5786 *Inorg. Chem.* **2010**, *49*, 5786–5788
DOI: 10.1021/ic100501e

Inorganic Chemistry
Communication

Reactivity Studies of a Ge$^{\mathrm{I}}$–Ge$^{\mathrm{I}}$ Compound with and without Cleavage of the Ge–Ge Bond

Sakya S. Sen, Daniel Kratzert, Daniel Stern, Herbert W. Roesky,* and Dietmar Stalke

Institut für Anorganische Chemie, Universität Göttingen, Tammannstrasse 4, 37077 Göttingen, Germany

Received March 16, 2010

This Communication describes two strikingly different reactivities of a digermylene [{PhC(N*t*Bu)$_2$}$_2$Ge$_2$] (**1**) featuring a Ge$^{\mathrm{I}}$–Ge$^{\mathrm{I}}$ single bond. In the reaction with azobenzene, **1** affords the oxidative addition product LGeN(Ph)N(Ph)GeL [**2**; L = PhC(N*t*Bu)$_2$], with simultaneous cleavage of the Ge–Ge bond, whereas treatment of **1** with Fe$_2$(CO)$_9$ yields the Lewis acid–base adduct LGe[Fe(CO)$_4$]Ge[(Fe(CO)$_4$]L (**3**). Both compounds were characterized by single-crystal X-ray diffraction, NMR spectroscopy, electrospray ionization mass spectrometry, and elemental analysis.

The synthesis of alkyne analogues (REER) of the heavier congeners (E = Si–Pb) was only recently accomplished. In 2002, Power and co-workers reported the first carmine red-orange digermyne [RGeGeR; R = 2,6-Trip$_2$C$_6$H$_3$ (Trip = 2,6-*i*Pr$_2$C$_6$H$_3$)] by means of a tailor-made terphenyl-substituted starting material.[1a] Following this, Jones et al. reported the amidinato- and guanidinato-stabilized germanium(I) dimer {Ge(Piso)}$_2$ and {Ge(Giso)}$_2$ [Piso = (ArN)$_2$C*t*Bu, Giso = (ArN)$_2$CN*i*Pr$_2$, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$].[2] Recently, we successfully synthesized the first *gauche*-bent amidinato-stabilized germanium(I) dimer [PhC(N*t*Bu)$_2$]$_2$Ge$_2$ (**1**) with the *t*Bu substituents on the nitrogen atoms.[3] The series was extended when Driess et al. documented a unsymmetrically substituted digermylene with a Ge$^{\mathrm{I}}$–Ge$^{\mathrm{I}}$ bond [LGe–GeL′, L = C(Me)CHC(Me)N(2,6-*i*Pr$_2$-C$_6$H$_3$), L′ = CH(CMeNR)$_2$, R = 2,6-*i*Pr$_2$C$_6$H$_3$) R = 2,6-*i*Pr$_2$C$_6$H$_3$].[4] The main difference in Power's digermyne and the other germanium(I) dimers is the central Ge–Ge bond length. Inspection of structural data of the latter affords the Ge–Ge bond distance as 2.28(6) Å,[1] which is commonly interpreted as a double bond because it is significantly shorter than a single bond. Differently are the Ge–Ge bond distances in Jones' germanium(I) dimer and in **1**. They are 2.63(8) and 2.57(5) Å, respectively, and hence much closer to the bond length found in a Ge–Ge single bond (2.61 Å mean).[5] The reactivity of digermynes has been studied extensively,[6] but to the best of our knowledge, the reactivity of a germanium(I) dimer where the Ge–Ge bond length has to be regarded as a single bond has not been reported so far. Furthermore, a detailed theoretical calculation proposed that **1** features two stereoactive lone pairs, which prefer to remain nonbonded at each germanium atom.[3] Fueled by this unprecedented electronic structure, we embarked to study the reactivity of **1**. Unequivocally, this

---

*To whom correspondence should be addressed. E-mail: hroesky@gwdg.de.

