Angewandte Chemie

Germanium(0) Compounds

DOI: 10.1002/ange.201309421

A Coordination Compound of Ge^0 Stabilized by a Diiminopyridine Ligand**

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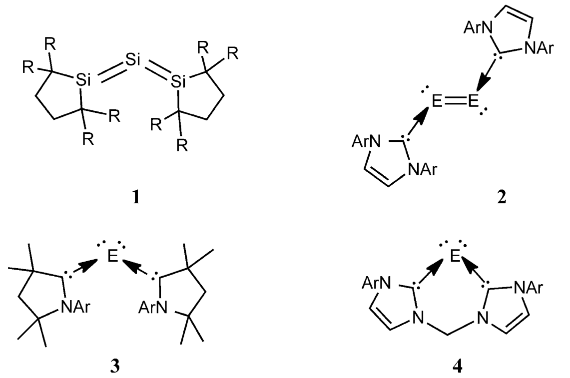
Dedicated to Professor Nikolai A. Ustynyuk on the occasion of his 70th birthday

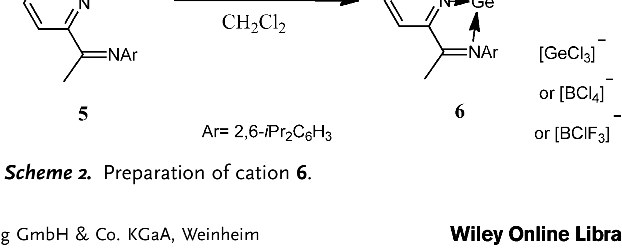
Abstract: *Reduction of the cationic Ge^{II} complex [dimpyrGeCl][$GeCl_3$] (dimpyr = 2,6-(ArN = CMe)$_2$NC$_5$H$_3$, Ar = 2,6-iPr$_2$C$_6$H$_3$) with potassium graphite in benzene affords an air sensitive, dark green compound of Ge^0, [dimpyrGe], which is stabilized by a bis(imino)pyridine platform. This compound is the first example of a complex of a zero-valent Group 14 element that does not contain a carbene or carbenoid ligand. This species has a singlet ground state. DFT studies revealed partial delocalization of one of the Ge lone pairs over the π*(C=N) orbitals of the imines. This delocalization results in a partial multiple-bond character between the Ge atom and imine nitrogen atoms, a fact supported by the X-ray crystallography and IR spectroscopy data.*



Scheme 1. Examples of Si^0 and Ge^0 compounds.

The chemistry of the Group 14 elements in low oxidation states has recently received renewed attention.[1–3] In particular, the unique zero oxidation state, E(0), has recently been realised. Following the pioneering report by Kira et al.[4] on trisilaallene (**1**) and its heavier congeners,[5–7] a series of E(0) compounds were prepared, all showing the same prominent feature: coordination of the Group 14 centre in the zero oxidation state to a carbene or silylene ligand. These compounds can be placed into two major categories: the double-bonded species L→E = E←L (E = Si,[8] Ge,[9] Sn;[10] L = NHC carbene; **2** in Scheme 1)[11] and a wider class of so-called ylidones, L→E←L, in which the central atom is bound to two carbenoid ligands by means of donor–acceptor bonds.[7,12] The valence electrons of the central atom of ylidones are retained as two lone pairs. Recently, the research groups of Roesky and Driess reported the carbene-stabilized E(0) compounds **3**[13] and **4**[14] (Scheme 1). The extension of the E(0) chemistry to other types of ligand environments, and in particularly to those based on hard N and O donors, is of interest because it can provide new structural and reactivity patterns. Herein, we report the first Ge^0 coordination compound that is stabilized by a trinitrogen platform and free from soft carbene or carbenoid ligands. During the revision of this paper, Fischer and Flock et al. disclosed a closely related Sn^0 compound supported by a diiminopyridine ligand.[15]

