

# Isolable Metallo-Germylene and Metallo-Stannylene $\sigma$ -Complexes with Iron

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Conversion of the  $\beta$ -diketiminato Ge(II) chloride LGeCl [L = CH{CMe(NAr)}<sub>2</sub>, Ar = 2,6<sup>-1</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>] (1) and its tin homologue LSnCl (2) with the anionic iron complex K[Fe( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>] leads to the iron-germylene LGeFe( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub> (3) and iron-stannylene LSnFe( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub> (4), respectively. The compounds 3 and 4 were characterized by NMR, IR, and UV-vis spectroscopy as well as theoretical studies. The structure of 3 was also determined by X-ray crystallography. The experimental and computed structures show clealy that the Fe-E (E = Ge, Sn) bond is a single bond in compounds 3 and 4. They represent the isolable iron-germylene and -stannylene  $\sigma$ -complexes. Notably, compound 3 is the first example of iron-germylene  $\sigma$ -complexes ever characterized by X-ray analysis.

### Introduction

Since the first striking isolation of germylenes and stannylenes by Lappert and co-workers in 1974,<sup>1</sup> low-valent germanium and tin compounds have attracted considerable interest during the last three decades.<sup>2</sup> Germylenes and stannylenes  $R_2E$ : (E = Ge, Sn; R = amido, alkyl, aryl) are suitable ligands for the synthesis of transition metal complexes with potential applications in homogeneous catalysis. The ability of ER<sub>2</sub> systems to serve as  $\sigma$ -donors and  $\pi$ -acceptors toward transition metal centers can be tuned by the nature of the substituents R. While numerous carbene-like transition metal complexes of the type M=ER<sub>2</sub> have been reported, only a few examples of isolable metallo-germylenes and -stannylenes with a M-E(II)  $\sigma$ -bond and a bent M-E-R configuration (M = transition metal, E = Ge, Sn) have been synthesized to date.<sup>3-5</sup> The latter type of metallo-ylidenes are interesting and represent congeners of as yet unknown  $\sigma$ -metallocarbenes [M]-C-R. In 1994, Jutzi and Leue synthesized the first

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## Chart 1. Metallo-germylenes and -stannylenes



metallogermylene derivatives of iron Ia,b (Chart 1), but the latter have not been characterized structurally.<sup>3</sup> The metallogermylenes IIa,b<sup>4</sup> and metallostannylenes IIIa–f<sup>5</sup> have been reported by Power and co-workers and structurally characterized by X-ray diffraction (Chart 1). Interestingly, Tilley and co-workers reported the tautomerization of the osmium stannylene complex Cp\*(<sup>i</sup>Pr<sub>3</sub>P)(H)Os=Sn(H)R to give the osmostannylene IV, which has been characterized by means of spectroscopy (Chart 1).<sup>6</sup> Pandey and co-workers reported on the electronic structure and bonding features of metallogermylenes and metallostannylenes by theoretical studies.<sup>7</sup> The latter results suggested that the  $\pi$ -bonding contribution in metallo-ylidenes is smaller than those in metal-ylidynes, while

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Figure 1. ORTEP drawing of compound 3, top view (left) and side view (right). Thermal ellipsoids are shown with 30% probability, and hydrogen atoms have been omitted for clarity. Compound 3 is disordered; only the major positions are shown here.





the  $\sigma$ -bonding contribution in the former compounds is larger than those in the metallo-ylidynes. Up to now, no structural characterization of an iron-germylene and -stannylene complex has been reported. We report here the synthesis and isolation of the new iron-germylene and -stannylene complexes **3** and **4**, starting from the N-heterocyclic E(II) chloride precursors **1** (E = Ge) and **2** (E = Sn), respectively. The molecular structure of **3** has also been elucidated by X-ray diffraction.