(1) (a) Stender, M.; Phillips, A. D.; Wright, R. J.; Power, P. P. *Angew. Chem.* **2002**, *114*, 1863–1865. *Angew. Chem., Int. Ed.* **2002**, *41*, 1785–1787. (b) Power, P. P. *Chem. Commun.* **2003**, 2091–2101.

(2) Green, S. P.; Jones, C.; Junk, P. C.; Lippert, K.-A.; Stasch, A. *Chem. Commun.* **2006**, 3978–3980.

(3) Nagendran, S.; Sen, S. S.; Roesky, H. W.; Koley, D.; Grubmüller, H.; Pal, A.; Herbst-Irmer, R. *Organometallics* **2008**, *27*, 5459–5463.

(4) Wang, W.; Inoue, S.; Yao, S.; Driess, M. *Chem. Commun.* **2009**, 2661–2663.

(5) Determined by the survey of the Cambridge Crystallographic Database.

(6) (a) Cui, C.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **2004**, *126*, 5062–5063. (b) Cui, C.; Brynda, M.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **2004**, *126*, 6510–6511. (c) Power, P. P. *Appl. Organomet. Chem.* **2005**, *19*, 488–493. (d) Spikes, G. H.; Fettinger, J. C.; Power, P. P. *J. Am. Chem. Soc.* **2005**, *127*, 12232–12233. (e) Cui, C.; Olmstead, M. M.; Fettinger, J. C.; Spikes, G. H.; Power, P. P. *J. Am. Chem. Soc.* **2005**, *127*, 17530–17541. (f) Power, P. P. *Organometallics* **2007**, *26*, 4362–4372. (g) Rivard, E.; Power, P. P. *Inorg. Chem.* **2007**, *46*, 10047–10064. (h) Power, P. P. *Nature* **2010**, *463*, 171–177.

(7) All manipulations were carried out in an inert atmosphere of N$_2$ using standard Schlenk techniques and in a N$_2$-filled glovebox. (a) **2:** A mixture of **1** (0.2 g, 0.33 mmol) and PhNNPh (0.06g, 0.33 mmol) in toluene (20 mL) was stirred at room temperature overnight. The solvent was removed under reduced pressure, and the remaining powder was washed with *n*-hexane (10 mL). Further recrystallization from toluene (5 mL) at room temperature afforded colorless crystals of **2** (0.16 g, 61.5%). Mp: 148–155 °C. Elem anal. Calcd for C$_{42}$H$_{56}$Ge$_2$N$_6$ (790.20): C, 63.84; H, 7.14; N, 10.64. Found: C, 64.16; H, 8.04; N, 10.35. ^{1}H NMR (300 MHz, C$_6$D$_6$, 25 °C): δ 1.25 (s, 36 H, *t*Bu), 7.26–7.33 (m, 10 H, Ph), 6.85–7.50 (m, 20 H, Ph). ^{13}C{^{1}H} NMR (125.75 MHz, C$_6$D$_6$, 25 °C): δ 32.47(C*Me*$_3$), 53.81 (*C*Me$_3$), 123.29, 125.64, 127.54, 127.81, 128.00, 128.10, 128.19, 128.29, 128.41, 128.44, 128.51, 128.53, 129.15, 129.25, 129.27, 129.51, 131.08, 136.37, 140.88 (Ph), 166.08 (NCN). EI-MS: *m*/*z* 790 [M^{+}](100%). (b) **3:** THF (40 mL) was added to the mixture of **1** (0.2 g, 0,33 mmol) and diiron nonacarbonyl (0.24 g, 0.67 mmol) at ambient temperature under N$_2$. After stirring for 40 h, the initially light-orange solution became darker in color to ultimately afford a garnet-brown solution. The solvent was then removed in vacuum, and the residue was extracted with toluene (30 mL). The insoluble solid was filtered off. The garnet-brown filtrate was concentrated and stored at −30 °C in a freezer to yield a red-brown solid of **3** (0.52 g, 61%). Mp: 180–185 °C. Elem anal. Calcd for C$_{38}$H$_{46}$Fe$_2$Ge$_2$N$_4$O$_8$ (943.67): C, 48.36; H, 4.91; N, 5.94. Found: C, 47.51; H, 4.33; N, 5.85. ^{1}H NMR (200 MHz, C$_6$D$_6$, 25 °C): δ 1.41 (s, 36H, *t*Bu), 7.56–7.82 (m, 5H, Ph). ^{13}C{^{1}H} NMR (125.75 MHz, C$_6$D$_6$, 25 °C): δ 31.3 (C*Me*$_3$), 54.9 (*C*Me$_3$), 127.8, 128.2, 128.3, 129.2, 130.0, 130.7 (*Ph*), 171.1 (N*C*N), 220.5 (*C*O). IR (Nujol, cm^{-1}): ν 2029 (m), 1974 (s), 1920 (s) (CO). EI-MS: *m*/*z* (%) 943 [M^{+}] (100).

