Preparation of iron carbonyl complexes of germanium(II) and tin(II) each with a terminal fluorine atom

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ABSTRACT

The reaction of β-diketiminate substituted germanium(II) and tin(II) fluorides (LGeF (**1**) and LSnF (**2**)) (L = CH{(CMe)$_2$(2,6-iPr$_2$C$_6$H$_3$N)$_2$}) with diiron nonacarbonyl, Fe$_2$(CO)$_9$ at room temperature, leads to the iron carbonyl complexes of germanium(II) LGeFFe(CO)$_4$ (**3**) and tin(II) LSnFFe(CO)$_4$ (**4**), respectively. Compounds **3** and **4** were characterized by elemental analysis, NMR spectroscopy, and mass spectrometry. Furthermore, both complexes (**3** and **4**) were investigated by X-ray structural analysis which shows that both compounds are monomeric in the solid state containing terminal fluorine atoms.
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1. Introduction

Organometallic fluoride complexes have received considerable interest with regard to their catalytic properties and reactions [1]. In the solid state, GeF$_2$ is a strongly fluorine-bridged chain polymer in which the parallel chains are cross-linked by weak fluorine bridges. The structural unit of the strongly bridged chains is a trigonal pyramid of three fluorine atoms and an apical germanium atom [2]. SnF$_2$ exists as a tetramer containing a puckered eight-membered ring in which Sn and F atoms are alternately arranged [3]. Therefore, the parent germanium(II) and tin(II) fluoride compounds have low solubilities in common organic solvents and it is difficult to study their reactions in solution. In this context we reported on hydrocarbon soluble three-coordinate germanium(II) and tin(II) fluorides that originate from the reaction of a germanium(II) chloride [4] and tin(II) methyl [5] compound, respectively with the fluorine source Me$_3$SnF. SnF$_2$ is widely used in toothpaste as a source of fluoride to harden dental enamel [6]. In the enamel it converts apatite into fluoroapatite, which is more resistant to attack by acids generated by bacteria. Here it is worth mentioning that our group reported on the first soluble CaF$_2$ complex [(Cp*TiF$_2$)$_6$CaF$_2$(THF)$_2$] (Cp* = C$_5$Me$_5$), and subsequently prepared β-diketiminate substi-

tuted calcium and strontium fluorides [7–9]. There are only a few reports on the synthesis of compounds with substituted germanium(II) and tin(II) fluoride in the literature, but no records of their reaction chemistry [10,11]. Herein we present the reaction of germanium(II) and tin(II) fluorides (LGeF (**1**) and LSnF (**2**)) with diiron nonacarbonyl, Fe$_2$(CO)$_9$ leading to the formation of the iron carbonyl complexes (LGeFFe(CO)$_4$ (**3**) and LSnFFe(CO)$_4$ (**4**)), with terminal fluorine atoms and their characterization by mass spectrometry, multinuclear magnetic resonance spectroscopy, and single-crystal X-ray structural analysis.

2. Results and discussion

We have already reported the synthesis of hydrocarbon-soluble monomeric germanium(II) and tin(II) fluoride [4,5]. LGeF (**1**) and LSnF (**2**) can be used as efficient precursors for the preparation of heterobimetallic germanium(II) and tin(II) iron carbonyl compounds. The reaction of LGeF (**1**) and LSnF (**2**) with diiron nonacarbonyl, Fe$_2$(CO)$_9$ in THF leads to the complexes LGeFFe(CO)$_4$ (**3**) and LSnFFe(CO)$_4$ (**4**), respectively, in good yields (Scheme 1).

The ^{19}F NMR spectra of **3** and **4** in C$_6$D$_6$ each revealed singlet resonances (δ −102.81 and −132.91 ppm) for the fluorine as a singlet, which are different from those of the starting materials **1** and **2** (δ −112 and −125.29 ppm). In the ^{13}C NMR spectra, CO resonances are observed at δ 213.58 and 212.90 ppm, respectively, comparable to those of the isoelectronic compounds having the
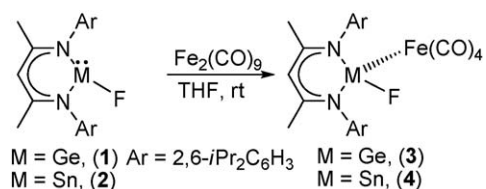
Scheme 1. Preparation of compounds 3 and 4.

