC 833301 (**2**) 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.
[14] J. S. Kasper, S. M. Richards, *Acta Crystallogr.* **1964**, *17*, 752 – 755.
[15] a) A. Schnepf, R. Köppe, *Angew. Chem.* **2003**, *115*, 940 – 942; *Angew. Chem. Int. Ed.* **2003**, *42*, 911 – 913; b) A. F. Richards, H. Hope, P. P. Power, *Angew. Chem.* **2003**, *115*, 4205 – 4208; *Angew. Chem. Int. Ed.* **2003**, *42*, 4071 – 4074.
[16] Y. Peng, H. Fan, H. Zhu, H. W. Roesky, J. Magull, C. E. Hughes, *Angew. Chem.* **2004**, *116*, 3525 – 3527; *Angew. Chem. Int. Ed.* **2004**, *43*, 3443 – 3445.
[17] a) The quantum chemical methods are described in the Supporting Information. b) The cyclic structure of **1** is remarkably different from its NHC stabilized, chain like congeners LE = EL with a distinct multiple bond situation between the main group elements (E = Si, Ge; L = NHC).[1,2] The NHGa prefers the bridging position in contrast to the terminal bonded NHC. The NHC and NHGa ligand properties are characteristically different which has consequences for the Ge–Ge bond situation.
[18] V. Jonas, G. Frenking, M. T. Reetz, *J. Am. Chem. Soc.* **1994**, *116*, 8741 – 8753.
[19] R. S. Ghadwal, H. W. Roesky, K. Pröpper, B. Dittrich, S. Klein, G. Frenking, *Angew. Chem.* **2011**, *123*, 5486 – 5490; *Angew. Chem. Int. Ed.* **2011**, *50*, 5374 – 5378.
[20] One referee suggested that the reason for the Ge-Ge π bonding could be the slightly larger electronegativity of Ge compared with Ga. We checked this by calculating the silicon and tin

homologues of **1M**. The electronegativities of Si (1.7) and Sn (1.7) are smaller than that of Ga (1.8) but the electronic structure of the group-14 homologues showed also Si-Si and Sn-Sn π bonding, respectively.

[21] A. D. Becke, K. E. Edgecombe, *J. Chem. Phys.* **1990**, *92*, 5397 – 5403.

[22] One referee suggested that related cases of π bonding between main-group elements have been discussed in early works by Passmore and co-workers[23] and in recent studies by Bertrand[24a] and Driess.[24b] The article of Passmore present sketches of Lewis structures for S_8^{2+}[23a] and $S_2I_4^{2+}$[23b] which can not be considered as proof for π bonding without σ bonding. Moreover, the authors suggest that in $S_2I_4^{2+}$[23b] π* orbitals of the S_2 and I_2 fragments interact such that the valence p orbitals of the atoms are aligned along the bond which yields σ bonding. We want to point out that σ and π define the symmetry of orbitals of a bond A-B with respect to a plane that contains the bond. The π*-π* interactions which are suggested for the bonding in $S_2I_4^{2+}$[23b] refer to orbitals which have π symmetry with respect to the S_2 and I_2 fragments but the S–I bonding orbitals have σ symmetry. A similar situation is presented in the work of Bertrand[24a] and Driess.[24b] Figure 4 in the former article shows nicely how two P-P π* orbitals of three-membered cyclic fragments yield P-P σ bonds. The same holds true for the related systems which are described by Driess[24b] where two S-S π* orbitals of three-membered cyclic fragments yield S-S σ bonds.

[23] a) C. G. Davies, R. J. Gillespie, J. J. Park, J. Passmore, *Inorg. Chem.* **1971**, *10*, 2781 – 2785; b) J. Passmore, G. Sutherland, T. Whidden, P. S. White, *J. Chem. Soc. Chem. Commun.* **1980**, 289 – 290.

[24] a) Y. Canac, D. Bourissou, A. Baceiredo, H. Gornitzka, W. W. Schoeller, G. Bertrand, *Science* **1998**, *279*, 2080 – 2082; b) S. Yao, C. Milsmann, E. Bill, K. Wieghardt, M. Driess, *J. Am. Chem. Soc.* **2008**, *130*, 13536 – 13537.