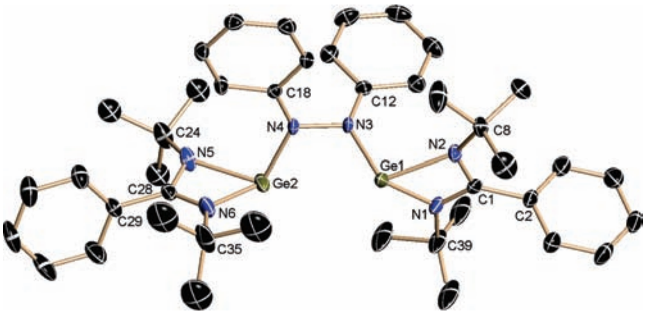
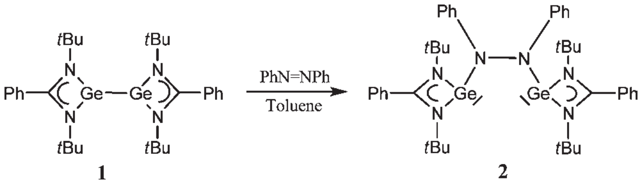


Figure 1. Anisotropic displacement parameters, depicted at the 50% probability level of **2**. Hydrogen atoms and two toluene lattice molecules are omitted for clarity. All four *t*Bu groups are rotationally disordered about the N−C axis. Selected bond lengths [Å] and angles [deg]: N2−Ge1 2.050(3), Ge1−N3 1.911(3), Ge2−N4 1.902(3), N3−C12 1.401(4), N3−N4 1.436(4); C28−N5−Ge2 91.1(2), C24−N5−Ge2 133.1(2), C28−N6−Ge2 92.7(2), C35−N6−Ge2 136.3(3), N4−Ge2−N5 105.6(13), N4−Ge2−N6 103.6(14), C12−N3−Ge1 134.5(2), N4−N3−Ge1 110.8(2), C18−N4−Ge2 132.7(2), N3− N4−Ge2 110.9(2), C1−N1−Ge1 93.0(2), C39−N1−Ge1 135.4(3), C1−N2−Ge1 91.7(2), C8−N2−Ge1 134.2(2), N3−Ge1−N1 104.4(13), N3− Ge1−N2 105.1(12), N1−Ge1−N2 64.1(12).

Scheme 1. Preparation of **2**



is of great interest to both organic and organometallic chemists. Our initial results are reported herein.

In order to derivatize **1**, a reaction was performed with azobenzene (PhN═NPh) in a 1:1 molar ratio in toluene at room temperature (Scheme 1). This afforded **2** as colorless crystals in good yield.[7a] The product is stable under an inert atmosphere and soluble in organic solvents like ether, toluene, and tetrahydrofuran (THF).