compositions $LGe(OH)Fe(CO)_4$ (δ 214.8 ppm) [12] and $LSn(OH)$-$Fe(CO)_4$ (δ 213.15 ppm) [13]. Moreover, compound **4** shows a doublet at δ −14.16 ppm with a coupling constant of $^2J(Sn–F) = 3172.2$ Hz in the ^{119}Sn NMR spectrum. The chemical shift is quite different but the coupling constant is similar to those of the starting material LSnF (**2**) (δ −371.52 ppm, $^2J(Sn–F) = 3100$ Hz).

The molecular structures of **3** and **4** were determined by single-crystal X-ray diffraction. Single crystals of **3** were obtained from a saturated toluene solution as light brown crystals. Compound **3** crystallizes in the monoclinic space group $P2_1/n$. In **3**, a germanium atom binds to a monoanionic β-diketiminate ligand, to a fluorine atom, and to an iron carbonyl fragment, generating a four-coordinate germanium center, which adopts a distorted-tetrahedral geometry. One can therefore argue that germanium occupies the axial position of a distorted trigonal bipyramid at the iron center (Fig. 1).

The Ge–Fe bond length in **3** (2.3262(7) Å) is comparable to that in $LGe(OH)Fe(CO)_4$ (2.330(1) Å) [9] but is slightly longer in comparison with that in $L^1Ge(Cl)Fe(CO)_4$ (2.298(2) Å; $L^1 = HC[(CMe)(NPh)]_2$) [14]. Moreover, a longer Ge–F bond length in **3** (1.868(2) Å) is observed compared with that in LGeF (1.805(17) Å) [4], and this value is even longer than that in LGe(S)F (1.848(2) Å) with the same coordination number [15]. As expected the Ge(II)–F bond of **3** is longer when compared with Ge(IV)–F bonds such as those of $[(CH_3)_4N][(CF_3)_3GeF_2]$ (av. 1.810(4) Å) [16] and of $[N(CH_2CH_2O)_3GeF]$ (1.781(10) Å) [17].

Compound **4** crystallizes in the same monoclinic space group $P2_1/n$ as **3**, with one molecule of **4** in the asymmetric unit. In **4**, the coordination polyhedron around the tin atom is similar to that in **3** (Fig. 2).
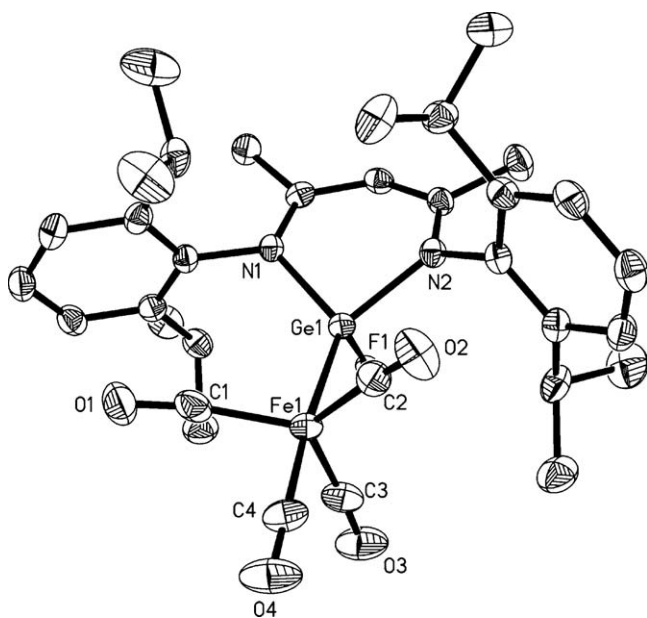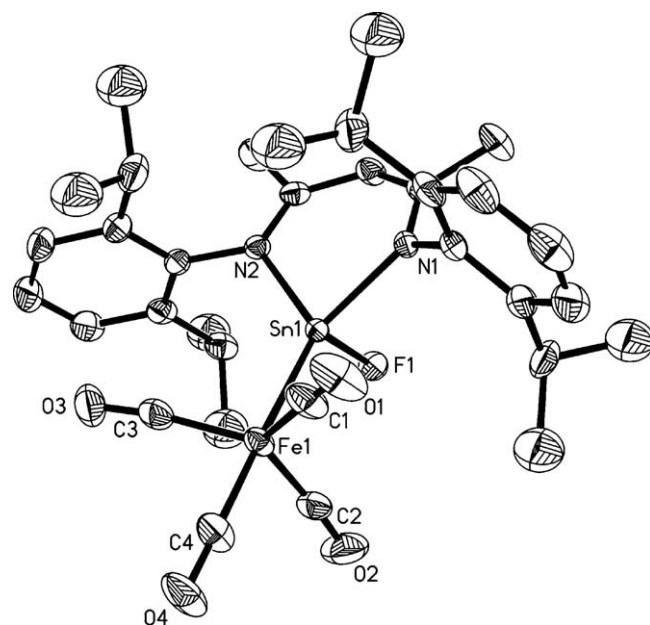

