Metallylenes **Hot Paper**

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A Bis(silylenyl)pyridine Zero-Valent Germanium Complex and Its Remarkable Reactivity

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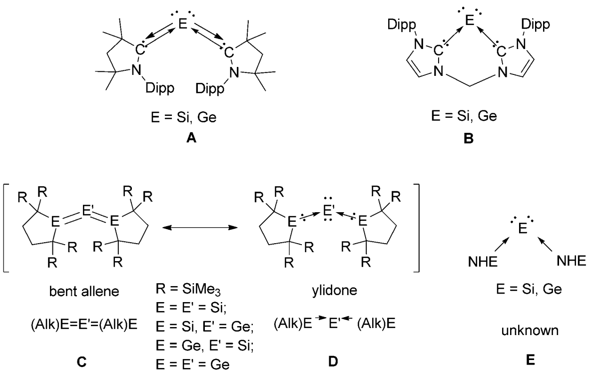
In memory of Manfred Weidenbruch

Abstract: *The synthesis, reactivity, and electronic structure of the unique germylone iron carbonyl complex* ***[SiNSi]Ge***$^{0}\rightarrow$ *Fe*$(CO)_4$ *is reported. The compound was obtained in 49% yield from the reaction of the bis(N-heterocyclic silylenyl)pyridine pincer ligand* ***SiNSi*** *(1,6-*C_5NH_3*-[EtNSi(N*^{t}*Bu)*$_2$*CPh]*$_2$*) with* $GeCl_2$*·(dioxane) to give the corresponding chlorogermyliumylidene chloride precursor* ***[SiNSi]Ge***^{II}***Cl***$^{+}$ ***Cl***$^{-}$*, which was further reduced with* $K_2Fe(CO)_4$*. Single-crystal X-ray diffraction analysis of* ***[SiNSi]Ge***$\rightarrow$*Fe*$(CO)_4$ *revealed that the* Ge^0 *center adopts a trigonal-pyramidal geometry with a Si-Ge-Si angle of 95.66(2)°. Remarkably, one of the* Si^{II} *donor atoms in the complex is five-coordinated because of additional (pyridine)N*$\rightarrow$*Si coordination. Unexpectedly, the reaction of* ***[SiNSi]Ge***$\rightarrow$*Fe*$(CO)_4$ *with* $GeCl_2$*·(dioxane) (one molar equivalent) yielded the first push–pull germylone–germylene donor–acceptor complex,* ***[SiNSi]Ge***$\rightarrow GeCl_2\rightarrow$*Fe*$(CO)_4$ *through the insertion of* $GeCl_2$ *into the dative* $Ge^0\rightarrow$*Fe bond. The electronic features of the new compounds were investigated by DFT calculations.*

Recently, members of a new class of compounds named “ylidones”, which feature formally zero-valent Group 14 elements E^0 (E = C, Si, Ge) with two lone pairs of electrons stabilized by suitable donor ligands L, could be isolated.[1] It was shown that N-heterocyclic carbenes (NHCs)[2] and their heavier analogues (“metallylenes”) or related π-delocalized imino donors are suitable ligands L for ylidone species.[3] For instance, in 2013, Roesky and co-workers reported silylone and germylone **A** (Scheme 1), which are stabilized by cyclic alkyl amino carbenes (cAACs). However, because cAAC ligands are strong π acceptors, compounds **A** have a singlet ground state and relatively short C–E distances (E = Si: 1.841(2) Å; E = Ge: 1.9386(16)–1.9417(15) Å).[2a,d] At the same time, our group reported the formation of silylone and germylone **B**, which were stabilized by a bis-NHC ligand that is a relatively strong σ donor and weak π acceptor, which resulted in longer C–E distances (E = Si: 1.864(1)–1.874(1) Å; E = Ge: 1.965(3)–1.961(3) Å) and more electron-rich E^0 atoms.[2b,c] Interestingly, the heavier E=E′=E allenes **C** (E, E′ = Si, Ge: trisilaallenes, trigermaallenes, 1,3-digermasilaallenes, and 2-germadisilaallene) reported by Kira et al.[4] and a tristannaallene describe by Wiberg and co-workers[5] have non-classical bent structures with E-E′-E angles of 122–156°. Theoretical calculations suggested that compounds **C** can also be described as ylidones **D**, in which the central E′ atoms are in the zero-valent state and bear two lone pairs of electrons, taking advantage of donor–acceptor interactions with the cyclic dialkyl metallylene ligands (e.g., the cyclic dialkyl silylene 2,2,5,5-tetrakis(trimethylsilyl)silacyclopentane-1,1-diyl).[6]



Scheme 1. Ylidones stabilized by carbenes and their heavier analogues. Dipp = 2,6-$^{i}Pr_2$-C_6H_3.