The molecular graph from the crystal structure determination of **2** is shown in Figure 1.[8] Compound **2** crystallizes in the monoclinic space group *Pbcn*. The most striking result of the reaction is the unambiguous cleavage of the Ge−Ge bond and the insertion of the substituted N_2 motif of the azobenzene. The formal oxidation state of both germanium atoms in **2** is increased to 2+. The N−N bond distance of 1.44(4) Å is consistent with the interpretation as a single bond.[9] In addition, the N−C bond distances remain unchanged. Therefore, the reaction of **1** with PhN═NPh has to be regarded as an oxidative addition with simultaneous Ge−Ge bond cleavage. As a result, **2** is a molecular chain containing four elements each with a lone pair of electrons. Here it is worth mentioning that a similar kind of Ge−Ge bond cleavage was reported by Power et al. when RGeGeR [R = 2,6-$\mathrm{Trip_2C_6H_3}$ (Trip = 2,6-*i*$\mathrm{Pr_2C_6H_3}$)] was reacted with azobenzene.[8c] In addition to that, the Ge−N bond lengths [1.882(4) and 1.875(4) Å] and the N−N bond distance [1.45(3) Å] in RGe{(Ph)NN(Ph)}GeR coincide very well with those of **2**. Both germanium atoms are tricoordinate and each exhibit a distorted trigonal-pyramidal geometry with a stereochemically active lone pair at one apex. The three other sites at the germanium atom are occupied by the two nitrogen atoms of the amidinato ligand and one nitrogen atom of the bridging azobenzene. The coordination of the nitrogen atoms is almost planar with angular sums $\sum\angle$N3,4 of 359.8(2)°. The Ge−N bond length [1.905(3) Å] is within the range found for other germanium(II) amides.[9]

Additionally, **2** was characterized by NMR spectroscopy, electron impact mass spectrometry (EI-MS), elemental analysis. The ^{1}H NMR spectrum of **2** exhibited three sets of resonances, one from the *t*Bu protons of the amidinato ligand, the second one of the phenyl rings of the same ligand, and the third one of the phenyl substituents of azobenzene. In the EI-MS spectrum, the molecular ion appeared as the most abundant peak with the highest relative intensity at *m*/*z* 790.

In the aforementioned experiment, the Ge−Ge bond in **1** was cleaved by insertion of azobenzene. However, we were curious to see a reactivity where the Ge−Ge bond will remain intact. In order to obviate such a possibility and minimize the opportunity of cleavage, we wanted to employ the lone pair at the $\mathrm{Ge^I}$ atom in bonding. According to Pearson's hard and soft acids and bases concept, **1** can be considered as a soft base.[10] So, the simplest idea is to treat **1** with a soft Lewis acid and check whether it can form the Lewis acid−base adduct. Therefore, diiron nonacarbonyl, $\mathrm{Fe_2(CO)_9}$, with iron in the formal oxidation state zero, was judiciously chosen as a probe to investigate the reaction behavior. It is known to form metal complexes with N-heterocyclic silylene.[11] In our case, the reaction successfully affords the target complex, a unique example of a Lewis acid−base adduct employing both germanium(I) centers with adjacent lone pairs as Lewis bases.

The treatment of **1** with 2 equiv of $\mathrm{Fe_2(CO)_9}$ in THF for 1 day afforded **3** (Scheme 2).[7b] After the reaction, the solvent was removed in vacuum and the residue extracted with toluene. The insoluble solid was filtered off, and the filtrate was concentrated and stored at −30 °C in a freezer to yield red crystals of **3**, suitable for the X-ray diffraction study.