Chirik et al. reported a series of diiminopyridine complexes of iron in the formal zero oxidation state.[16] The unique ability of diiminopyridine (dimpyr) ligands to stabilize low oxidation states was related to its non-innocent redox-active nature, which allows for partial delocalization of electron density from an electron rich metal to the ligand. This redox activity of dimpyr ligands makes them promising for the stabilization of the low oxidation states of main-group-element centers.[17] Roesky et al. recently reported that the bulky dimpyr compound 2,6-(ArN = CMe)$_2$NC$_6$H$_3$ (**5**, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) reacts with two equivalents of $GeCl_2$·diox (diox = 1,4-dioxane) to give a Ge^{II} cation [ClGe(dimpyr)]$^+$ (**6**; Scheme 2).[18] We independently observed a similar reac-



Scheme 2. Preparation of cation **6**.

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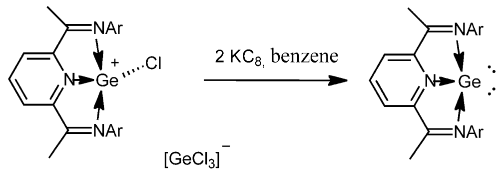
[**] G.I.N. thanks the Petroleum Research Fund for support and CFI/OIT for an equipment grant.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201309421.

tion. The cation **6** can also be cleanly generated by reacting the diiminopyridine **5** with one equivalent of $GeCl_2$·diox in the presence of one equivalent of BCl_3 or $Et_2O·BF_3$ to give the salts $[ClGe(dimpyr)]^+[BCl_4]^-$ and $[ClGe(dimpyr)]^+[BClF_3]^-$. These products were characterized by ^1H, ^{13}C, ^{11}B, and ^{19}F NMR spectroscopy, IR spectroscopy, and by comparison to the related data for $[ClGe(dimpyr)]^+[GeCl_3]^-$. The molecular structure of **6**$[GeCl_3]$ was established by X-ray analysis.[19] It differs from that reported by Roesky et al. by the presence of a solvent molecule but is otherwise very similar.

The reduction of compound **6**$[GeCl_3]$ by two equivalents of potassium graphite in benzene affords dark green compound **7**, which can be classified as a complex of Ge^0 with the ligand **5** (Scheme 3). Complex **7** is extremely air and moisture sensitive. It was characterized by ^1H and ^{13}C NMR spectroscopy and IR spectroscopy, and its structure was confirmed by X-ray analysis. Solution NMR spectra of **7** in C_6D_6 are consistent with an NMR-averaged C_{2v} geometry. In particular, the *i*Pr groups of the ligand are equivalent and give rise to two doublets at $\delta = 1.08$ ppm and 1.16 ppm, both coupled to a septet at $\delta = 2.66$ ppm ($^3J_{H\text{-}H} = 6.9$ Hz) integrated as four protons. The iminoacyl signal was observed as a singlet at $\delta = 2.04$ ppm (N=C−CH_3) integrated as six protons. The NMR-averaged C_{2v} symmetry of **7** is persistent in $[D_8]$toluene in the temperature range −70–+25 °C. In the IR spectrum of **7**, the N=C(imine) stretch at 1575 cm^{-1} is bathochromically shifted relative to the free ligand (1642 cm^{-1}) and the cation **6** (1655 cm^{-1}), thus suggesting decreased C=N bond order.



6 **7**

Scheme 3. Preparation of compound **7**.