#### **Results and Discussion**

Synthesis of LGeFe( $\eta^{5}$ -C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub> and LSnFe( $\eta^{5}$ -C<sub>5</sub>H<sub>5</sub>)-(CO)<sub>2</sub>. The N-heterocyclic  $\beta$ -diketiminato Ge(II) chloride LGeCl [L = CH{CMe(NAr)}<sub>2</sub>, Ar = 2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>] (1) and its tin homologue **2** were employed as precursors for the synthesis of the iron-germylene **3** and -stannylene **4**, respectively (Scheme 1).<sup>8</sup> Thus **1** was allowed to react with 1 molar equiv of anionic iron complex K[Fe( $\eta^{5}$ -C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>]<sup>9</sup> in diethyl ether at ambient temperature, affording a dark red solution, from which dark red crystals of the desired iron-germylene LGeFe( $\eta^{5}$ -C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub> (**3**) can be isolated in 71% yield. In a similar manner, treatment of LSnCl (**2**) with K[Fe( $\eta^{5}$ -C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>] yields the corresponding iron complex LSnFe-( $\eta^{5}$ -C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub> (**4**) in 53% yield (Scheme 1).

The composition and constitution of **3** and **4** were characterized by elemental analysis and spectrocopy, as well as X-ray diffraction analysis.<sup>10</sup> The <sup>1</sup>H NMR spectra of **3** and **4** display resonance signals from the cyclopentadienyl and the  $\gamma$ -CH protons of the C<sub>3</sub>N<sub>2</sub>M (M = Ge (3), Sn (4)) ring in an intensity ratio of 5:1. Furthermore, four signals for methyl groups of isopropyl groups and two siganals for the CH of isopropyl groups are observed. It is suggested that there is no free rotation around the N-C bond of the Ar group due to steric hindrance. This pattern is similar to those observed for LGeCl 1 and LSnCl 2.8 Compound 4 was also characterized by <sup>119</sup>Sn NMR spectroscopy, which revealed a singlet at  $\delta = -645$  ppm. Apparently, the <sup>119</sup>Sn nucleus in **4** is more shielded than that in the precursor 2 ( $\delta = -224$  ppm). In the UV-vis spectra, absorption bands are observed at 428 and 410 nm for 3 and 4, respectively, which can be assigned to n-p transitions. This pattern is similar to that observed for metallogermylenes II and metallostannylenes III.<sup>4,5</sup> In addition, the infrared spectra of 3 and 4 in KBr revealed each two expected strong stretching vibration modes in the carbonyl region. The observed stretching frequencies of 3 (1968 and  $1918 \text{ cm}^{-1}$ ) and 4 (1961 and 1907 cm<sup>-1</sup>) resemble that of related compounds and are in good agreement with the DFT-calculated values (3:1977 and 1933 cm<sup>-1</sup>; 4: 1978 and 1945 cm<sup>-1</sup>). Moreover, compared with iron-substituted germylenes Ia (1969 and 1920  $\text{cm}^{-1}$ ) and Ib (2004 and 1950 cm<sup>-1</sup>),<sup>3</sup> the  $\beta$ -diketiminato germylene and stannylene ligands are slightly stronger  $\sigma$ -donors than aryl-substituted germylene ligands.

**X-ray Structure Analysis.** The molecular structure of **3** is shown in Figure 1. Two carbonyl ligands, a cyclopentadienyl ligand, and the  $\beta$ -diketiminato germylene ligand are coordinating to the iron center of **3**. The Ge–Fe bond length of 2.4961(17) Å in **3** is longer than typical Ge–Fe single bonds; for example, 2.357(4) Å is found in Cl<sub>2</sub>Ge[Fe( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)-(CO)<sub>2</sub>] <sub>2</sub>.<sup>11</sup> The Ge–N bond lengths of **3** (2.059(4) and 2.080(4) Å) are longer than those of LGeCl **2** (1.988(4) and

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**Figure 2.** Molecular orbitals of **3**, HOMO(left) and HOMO–11-(right). DFT calculations were performed at the B3LYP level using the 6-31G(d) basis set for Ge, N, C, and H atoms and the LANL2DZ level for the Fe atom.



**Figure 3.** Molecular orbitals of **4**, HOMO(left) and HOMO–11-(right). DFT calculations were performed at the B3LYP level using the 6-31G(d) basis set for Ge, N, C, and H atoms and the LANL2DZ level for the Fe and Sn atoms.