The solid-state structure of **3** is shown in Figure 2.[8] **3** crystallizes in the centrosymmetric monoclinic space group *C*2/*c*. The most striking feature of the structure is the unbroken Ge−Ge bond. This bond length is 2.55(5) Å and, hence, is reduced a little in comparison to **1** [2.57(5) Å]. In **3**, each germanium atom binds to two nitrogen atoms from the monoanionic chelating amidinato ligand, to another $\mathrm{Ge^I}$ atom, and to a $\mathrm{Fe(CO)_4}$ moiety, leaving the germanium atom

---

(8) (a) Kottke, T.; Stalke, D. *J. Appl. Crystallogr.* **1993**, *26*, 615–619. (b) Stalke, D. *Chem. Soc. Rev.* **1998**, *27*, 171–176. (c) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122. Shock-cooled crystals were selected and mounted under nitrogen atmosphere using X-TEMP2. The structure was solved by direct methods (SHELXS) and refined against F^2 using full matrix least squares methods of SHELXL. Crystal data for **2**: M_r = 881.23, orthorhombic, space group *Pbcn*, a = 16.831(2) Å, b = 17.077(3) Å, c = 32.576(5) Å, V = 9364(2) Å^3, $Z = 8$, ρ_{calcd} = 1.250 g/cm^3, μ(Mo Kα) = 1.323 mm^{-1}, T = 100(2) K, R1 = 0.0531 [$I > 2\sigma(I)$], wR2 = 0.1374. Crystal data for **3**: M_r = 943.71, monoclinic, space group $C2/c$, a = 21.491(2) Å, b = 10.420(1) Å, c = 18.889(2) Å, β = 105.965(1)°, V = 4066.9(7) Å^3, $Z = 4$, ρ_{calcd} = 1.541 g/cm^3, μ(Mo Kα) = 2.217 mm^{-1}, T = 100(2) K, R1 = 0.0249 [$I > 2\sigma(I)$], *w*R2 = 0.0638.

(9) (a) The N−N bond length in $\mathrm{(H_3Si)_2NN(SiH_3)_2}$ is 1.46 Å: Glidewell, C.; Rankin, D. W. H.; Robiette, A. G.; Sheldrick, G. M. *J. Chem. Soc. A* **1970**, 318–320. (b) Veith, M.; Rammo, A. *Z. Anorg. Allg. Chem.* **2001**, *627*, 662–668.

(10) (a) Pearson, R. J. *Science* **1966**, *151*, 172–177. (b) Pearson, R. J. *J. Am. Chem. Soc.* **1963**, *85*, 3533–3539.

(11) Yang, W.; Fu, H.; Wang, H.; Chen, M.; Ding, Y.; Roesky, H. W.; Jana, A. *Inorg. Chem.* **2009**, *48*, 5058–5060.

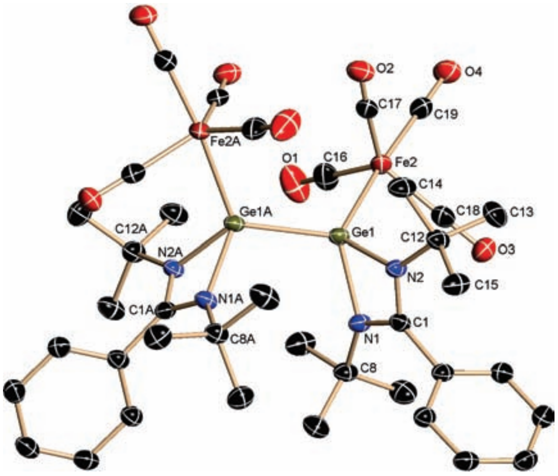
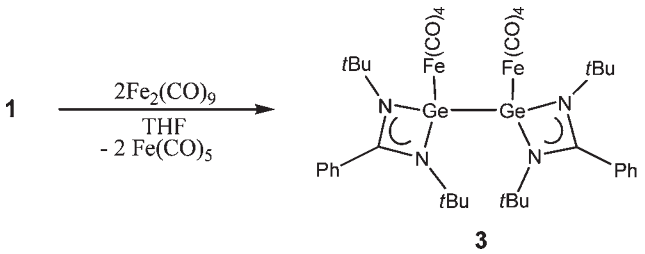


Figure 2. Anisotropic displacement parameters, depicted at the 50% probability level of **3**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]:Ge1−Ge1A 2.5512(5), Ge1−N1 1.9623(16), Ge1−N2 1.9817(16), Fe2−C16 1.791(2), Fe2−Ge1 2.3402(4); C18−Fe2−C19 92.34(9), N1−Ge1−N2 66.60(6), N1−Ge1−Fe2 118.44(5), N2−Ge1−Fe2 114.94(5), N1−Ge1−Ge1A 111.66(5), N2−Ge1−Ge1A 108.00(5), Fe2−Ge1−Ge1A 123.211(10).