In sharp contrast to Kira’s cyclic dialkyl silylene, which serves as a strong π acceptor, N-heterocyclic silylenes (NHSis) are more electron-rich donor ligands (e.g., the amidinate-stabilized silylene [PhC(N^{t}Bu)$_2$]SiCl), even exceeding the donor ability of NHCs.[7] In the last two decades, NHSi derivatives have been successfully introduced as supporting ligands in coordination chemistry.[8] Recently, by employing the amidinate-based silylene ligand [PhC(N^{t}Bu)$_2$]SiN(SiMe$_3$)$_2$, So and co-workers reported the synthesis of the first digermanium(0) complex, NHSi→**:**Ge=Ge**:**←NHSi.[9] However, to the best of our knowledge, mononuclear E^0 complexes (ylidones) of type **E**, NHE→ :E:←NHE, are currently unknown, but have been predicted to be isolable species by Frenking and co-workers.[10] Encouraged by the latter theoretical predictions and the successful

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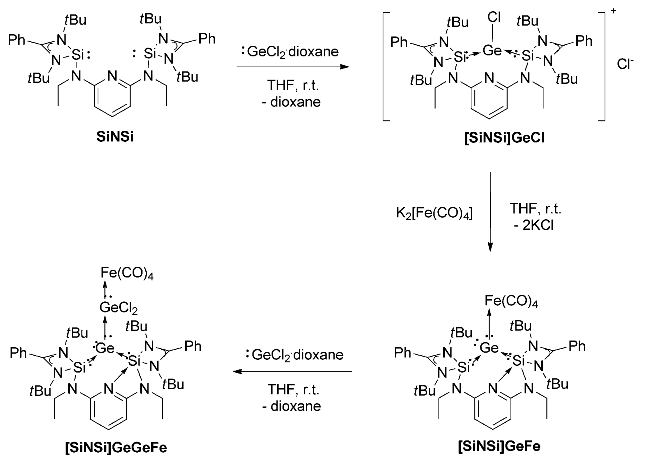

Scheme 2. Synthesis of the chlorogermyliumylidene chloride **[SiNSi]GeCl**, the germylone iron carbonyl complex **[SiNSi]GeFe**, and the $Ge^0 \rightarrow GeCl_2 \rightarrow Fe(CO)_4$ push–pull adduct **[SiNSi]GeGeFe** stabilized by the bis(NHSi)pyridine pincer **SiNSi** ligand.

synthesis of ylidones **B**, we tested whether or not the strong σ donor bis(silylenyl)pyridine pincer-type ligand **SiNSi** (Scheme 2)[11] can stabilize heavier ylidone species of type **E**. Herein, we report the first example of an NHSi donor and $Fe(CO)_4$ acceptor supported germylone complex and its remarkable reactivity towards $GeCl_2$ to form an unprecedented germylone→germylene complex.

The reaction of the bis(NHSi)pyridine pincer ligand **SiNSi** with $GeCl_2$·dioxane in THF at room temperature furnished the first chlorogermyliumylidene cation as **[SiNSi]GeCl** stabilized by a bis(NHSi) ligand, which could be isolated as a yellow powder in 62% yield. **[SiNSi]GeCl** is almost insoluble in THF and toluene but soluble in dichloromethane owing to its ionic nature. Its ^{29}Si NMR spectrum shows a singlet resonance at $\delta = 3.60$ ppm, which is further downfield than that of the free **SiNSi** ligand ($\delta = -14.9$ ppm) owing to the donor coordination of the Si^{II} atoms. Single crystals of **[SiNSi]GeCl** that were suitable for X-ray diffraction analysis could be obtained by crystallization from a mixture of THF/toluene (1:1) at room temperature; the compound crystallizes in the space group $P2_1/c$ (see the Supporting Information, Figure S4). The Ge1−Cl1 bond (2.3757(6) Å) is longer than those observed in germyliumylidene cations stabilized by a bis(NHC) (2.310(1) Å),[2b] a bis(tributylphosphazenyl)naphthalene (2.278(1) Å),[12] or a diiminopyridine ligand (2.2433(9) Å).[13] The Ge1−Si1 and Ge1−Si2 distances of 2.3503(6) Å and 2.3513(6) Å, respectively, are drastically shorter than that in a $GeCl_2$ mono-NHSi adduct (2.5259(13) Å),[9] presumably owing to the stronger donor coordination of the chelating **SiNSi** ligand. However, the Ge1−N1 distance of 2.594 Å in **[SiNSi]GeCl** is substantially longer than that of a germyliumylidene stabilized by a diiminopyridine pincer ligand (2.071(2) Å),[13] suggesting that the pyridine N atom is only weakly coordinated to the Ge^{II} center.