Table 1. Selected Bond Distances (Å) and Angles (deg) in Compound 3

Ge1-Fe1	2.496(2)	N2-Ge1-N1	88.92(16)
Ge1-N1 Ge1-N2 Fe1-C35 <sub>(carbonyl)</sub> Fe1-C36 <sub>(carbonyl)</sub>	2.059(4) 2.080(4) 1.807(10) 1.738(11)	N2-Ge1-Fe1 N1-Ge1-Fe1 C4-N2-Ge1 C2-N1-Ge1	110.86(12) 109.91(12) 115.3(3) 120.0(3)

1.997(4) Å), probably owing to the steric congestion around the Ge(II) atom. The  $C_3N_2$  plane of the  $C_3N_2$ Ge ring in the compound **3** is nearly planar, but the Ge atom is out of the plane by 32.7°. The angle between the Ge–Fe bond and the Ge1–N1–N2 plane is 102.9°. The large distorted structure of **3** is consistent with the presence of a lone pair on the germanium atom. Accordingly, it is obvious that the bending feature of **3** is different from germylyne complexes. For instance, the structures of germylyne complexes having a triple bond between the transition metal and germanium atom show a nearly linear structure (bent angles around  $172.0-178.9^\circ$ ).<sup>4,12</sup> The structure of **4** was unambiguously

 Table 2. Crystal and Refinement Data for 3

empirical formula	C <sub>36</sub> H <sub>46</sub> FeGeN <sub>2</sub> O <sub>2</sub>	
$M^{-}$	667.19	
cryst syst	monoclinic	
space group	$P2_1/n$	
a/Å	9.0894(2)	
b/Å	21.8257(5)	
c/Å	17.4797(4)	
a/deg	90	
$\beta/\text{deg}$	102.984(2)	
$\gamma/\text{deg}$	90	
$V/\text{\AA}^3$	3379.01(13)	
Z	4	
$d_{\rm calc}/{\rm Mg}{\rm m}^{-3}$	1.312	
$\mu$ (Mo K $\alpha$ )/mm <sup>-1</sup>	1.352	
reflns collected	28 511	
indep reflns	5925	
R(int)	0.064	
reflues with $I > 2\sigma(l)$	4055	
Data/params	486	
final $\hat{R}$ indices $[I > 2\sigma(I)], R_1$	0.0825	
R indices (all data), $wR_2$	0.1537	

determined by X-ray analysis. The structural features of **4** are quite similar to those of **3**; however, the X-ray data were not sufficient for further discussion.

**Theoretical Calculations.** In order to obtain more information about the electronic structure and bonding nature of **3** and **4**, we performed quantum chemical calculations at the gradient-corrected DFT level using the exchange–correlation functional B3LYP of the geometries of **3** and **4**, as initial structures that were obtained by X-ray crystallographic analysis.<sup>13</sup> The HOMO of **3** represents mainly the lone pair at the Ge(II) atom with somewhat in-plane pseudo- $\pi$ -bonding contributions (Figure 2, left). The HOMO–11 of **3** shows mainly the Ge–Fe  $\sigma$ -bonding orbital (Figure 2, right). Molecular orbitals of **4** are shown in Figure 3. The HOMO and HOMO–11 of **4** are fairly similar to those of **3** (HOMO, right; HOMO–11, left).

As expected from the geometric features, there is no pure  $\pi$ -bonding orbital in 3 and 4. An NBO analysis of 3 and 4 shows that the  $\sigma$ -type E–Fe orbitals are highly filled (3: 1.68*e*, 4: 1.72*e*) and strongly polarized toward the iron atom (Fe = 72.29% in 3, 78.11% in 4). Furthermore, the E–Fe bond of 3 and 4 consists of highly overlapped np-valence orbitals of E (3: Ge 4s 10.53%, 4p 89.37%, 4: Sn 5s 8.33%, 5p 91.67%). Additionally, the single  $\sigma$ -bond character of 3 and 4 is supported by the WBI values of the E–Fe bond (0.7031 (3) and 0.6084 (4)). In fact, the electronic features and molecular orbitals of 4 are similar to those of 3. The molecular orbital characteristics of the iron-germylene and -stannylene derivatives presented here are in good agreement with those reported by Pandey and co-workers.<sup>7</sup>

## Conclusions

In this work, we investigated the synthesis and characterization of novel iron-germylene complex **3** and iron-stannylene complex **4**. The facile synthesis and stability of **3** and **4** may be attributed to the stabilizing property of the N-heterocyclic  $\beta$ -diketiminato substituent. They represent isolable iron-germylene and -stannylene  $\sigma$ -complexes. Notably, compound **3** is the first example of an iron-germylene  $\sigma$ -complex that is structurally characterized. The compounds **3** and **4** are unique because not only are they the first isolable