Scheme 2. Preparation of **3**



four-coordinate in a distorted tetrahedral coordination geometry. Each iron atom is centered in a trigonal-bipyramidal polyhedron; four sites are occupied by carbonyl groups and one by a germanium atom. The Fe^I-Ge^I bond distance in **3** is 2.34(4) Å, which is very similar to those found in $LGe(OH)Fe(CO)_4$ [2.33(1) Å; L = $HC(CMeNAr)_2$ with Ar = 2,6-$i$$Pr_2C_6H_3$][12a] and [$\eta^3$-($\mu$-$t$BuN)$_2$(SiMeN$t$Bu)$_2$)-GeFe(CO)$_4$] [2.348(1) Å][12b] and also slightly longer compared with that of $LGe(Cl)Fe(CO)_4$ [2.29(2) Å; L = $HC(CMeNPh)_2$.[12c] In all of the mentioned examples, the $Fe(CO)_4$ fragment is bonded to germanium atoms in the formal oxidation state of 2+. However, to the best of our knowledge, **3** is the first example where the $Fe(CO)_4$ moiety is attached to a germanium atom in the formal oxidation state of 1+.

Additionally, **3** was characterized by mass spectrometry, NMR spectroscopy, and elemental analysis. All obtained data are in accordance with the structure of **3**. The ^{1}H NMR spectrum of **3** shows a singlet at 1.41 ppm for the 36 protons of four tBu groups and another multiplet for 10 aromatic protons (7.56−7.82 ppm). In the ^{13}C NMR spectrum, the chemical shift of the carbonyl group in **3** (220.56 ppm) is similar to that observed for the N-heterocyclic silylene complex with $Fe(CO)_4$.[11] The molecular ion in the EI-MS spectrum appeared as the most abundant peak at m/z 943.

Carbonyl stretching frequencies are used as a probe to compare the electronic properties of a series of complexes. The CO stretching frequencies of **3** [2029 (m), 1974 (s), and 1920 (s) cm^{-1}] are very similar to those of $LGe(OH)Fe(CO)_4$ [L = $HC(CMeNAr)_2$ with Ar = 2,6-$i$$Pr_2C_6H_3$; 2039 (s), 1956 (s), and 1942 (s) cm^{-1}][12a] and the N-heterocyclic silylene complex with $Fe(CO)_4$ [2026 (m), 1949 (s), and 1899 (s) cm^{-1}].[11]

In summary, we have shown for the first time two contrasting reactivities of a germanium(I) dimer featuring a Ge−Ge single bond toward azobenzene and diiron nonacarbonyl. In the former case, cleavage of the Ge−Ge bond occurs to form a vicinal digermahydrazine derivative, whereas in the latter case, a Lewis acid−base adduct is formed, keeping the Ge−Ge bond intact. Further reactivity studies are ongoing in our laboratory and will be reported in due course.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft.

Supporting Information Available: Crystallographic data in CIF format for **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

---

[12] (a) Pineda, L. W.; Jancik, V.; Colunga-Valladares, J. F.; Roesky, H. W.; Hofmeister, A.; Magull, J. *Organometallics* **2006**, *25*, 2381–2383. (b) Saur, I.; Rima, G.; Miqueu, K.; Gornitzka, H.; Barrau, J. *J. Organomet. Chem.* **2003**, *672*, 77–85. (c) Veith, M.; Becker, S.; Huch, V. *Angew. Chem.* **1990**, *102*, 186–188. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 216−218.