Attempts to synthesize the respective Ge^0 complex, **[SiNSi]Ge**, through reductive dechlorination of **[SiNSi]GeCl** with KC_8 or sodium naphthalenide were unsuccessful. We presume that **[SiNSi]Ge** is too labile under the reaction conditions owing to the great σ donor strength of the bis(NHSi) pyridine pincer ligand, which oversaturates the Ge^0 center electronically. DFT calculations (using the Gaussian 09, Revision D01 program suite at the B3LYP-D3(BJ)/6-311G(d,p) level of theory; see the Supporting Information for details) of hypothetical **[SiNSi]Ge** revealed an s-type orbital lone pair on the Ge that is occupied by 1.9 electrons and a relatively short Ge1−Si2 bond (2.311 Å; Figure S7); the corresponding Wiberg bond index of 1.45 suggests significant Si−Ge double-bond character, which is also reflected in the NBO orbitals (Figure S8). The electronic situation indicates that the highly electron-rich Ge center could gain substantial stabilization through coordination to a strong electron acceptor.

Thus we considered that the introduction of the Lewis acidic $Fe(CO)_4$ complex fragment as an electron acceptor bonded to the Ge^0 atom might increase the stability of the germylone complex. In fact, this could be achieved through the reaction of Collman's reagent, $K_2Fe(CO)_4$, with **[SiNSi]GeCl**, which afforded the desired germylone–iron carbonyl complex **[SiNSi]GeFe** in 49% yield as a red powder. **[SiNSi]GeFe** crystallizes in the monoclinic space group $P2_1/c$ (Figure 1). Its Ge1−Si1 and Ge1−Si2 distances of 2.3875(6) and 2.3729(6) Å, respectively, are significantly longer than those in Kira's analogous SiGeSi allene (2.2366(7) and 2.2373(7) Å)[4d] and in **[SiNSi]GeCl**, but shorter than the Si−Ge bond in So's NHSi-stabilized digermanium(0) complex (2.406(2) Å).[9] Unexpectedly, the pyridine N atom is not coordinated to the Ge atom but to one of the Si^{II} atoms, resulting in a five-coordinate Si^{II} center. Similar behavior has also been reported for bis[*N*,*N′*-diisopropylbenzamidinato]silicon(II) species, where a change from three-coordinate to five-coordinate Si^{II} sites also occurred upon additional coordination.[14] The Si1−N1 distance of 2.1038(19) Å) is longer than those of Si1−N4 and Si1−N5 as well as the Si−N distance in *para*-dimethylaminopyridine (DMAP) stabilized NHSi,[15] but comparable to the values reported for five-coordinate Si^{II} complexes.[14] The Si2-Ge1-Si1 angle of 95.66(2)° is larger than the C-Ge-C angle in germylone **B** stabilized by a bis(NHC) ligand (86.6(1)°),[2b] but smaller than those of cAAC-stabilized germylones **A**

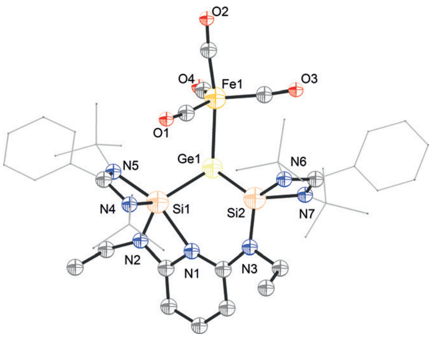

Figure 1. Molecular structure of the bis(NHSi)pyridine-stabilized germylone $Fe(CO)_4$ complex, **[SiNSi]GeFe**. Thermal ellipsoids set at 50% probability. Hydrogen atoms and solvent molecules are omitted for clarity.