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<sup>(13)</sup> Calculations were carried out using the *Gaussian 03*, Revision E.01 series of programs, and also see the Supporting Information.

metallo-germylene and metallo-stannylene  $\sigma$ -complexes with iron, but also they may lead to novel iron germylyneand stannylyne-complexes. For example, Power and coworkers have synthesized germylyne complexes from metallogermylenes by photolysis or thermolysis reactions.<sup>4</sup> The reactivity of **3** and **4**, including the synthesis of germylyne or stannylyne complexes, is currently under investigation.

#### **Experimental Section**

**General Considerations.** All experiments and manipulations were carried out under dry oxygen-free nitrogen using standard Schlenk techniques or in an MBraun inert atmosphere glovebox containing an atmosphere of purified nitrogen. Solvents were dried by standard methods and freshly distilled prior to use. The starting materials LGeCl 1, <sup>8</sup> LSnCl 2<sup>8</sup> (L = HC[C(Me)NAr]<sub>2</sub>, Ar = 2,6- $^{1}Pr_{2}C_{6}H_{3}$ ), and K[Fe( $\eta^{5}$ -C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>]<sup>9</sup> were prepared according to literature procedures. The NMR spectra were recorded on a Bruker AV 400 spectrometer. The <sup>1</sup>H and <sup>13</sup>C-{<sup>1</sup>H} NMR spectra were referenced to the residual solvent signals as internal standards, and the <sup>119</sup>Sn NMR spectra was referenced to SnMe<sub>4</sub> as an external standard. Abbreviations: s = singlet; d = doublet; t = triplet; sept = septet; mult = multiplet; br = broad.

LGeFe( $\eta^{5}$ -C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>(3). To a mixture of LGeCl 1 (1.013 g, 1.93 mmol) and K[Fe( $\eta^2$ -C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>] (417 mg, 1.93 mmol) was added dry Et<sub>2</sub>O (30 mL), and then the reaction mixture was stirred at room temperature for 4 h. Volatiles were removed under reduced pressure, and the residue was extracted with hexane (50 mL). The filtrate was concentrated and stored at -30 °C for 2 days, yielding 3 as dark red crystals (913.8 mg, 1.37 mmol, 71%). Mp: 151 °C (dec). <sup>1</sup>H NMR (400.13 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  1.07 (d,  ${}^{3}J_{HH} = 7$  Hz, 12 H, CHMe2), 1.11 (d,  ${}^{3}J_{HH} =$ 7 Hz, 12 H, CHMe2), 1.51 (d,  ${}^{3}J_{HH} =$  7 Hz, 12 H, CHMe2), 1.57  $(d, {}^{3}J_{HH} = 7 \text{ Hz}, 12 \text{ H}, \text{CH}Me2), 1.61 (s, 6 \text{ H}, \text{NC}Me), 3.77 - 4.01$ (m, 4 H, CHMe2), 3.88 (s, 5 H, CpH), 4.63 (s, 1 H,  $\gamma$ -CH), 7.08–7.13 (m, 6 H, 2,6-<sup>1</sup>Pr2C6H3). <sup>13</sup>C{<sup>1</sup>H} NMR (100.61 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ 24.3 (NCMe), 25.8, 25.9, 26.0, 26.5 (CHMe2), 27.9, 29.3 (CHMe2), 85.0 (Cp), 95.0 (γ-C), 125.7, 125.9, 127.3, 141.6, 144.8, 145,5 (2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) 168.7 (NCMe), 217.4 (CO). UV-vis λ [nm]: 428 (2150), 582 (100). IR (KBr, cm<sup>-1</sup>): 441 (w), 509 (m), 571 (m), 645 (m), 747 (m), 758 (w), 795 (m), 818 (m), 842 (w), 932 (w), 984 (m), 1053 (w), 1103 (m), 1155 (s), 1240 (s), 1314 (s), 1376 (s), 1436 (m), 1461 (m), 1522 (m), 1548 (m), 1611 (w), 1648 (w), 1910 (s), 1966 (s), 2868 (w), 2928 (w), 2962 (m), 3056 (w), 3483 (w). Anal. (%) Calcd for C36H46FeGeN2O2: C, 64.80; H, 6.95; N, 4.20. Found: C, 64.57; H, 6.85; N, 4.14.