An interesting feature of the ^1H NMR spectrum of **7** is the upfield shift of the *para*-CH resonance of the pyridine ligand upon formation of the complex: $\delta = 6.35$ ppm (t, $^3J_{H\text{-}H} = 7.6$ Hz) in **7** versus $\delta = 7.29$ ppm in the free ligand. An analogous feature is observed for the related dimpyr complex of Sn^0, which shows increased shielding of the *p*-CH(pyr) signal at $\delta = 6.23$ ppm,[15] and for the isoelectronic dimpyr complex of P^I, $[P(FcN{=}CH)_2NC_6H_3]^+$ (Fc = ferrocenyl): $\delta = 7.12$ ppm versus $\delta = 7.84$ ppm in the free ligand (in D_3CCN).[17] Our initial interpretation of this unusual shift was that it might be related to the availability of a low-lying triplet state with increased hyperfine coupling to the *p*-CH. Indeed, EPR spectra taken of the crude reaction mixture and of recrystallized complex **7** showed a weak signal, the simulation of which was consistent with significant spin localization in the *para* position of the ring.[20] However, multiple recrystallizations of **7** caused a marked decrease in the intensity of the EPR signal and DFT calculations (see below) showed that the lowest triplet state of **7** lies 17.7 kcal mol^{-1} above the singlet ground state. Moreover, VT ^1H NMR spectra did not show any significant temperature dependence, which must occur in the case of temperature accessible excitation to the triplet state. Finally, we discovered that mixing a sample of purified **7** with the starting complex **6**$[GeCl_3]$ results in the appearance of the same EPR signal but with a roughly 20-fold increase in intensity (see Figure S18 in the Supporting Information). Thus, we tentatively assign the EPR-active species to a radical formed by the reduction of **6** by **7**.[21]

The molecular structure of **7** is shown in Figure 1. The molecule is bisected by a crystallographically imposed mirror plane so that the left side of the molecule is a reflection of the right side. The coordination sphere of germanium in **7** is comprised of three nitrogen atoms: one from the central pyridine core and two from the imine groups. The imine nitrogen atoms, N2 and N2a, coordinate to the Ge centre from opposite sides. Refinement of the Ge atom in the special position results in significant elongation of its thermal ellipsoid in parallel with the N2-N2a vector, thus suggesting disorder. This disorder was successfully modeled by shifting the Ge atom in the plane of the pyridine fragment towards one of the imine nitrogen atoms. The resulting Ge1−N2 bond of 2.047(7) Å is noticeably shorter than the Ge1−N2a distance of 2.306(7) Å. The latter value is still comparable to the Ge−imine bonds in **6**$[GeCl_3]$ (2.2757(17) and 2.2623(17) Å), however. The Ge1 atom is located 1.8988(18) Å away from the pyridine nitrogen N1, a distance shorter than the corresponding distance (2.0739(18) Å) in the cation **6**$[GeCl_3]$. Neither of these distances is longer than the N−Fe^0 bond in the complex $[dimpyrFe(N_2)_2]$ (1.8362(14) Å),[16a] although the covalent radius of iron (1.32(3) Å) is larger than the covalent radius of germanium (1.20(4) Å).[22] This feature likely reflects the higher effective oxidation state of iron in the dimpyr complex[23] and the hybridization of the germanium atom in **7**. That is, the N−Ge bonds have increased Ge p-character so that the orbitals hosting the lone pairs of germanium have increased s-character.[24] The N2–Ge1–N2a

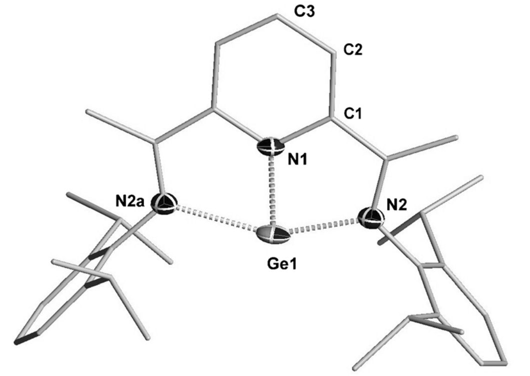
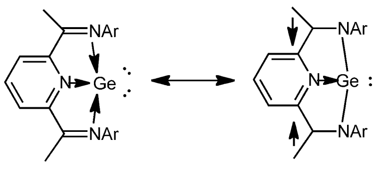


Figure 1. Molecular structure of complex **7** (thermal ellipsoids are set at 50% probability; hydrogen atoms and thermal ellipsoids for the ligand carbon atoms are omitted for clarity). The left-hand part of the molecule is related to the right-hand part by a crystallographically imposed mirror plane that runs through C3 and N1. The Ge1 atom is disordered but only one position is shown for clarity.