Fig. 2. Molecular structure of **4**. Thermal ellipsoids are shown at 50% probability. H atoms are omitted for clarity reasons. Selected bond lengths [Å] and angles [°]: Sn1–F1 1.9497(19), Sn1–Fe1 2.4577(6), Sn1–N1 2.099(2), Fe1–C1 1.796(4), C1–O1 1.146(4); N1–Sn1–N2 89.69(9), N1–Sn1–F1 92.08(8), N1–Sn1–Fe1 129.80(7).

Interestingly, a shorter Sn–F bond length is observed in **4** (1.9497(19) Å) compared with that in **2** (1.988(2) Å). This is in contrast to the trend observed for the germanium compounds **1** (1.805(17) Å) and **3** (1.868(2) Å). Moreover, the Sn(II)–F bond of **4** is shorter when compared with those of Sn(IV)–F bonds such as $\{2,6-[P(O)(OEt)_2]_2-4-tBu-C_6H_2\}SnF_2Ph\cdot0.5H_2O$ (av. 2.015(2) Å) [18], $\{\{2,6-[P(O)(OEt)_2]_2-4-tBu-C_6H_2\}SnF_2OH\}_2$ (av. 1.949(3) Å) [18], and $[CH(SiMe_3)C_9H_6N-8]_2SnF_2$ (av. 1.980(4) Å) [19]. The difference in the Sn–F bond length of **4** (CN 4) compared with those of $\{2,6-[P(O)(OEt)_2]_2-4-tBu-C_6H_2\}SnF_2Ph\cdot0.5H_2O$ (CN 6), $\{\{2,6-[P(O)(OEt)_2]_2-4-tBu-C_6H_2\}SnF_2OH\}_2$ (CN 7), and $[CH(SiMe_3)C_9H_6N-8]_2SnF_2$ (CN 6) might be due to the different coordination numbers at tin (the coordination numbers, CN, are given in parentheses) or alternatively might be due to the two fluorine atoms in the latter cases that bind to each tin atom.

Compounds **3** and **4** are very soluble in benzene, toluene, diethyl ether, and THF, but to a lesser amount in *n*-hexane and *n*-pentane, which differs from the solubilities of the precursor materials, **1** and **2**.

3. Conclusion

In conclusion we have prepared the heterobimetallic complexes (**3** and **4**) containing group 14 elements (germanium and tin) and a transition metal (iron). Complexes **3** and **4** are monomeric in the solid state, and they are soluble in common organic solvents.

4. Experimental

All manipulations were performed under a dry and oxygen free atmosphere (N_2) using standard Schlenk techniques, or inside a MBraun glovebox maintained at or below 1 ppm of O_2 and H_2O. Solvents were purified with the MBraun solvent drying system. The starting materials **1** and **2** were prepared using literature procedures [4,5]. $Fe_2(CO)_9$ was purchased from Aldrich and used as received. ^1H, ^{13}C, ^{19}F, and ^{119}Sn NMR spectra were recorded on a Bruker Avance DRX 500 MHz instrument and referenced to the deuterated solvent in the case of the ^1H and ^{13}C NMR, and to $CFCl_3$,