(114.71(6)–117.24(8)°)[2d] and germadisilaallene **C** (132.38(2)°).[4d] The Ge center adopts a trigonal-pyramidal geometry (the sum of the angles around the Ge atom is 322.59°), which is similar to those in bis(NHC) germylone→$GaCl_3$ complexes,[16] but different from the situation of coplanar Ge centers in germylone mesoionic germylene metal complexes.[17] The IR stretching vibrations of CO in **[SiNSi]GeFe** appear at 1969, 1886, 1865, and 1830 cm^{-1}, which are red-shifted compared to those of the amino(imino)germylene iron carbonyl complex (2039, 1965, and 1930 cm^{-1}), indicating that the CO ligands act as strong electron acceptors at the Fe center.[18]

According to NBO analysis, the electronic structure of the model germylone iron carbonyl complex, **m-[SiNSi]GeFe**, exhibits a Ge s-type lone-pair orbital that is occupied by 1.77 electrons and a Ge p-type lone-pair orbital that is directed towards the Fe center and occupied by one electron. The Ge1–Si1 and Ge1–Si2 bonds are single bonds, each with an occupancy of about two electrons (Figure 2).[19] The WBIs of these bonds are 0.96 and 1.08, respectively. The NBO analysis does not yield a covalent Ge–Fe bond. The coordination between the $Fe(CO)_4$ fragment and the **[SiNSi]Ge** ligand is dictated by a very strong donor–acceptor interaction between the lone-pair p orbital on Ge and the $\sigma^*(\mathrm{Fe{-}C_{axial}})$ orbital (ΔE(second order perturbation) = 217 kcal mol^{-1}; Figure 2). The calculated Ge–Fe bond of 2.507 Å (exp. 2.499 Å, WBI = 0.39) is significantly longer than the Ge–Fe bond (2.378 Å) in the $Fe(CO)_4$ complex of Tip($SiClR_2$)Si=Ge←NHC[20] (Tip = 2,4,6-$^i Pr_3C_6H_2$) and in the amino(imino)germylene $Fe(CO)_4$ complex[18] (calc. 2.32 Å, exp. 2.30 Å, WBI = 0.56). The charge on the $Fe(CO)_4$ fragment is −0.73 electrons.

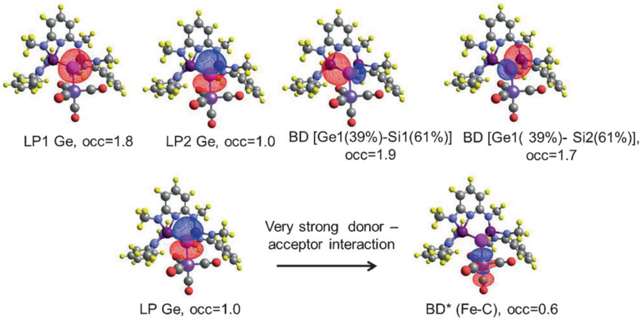

Figure 2. Selected NBO orbitals of the DFT-calculated model compound **m-[SiNSi]GeFe** where the ^{t}Bu groups at the amidinate N atoms in the synthesized complex were replaced by Me groups. LP = lone-pair orbital, BD = bonding orbital, BD* = antibonding orbital. The polarity of the BD orbitals is given by the percentage of the electron density on Ge and Si. occ is the occupancy of the orbital in electrons. Contour value = 0.03.

Featuring a lone pair of electrons on the germylone center, **[SiNSi]GeFe** undergoes an unexpected insertion reaction of $GeCl_2$ into the Ge^0→Fe donor–acceptor bond to give the **[SiNSi]GeGeFe** complex as orange crystals in 65 % yield. The compound crystallizes in the monoclinic space group $P2_1/c$, and single-crystal X-ray diffraction analysis revealed the presence of a mixed-valent Ge_2Cl_2 moiety stabilized by the bis(NHSi)pyridine ligand and the $Fe(CO)_4$ group (Figure 3). The Ge1–Ge2 distance of 2.4784(7) Å is significantly longer than that in NHSi:→:Ge=Ge:←:NHSi[9] and in the digermavinylidene $((\mathrm{HCDippN})_2\mathrm{B})_2$Ge=Ge:,[21] consistent with the Ge–Ge single bonds in dichlorogermylene oligomers reported by Rivard and co-workers.[22] The $GeCl_2$ group of the Ge_2Cl_2 moiety in **[SiNSi]GeGeFe** adopts a pyramidal geometry (the sum of the bond angles around Ge2 is 288.47°), which is, as expected, different from the coplanar configuration of the R_2E moiety in a digermavinylidene, R_2Ge=Ge:, reported by Aldridge[21] and co-workers as well as for other heavier vinylidene analogues described by the Filippou and Scheschkewitz groups.[20,23]