bond angle is more open in **7** than in **6**[GeCl$_3$] (152.76(8)° versus 146.50(7)°), thus reflecting the closer proximity of the Ge atom to the pyridine ring in the former. The N2−C4 bond of the imine fragment of **7** is elongated to 1.320(2) Å, thus indicating some decrease in multiple-bond character. A similar situation is observed in the Fe^0 complex [dimpyr-Fe(N$_2$)$_2$], which has a N=C(imine) bond of 1.332(2) Å,[16a] and in the related Sn^0 dimpyr compound (1.308(3) and 1.321(3) Å).[15] For comparison, the N=C(imine) bonds in **6**[GeCl$_3$] are normal at 1.278(3) and 1.274(3) Å. The C1−C2 and C2−C3 bond lengths in the pyridine ring of **7** (1.389(2) and 1.378(2) Å, respectively) are very close to the corresponding C−C distances in **6**[GeCl$_3$] (range 1.377–1.393(3) Å), whereas the pyridine N1−C1 distance of 1.4051(19) Å is elongated compared to 1.343(3) and 1.345(3) Å in **6**[GeCl$_3$], thus suggesting partial charge transfer to the ring.



A **B**

Scheme 4. Valence-bond representation of **7**.

From a qualitative perspective, the spectral and X-ray crystallography data for **7** suggest that its singlet ground state can be represented as a resonance of canonical forms **A** and **B** (Scheme 4). Form **B** is a singlet biradical[25] with unpaired electron density localized on the imine carbon atoms. It can be viewed as being the result of charge transfer from the Ge^0 center to the antibonding π*(C=N) orbital, which is primarily localized on the carbon atoms. The contribution of **B** accounts for the elongation of the N=C(imine) bond in **7** and the red shift of the N=C stretch in the IR spectrum of **7** in comparison with the free ligand **5**.

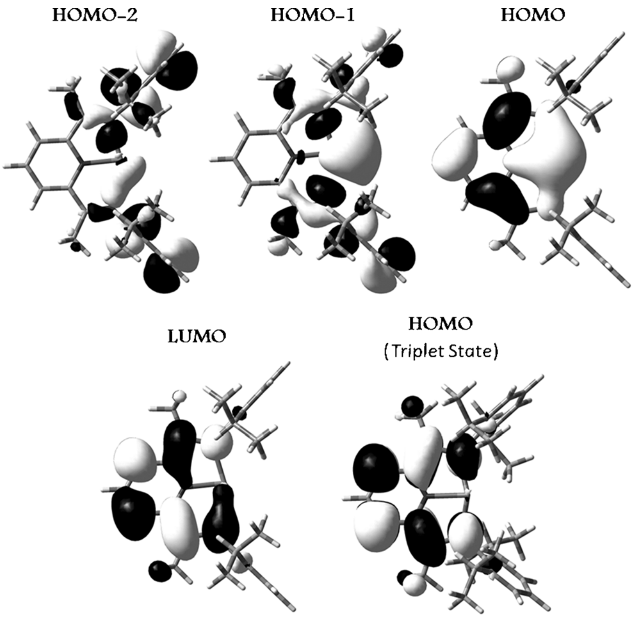


Figure 2. Calculated structure and orbital compositions of key frontier orbitals of the singlet state of **7**, and the HOMO of the triplet state.