Fig. 1. Molecular structure of **3**. Thermal ellipsoids are shown at 50% probability. H atoms are omitted for clarity reasons. Selected bond lengths [Å] and angles [°]: Ge1–F1 1.868(2), Ge1–Fe1 2.3262(7), Ge1–N1 1.927(2), Fe1–C1 1.798(3), C1–O1 1.149(4); N1–Ge1–N2 94.12(10), N1–Ge1–F1 94.99(8), N1–Ge1–Fe1 125.96(7).

and SnMe$_4$ in the cases of the ^{19}F and ^{119}Sn NMR spectra, respectively. Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. Infrared spectral data were recorded on a Perkin-Elmer PE-1430 instrument. EI-MS were measured on a Finnigan Mat 8230 or a Varian MAT CH5 instrument. Melting points were measured in sealed glass tubes with a Büchi melting point B 540 instrument.

4.1. Synthesis of LGeFFe(CO)$_4$ (3)

A flask was loaded with **1** (0.50 g, 1.0 mmol), Fe$_2$(CO)$_9$ (0.37 g, 1.0 mmol), and THF (30 mL). The solution was stirred for 24 h at ambient temperature. Afterwards the solid was removed by filtration over celite, resulting in a clear pale brown filtrate. From the resulting solution the volatiles were removed in vacuum, giving a pale yellow solid. Crystallization of the crude product was achieved from a saturated THF solution of **3**, stored it in a freezer at −30 °C. After three days, **3** deposited as pale yellow crystals. Yield of **3** 0.48 g (70%). Elemental analysis C$_{33}$H$_{41}$FFeGeN$_2$O$_4$: calcd. C 58.53, H 6.10, N 4.14; found: C 58.79, H 6.53, N 4.09. Mp 194 °C. EI-MS (70 eV; *m/z* (%)): 678 (100) [M]$^+$. ^{1}H NMR (500 MHz, C$_6$D$_6$, 25 °C): δ (ppm) 7.05–7.19 (m, 6H, Ar*H*), 5.09 (s, 1H; *γ*-C*H*), 3.66 (sept, 2H, C*H*(CH$_3$)$_2$), 2.92 (sept, 2H, C*H*(CH$_3$)$_2$), 1.51 (s, 6H; C*H*$_3$), 1.50 (d, 6H, CH (C*H*$_3$)$_2$), 1.30 (d, 6H, CH(C*H*$_3$)$_2$), 1.15 (d, 6H, CH(C*H*$_3$)$_2$), 1.01 (d, 6H, CH(C*H*$_3$)$_2$). ^{13}C NMR (125.75 MHz, C$_6$D$_6$, 25 °C): δ (ppm) 213.58 (*C*O), 168.68 (*C*N), 146.67, 143.99, 138.35, 129.62, 125.59, 124.97 (Ar*C*), 102.09 (*γ*-*C*), 29.62 (*C*H$_3$), 28.88 (*C*H(CH$_3$)$_2$), 25.04 (CH(*C*H$_3$)$_2$), 24.80 (CH(*C*H$_3$)$_2$), 24.53 (CH(*C*H$_3$)$_2$), 24.37 (CH(*C*H$_3$)$_2$), 24.12 (CH(*C*H$_3$)$_2$). ^{19}F NMR (188.29 MHz, C$_6$D$_6$, 25 °C): δ (ppm) −102.81.