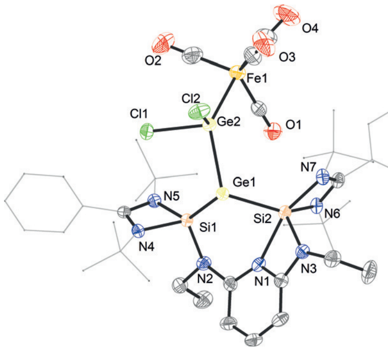

Figure 3. Molecular structure of the germylone iron complex **[SiNSi]GeGeFe**. Thermal ellipsoids set at 50% probability. Hydrogen atoms and solvent molecules are omitted for clarity.

To gain insight into the electronic structure, the model compound **m-[SiNSi]GeGeFe** was calculated, where the ^{t}Bu groups at the amidinate N atoms in the synthesized complex were replaced by Me groups (Figure 4). NBO analysis yielded a free s-type lone pair on Ge1 with an occupancy of 1.8 electrons and a p-type lone-pair orbital with an occupancy of one electron on Ge2. Ge1 and Ge2 are connected by a nonpolar single bond. Again, NBO analysis did not locate a covalent Ge2–Fe σ bond. Instead, the complexation between the dichlorogermylene and the $Fe(CO)_4$ fragment can be attributed to very strong hyperconjugative interactions between the lone pair on Ge2 and the $\sigma^*(\mathrm{Fe{-}C_{axial}})$ orbital (ΔE(second order perturbation) = 289 kcal mol^{-1}; Figure 4). The resulting Ge2–Fe distance is 2.389 Å (exp. 2.359 Å) with a WBI of 0.47. This distance is significantly shorter than the Ge–Fe distance in **m-[SiNSi]GeFe**, but very similar to the distances in the $Fe(CO)_4$ complex with Tip($SiClR_2$)Si=Ge←NHC[20] and in the amino(imino)germylene $Fe(CO)_4$ complex[18] (see above). The electronic structure predicted by NBO is in line with the description of **[SiNSi]GeGeFe** as a push–pull Ge^0→Ge^{II}→$Fe(CO)_4$ complex stabilized by a Lewis acid on one end and a Lewis base on the other. The charge on the **[SiNSi]Ge** fragment is +0.96 while the $GeCl_2$ (−0.45) and $Fe(CO)_4$ (−0.51) fragments are negatively charged (Table S7), which is consistent with the push–pull nature of this complex.

In summary, we have described the synthesis and isolation of the first bis(N-heterocyclic silylenyl)pyridine- and Fe-$(CO)_4$-stabilized germanium(0) complex, which was obtained by the reduction of the bis(NHSi)pyridine pincer ligand

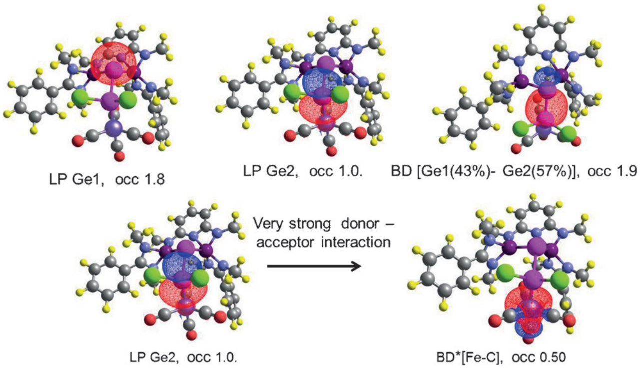

Figure 4. Selected NBO orbitals of the DFT-calculated model compound **m-[SiNSi]GeGeFe** where the ^{t}Bu groups at the amidinate N atoms in the synthesized complex were replaced by Me groups. LP = lone-pair orbital, BD = bonding orbital, BD* = antibonding orbital. The polarity of the BD orbitals is given by the percentage of the electron density on Ge and Si. occ is the occupancy of the orbital in electrons. Contour value = 0.03.

supported chlorogermyliumylidene chloride, **[SiNSi]GeCl**, with Collman's reagent, $K_2Fe(CO)_4$. Insertion of $GeCl_2$ into the $Ge^0 \rightarrow Fe$ bond in **[SiNSi]GeFe** afforded the germylone–germylene–iron complex **[SiNSi]GeGeFe**, which bears a push–pull $Ge^0 \rightarrow Ge^{II} \rightarrow Fe$ moiety.

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Keywords: germanium · metallylenes · pincer ligands · silicon · silylene

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