To gain additional insight into the electronic structure of **7**, DFT calculations at the [wB97XD/6-311G(d,p)] level were performed. The optimized singlet ground-state structure of **7** is shown in Figure 2. The calculated N1−Ge distance of 1.92 Å is close to the value determined by X-ray crystallography (1.899 Å). Interestingly, the DFT calculations confirm the C_s symmetry of **7** by showing two different Ge−N bond lengths to the imine nitrogen atoms N2 and N2a: 1.93 Å and 2.55 Å, respectively, which are in good agreement with the values of (2.047(7) Å and 2.306(7) Å) determined by X-ray crystallography. This difference represents about 14% displacement of the Ge atom from the central position. This asymmetry is indicative of a short-lived stationary point on a shallow double-well potential energy surface (derived from a fluxional exchange of the Ge atom between the two imine nitrogen atoms),[26] and indeed the VT NMR data discussed above suggest that exchange between two degenerate sites occurs very easily in solution even at very low temperature. Associated with the asymmetric nature of computed **7** is a slight yet measureable (1.28 Å vs. 1.36 Å) difference between the two N=C imine bond lengths, both of which are elongated when compared with those computed for the free ligand (1.27 Å). Consistent with our experimental observations, both N=C(imine) stretches in **7** (1726 cm^{-1} and 1401 cm^{-1}) were calculated to be of lower frequency than those of the free ligand (1772 cm^{-1} and 1777 cm^{-1}). Also consistent with the experimental data is an upfield shift of the *para*-CH resonance of the pyridine ligand in the computed NMR spectrum of **7** ($\delta = 6.75$ ppm) relative to the free ligand ($\delta = 7.96$ ppm).

For comparison, the computed triplet state of complex **7** (Figure 2) is symmetric and 17.7 kcal mol^{-1} higher in energy than the singlet state. Analysis of the spin density revealed that the largest component of the spin resides on Ge, with significant spin density on the pyridine backbone.[20] Structurally, the two imine bonds are equivalent in length (1.34 Å) and both the N2−Ge and the N2a−Ge bond lengths are 2.07 Å. Some additional features of the triplet include distortion of the Ge atom from the plane of the ligand, an elongated N1−Ge distance (1.96 Å), and slight twisting of the *N*-aryl ring systems with respect to the pyridine backbone, as opposed to the perpendicular relationship observed in the singlet state.

Molecular orbital (MO) analysis provided further insight into the structure of **7**. The HOMO of the singlet corresponds to a diffuse π-type orbital centered at the Ge^0 atom. This orbital spans the two bridging imine nitrogen atoms and includes what appears to be a back-bonding interaction between a Ge^0 4p orbital and a 2p orbital from the pyridine nitrogen (Figure 2). Another tell-tale feature of the HOMO is the presence of an antibonding interaction across the iminoacyl N=C(imine) bond, which accounts for the elongation of this metric observed by X-ray crystallography and the red shift of the imine stretch. Essentially, the HOMO of **7** can be viewed as being the result of delocalization of a Ge-centred lone pair over the π-system of the ligand, which is comprised of the imine and pyridinyl nitrogen atoms. We can therefore conclude that bonding of the Ge atom to the imine groups has a partial multiple-bond character, which allows us to account for the shorter Ge−N(imine) bonds in **7** relative to **6**[$GeCl_3$] observed in the X-ray studies (see above). On the other hand, the HOMO–1 corresponds to a Ge^0-centered σ-type lone pair, while the HOMO–2 is a bonding component of the 3c–4e interaction between an in-plane Ge 4p orbital and the two lone pairs of the imine nitrogen atoms N2 and N2a. The LUMO of **7** lies 0.21 eV above the HOMO and resides entirely on the ligand as is apparent from the lack of any orbital density at Ge. The HOMO of the triplet state closely resembles the LUMO of the singlet state in accordance with the Frank-Condon principle. Based on the computed energy difference, the triplet state is not thermally accessible.

Interestingly, NBO analysis also revealed the nonintuitive presence of four Ge-centred lone pairs. One lone pair sits in a σ orbital with an occupancy of 1.77e, which can be seen in the HOMO–1 and corresponds to a classic Lewis representation of a lone pair. The second lone pair, corresponding to the HOMO–2, has a low occupancy (0.27e) as a result of the above-mentioned delocalization into the π-system of the ligand. The third and fourth lone pairs also have small occupancies (0.55e and 0.50e, respectively), and are perhaps an artifact of the 3c–4e bond (i.e., a nonclassical Lewis representation). This is supported by strong donation of the imine nitrogen lone pairs into the orbitals assigned by NBO as the third and fourth lone pair of Ge^0 ($N(2a)_{LP}\rightarrow Ge_{LP(3)} = 0.11\ kcal\,mol^{-1}$, $N(2)_{LP}\rightarrow Ge_{LP(3)} = 42.3\ kcal\,mol^{-1}$, $N(2a)_{LP}\rightarrow Ge_{LP(4)} = 15.2\ kcal\,mol^{-1}$, $N(2)_{LP}\rightarrow Ge_{LP(4)} = 31.7\ kcal\,mol^{-1}$). Ultimately, this donation results in the measured excess of electron density assigned as the third and fourth lone pairs of the Ge^0 center.