4.2. Synthesis of LSnFFe(CO)$_4$ (4)

A flask was loaded with **2** (0.55 g, 1.0 mmol), Fe$_2$(CO)$_9$ (0.37 g, 1.0 mmol), and THF (35 mL). The solution was stirred 24 h at ambient temperature. The resulting solid was removed by filtration over celite, giving in a clear pale brown filtrate. From the resulting solution the volatiles were removed in vacuum forming a pale yellow solid. Crystallization of the crude product was achieved from a saturated toluene solution of **4**. After storing the solution for two days in a freezer at −30 °C, single crystals were obtained which are suitable for X-ray structural analysis. Yield of **4** 0.47 g (65%). Elemental analysis C$_{33}$H$_{41}$FFeN$_2$O$_4$Sn: calcd. C 54.80, H 5.71, N 3.87; found: C 54.76, H 6.13, N 3.80. mp 188 °C. EI-MS (70 eV; *m/z* (%)): 724 (100) [M]$^+$. ^{1}H NMR (500 MHz, C$_6$D$_6$, 25 °C): δ (ppm) 7.03–7.15 (m, 6H, Ar*H*), 4.95 (s, 1H; *γ*-C*H*), 3.73 (sept, 2H, C*H*(CH$_3$)$_2$), 2.96 (sept, 2H, C*H*(CH$_3$)$_2$), 1.52 (s, 6H; C*H*$_3$), 1.46 (d, 6H, CH (C*H*$_3$)$_2$), 1.30 (d, 6H, CH(C*H*$_3$)$_2$), 1.14 (d, 6H, CH(C*H*$_3$)$_2$), 1.02 (d, 6H, CH(C*H*$_3$)$_2$). ^{13}C NMR (125.77 MHz, C$_6$D$_6$, 25 °C): δ (ppm) 212.90 (*C*O), 169.87 (*C*N), 145.31, 142.90, 139.26, 129.05, 125.59, 124.79 (Ar*C*), 100.82 (*γ*-*C*), 29.41 (*C*H$_3$), 27.83 (*C*H(CH$_3$)$_2$), 25.41 (CH(*C*H$_3$)$_2$), 24.20 (CH(*C*H$_3$)$_2$), 24.14 (CH(*C*H$_3$)$_2$). ^{19}F NMR (188.31 MHz, C$_6$D$_6$): δ (ppm) −132.91. ^{119}Sn NMR (111.92 MHz, C$_6$D$_6$, 25 °C): δ (ppm) −14.16 (d, (^2J(Sn–F) = 3172.2 Hz), Sn–*F*).

4.3. X-ray crystallography

Suitable crystals of **3** and **4** were mounted on glass fibers and their data sets were collected on an IPDS II Stoe image-plate diffractometer (graphite monochromated Mo Kα radiation, λ = 0.71073 Å) at 133(2) K. The data was integrated with X-area. The structures were solved by Direct Methods (SHELXS-97) [20] and refined by full-matrix least square methods against F^2 (SHELXL-97) [20]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were

Table 1
Summary of crystal data and refinement results for compounds **3** and **4**.

Empirical formula	C$_{33}$H$_{41}$FFeGeN$_2$O$_4$	C$_{33}$H$_{41}$FFeN$_2$O$_4$Sn
Formula weight	677.12	723.22
CCDC-no.	745455	762752
T [K]	133(2)	133(2)
Crystal system	Monoclinic	Monoclinic
Space group	*P*2$_1$/*n*	*P*2$_1$/*n*
a [Å]	16.213(3)	11.132(2)
b [Å]	9.779(2)	19.793(4)
c [Å]	20.391(4)	17.180(3)
α [°]	90	90
β [°]	96.52(3)	108.65(3)
γ [°]	90	90
V [Å^3]	3212.2(11)	3586.5(12)
Z	4	4
$D_{calcd.}$ [g cm^{-3}]	1.4002(5)	1.3394(5)
μ [mm^{-1}]	1.432	1.140

refined isotropically on calculated positions using a riding model. It is common for iso-propyl groups that the terminal carbon atoms are rather of ellipsoidal than spherical shape due to their potential to rotate around the central carbon, which is in contrast to the terminal carbons that have only very small anisotropic atomic displacement parameters. This gives rise to a comparatively large U_{eq}(min)/U_{eq}(max) ratio for the respective carbon (and hydrogen) atoms. This is quite commonly observed in structures with the β-diketiminate ligand. In addition to the terminal carbon atoms of the iso-propyl groups the oxygen atoms of the carbonyl ligands at iron are elongated. Again this is connected to a potential structural flexibility, here now based on the trigonal bipyramidal coordination geometry around iron, which is known to be flexible enough to undergo pseudorotation. The latter is hindered in the solid state of this crystal structure, however, the carbonyl ligands and in particular the oxygen atoms, which are at a larger distance to iron are still flexible enough to move around their central position. As expected and due to the above explained reason for the elongation, the absorption correction did not influence the anisotropic atomic displacement parameters of the elongated atoms to a large extent. For instance the parameters for O4 in the structure of **3** changed from 0.03794, 0.02533, 0.08259, 0.00854, −0.01208 and 0.00178 to 0.03814, 0.02518, 0.083266, 0.00862, −0.01217 and 0.00176. The crystallographic data are summarized in Table 1.

Acknowledgment

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jfluchem.2010.03.011.

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