LSnFe( $\eta^{5}$ -C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub> (4). To a mixture of LSnCl 2 (819 mg, 1.432 mmol) and K[Fe( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>] (312 mg, 1.444 mmol) was added dry Et<sub>2</sub>O (25 mL), and then the reaction mixture was stirred at room temperature for 4 h. Volatiles were removed under reduced pressure and the residue was extracted with hexane (50 mL). The filtrate was concentrated and stored at -30 °C for 2 days, yielding 4 as dark red crystals (543 mg, 0.759 mmol, 53%). Mp: 140 °C (dec). <sup>1</sup>H NMR (400.13 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  1.06 (d,  ${}^{3}J_{HH} = 7$  Hz, 12 H, CHMe2), 1.15 (d,  ${}^{3}J_{HH} =$ 7 Hz, 12 H, CH*M*e2), 1.38 (d,  ${}^{3}J_{HH} = 7$  Hz, 12 H, CH*M*e2), 1.42 (d,  ${}^{3}J_{HH} = 7$  Hz, 12 H, CH*M*e2), 1.42 (d,  ${}^{3}J_{HH} = 7$  Hz, 12 H, CH*M*e2), 1.71 (s, 6 H, NC*M*e), 3.37 (sep, (d, 9 HH = 6.8 Hz, 2 H, CHMe<sub>2</sub>), 3.83 (s, 5 H, CpH), 3.96 (sep,  ${}^{3}J_{\text{HH}} = 6.8$  Hz, 2 H, CHMe<sub>2</sub>), 3.83 (s, 5 H, CpH), 3.96 (sep,  ${}^{3}J_{\text{HH}} = 6.8$  Hz, 2 H, CHMe<sub>2</sub>), 4.78 (s, 1 H,  $\gamma$ -CH), 7.05–7.16 (m, 6 H, 2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100.61 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) δ 23.8 (NCMe), 25.3, 25.4, 25.5, 26.6 (CHMe<sub>2</sub>), 28.2, 28.5 (CHMe<sub>2</sub>), 83.6 (Cp), 95.8 (γ-C), 125.1, 125.4, 126.5, 142.6, 143.8, 144,3 (2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) 169.0 (NCMe), 214.9 (CO). <sup>119</sup>Sn NMR ( $C_6D_6$ , 298 K):  $\delta$  –645 ppm. UV–vis  $\lambda$  [nm]: 435 (2600), 588 (100). IR (KBr, cm<sup>-1</sup>): 511 (w), 580 (w), 645 (w), 744 (m), 771 (m), 791 (m), 840 (w), 936 (w), 1001 (w), 1017 (m), 1057 (w), 1099 (m), 1172 (w), 1264 (m), 1316 (s), 1385 (s), 1436 (s), 1463 (m), 1519 (m), 1551 (s), 1623 (w), 1908 (s), 1961 (s), 2867 (w), 2927 (m), 2961 (s), 3057 (w), 3436 (w). Anal. (%) Calcd for C<sub>36</sub>H<sub>46</sub>FeSnN<sub>2</sub>O<sub>2</sub>: C, 60.62; H, 6.50; N, 3.93. Found C, 60.78; H, 6.39; N, 3.96.

Single-Crystal X-ray Structure Determinations. Crystals were each mounted on a glass capillary in perfluorinated oil and measured in a cold N<sub>2</sub> flow. The data of compounds **3** were collected on an Oxford Diffraction X calibur S Sapphire at 150 K (Mo K $\alpha$  radiation,  $\lambda = 0.71073$  Å). The structures were solved by direct methods and refined on  $F^2$  with the SHELX-97<sup>14</sup> software package. The positions of the H atoms were calculated and considered isotropically according to a riding model. The Ge atom and Fe atom in **3** are disordered over two orientations.

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**Supporting Information Available:** Details of the crystal structure determination for **3** (CIF) and tables with the Cartesian coordinates of the optimized geometries of **3** and **4**. This material is available free of charge via the Internet at http:// pubs.acs.org.

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