In summary, we have discovered the first coordination compound of Ge^0 stabilized by a rigid but non-innocent bis(imino)pyridine platform. The ground state of this species is a singlet. DFT studies indicate some multiple-bond character between the Ge atom and imine nitrogen atoms as a result of delocalization of a Ge lone pair onto the π*(C=N) orbitals. Investigation into the reactivity of this Ge^0 compound is in progress.

Experimental Section

All manipulations were performed using standard inert atmosphere (N_2 gas) glove-box and Schlenk techniques. Dichloromethane, hexanes, and benzene were dried by using a Grubbs-type solvent purification system. The deuterated solvent C_6D_6 was dried by distillation from K/Na alloy. NMR spectra were obtained with a Bruker DPX-300 (^1H 300 MHz; ^{13}C 75.5 MHz) instrument at room temperature. IR spectra were measured on a PerkinElmer 1600 FT-IR spectrometer. EPR spectra were collected on a Bruker Elexsys E580 instrument operating in cw mode. The simulation of the EPR spectrum was carried out by using EasySpin.[27] Elemental analysis was performed in the laboratories of the University of Toronto ("ANALEST") and McMaster University. $GeCl_2$·diox was purchased from Gelest; other materials were from Aldrich. Ligand **5** was prepared according to a reported procedure.[28]

(dimpyr)Ge (**7**): Benzene (30 mL) was added to a flask containing **6**[$GeCl_3$] (0.425 g, 0.553 mmol) and KC_8 (0.157 g, 1.161 mmol) and stirred for 2 h at room temperature. The dark green mixture was filtered and the residue was washed with benzene (3 × 5 mL). Volatile compounds were removed from the combined filtrate to give the product as a green solid (0.196 g, 0.354 mmol, 64 %). ^1H NMR (300 MHz, C_6D_6): $\delta = 7.18$ (m, 8 H, C_6H_3, *m-H* Py), 6.35 (t, 1 H, *p-H* Py, $^3J_{H\text{-}H} = 7.6$ Hz), 2.66 (hept, 4 H, $CH(CH_3)_2$, $^3J_{H\text{-}H} = 6.9$ Hz), 2.04 (s, 6 H, $NCCH_3$), 1.16 (d, 6 H, $CH(CH_3)_2$, $^3J_{H\text{-}H} = 6.8$ Hz), 1.08 ppm(d, 6 H, $CH(CH_3)_2$, $^3J_{H\text{-}H} = 7.0$ Hz). $^{13}C\{^1H\}$ (75 MHz, $CDCl_3$): $\delta = 146.1$ ($NCCH_3$), 141.7 (*ipso-C* Ph), 141.3 (*o-C* Ph), 137.4 (*o-C* Py), 125.9 (*p-C* Ph), 124.1 (*m-C* Py), 123.3 (*m-C* Ph), 113.9 (*p-C* Py), 28.4 ($CH(CH_3)_2$), 25.9, 23.4 ($CH(CH_3)_2$), 15.0 ppm ($NCCH_3$). IR (nujol): $\tilde{\nu} = 1575\ cm^{-1}$ (N=C). Elemental analysis Calcd for $C_{33}H_{43}GeN_3$: C, 71.50; H, 7.82; N, 7.58. Found: C, 70.89; H, 7.96; N, 7.15.

CCDC 968783 (**6**[$GeCl_3$]) and 968782 (**7**) 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.

Received: October 29, 2013
Revised: December 4, 2013

Keywords: DFT calculations · EPR spectroscopy · germanium · low oxidation states · pyridine

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