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Complexes of Ge(IV)- and Sn(IV)-Fluorides with Cyclic and Acyclic Carbenes: Bis(dialkylamino)-difluoromethylenes as Carbene Sources

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Ⓢ *Supporting Information*

ABSTRACT: Carbene complexes of Ge(IV)- and Sn(IV)-fluorides have been synthesized by oxidative addition of 2,2-difluoro-1,3-dimethylimidazolidine and bis(dimethylamino)difluoromethane to $GeCl_2$•dioxane and SnF_2. Chloride analogs of the Ge(IV) complexes were also isolated. All compounds were characterized in the solid state by single-crystal X-ray diffraction.

Diaminocarbenes have evolved during the past two decades from a chemical curiosity to a very well-established class of ligands in organometallic chemistry, alongside applications in technical and pharmaceutical processes.[1] The most common carbene ligands in coordination chemistry are N-heterocyclic carbenes (NHC) of *N,N'*-substituted imidazol-2-ylidenes, as they can be isolated in their free form as "bottleable carbenes", having coordination properties often compared with the well-established phosphine ligands.[2,3] In contrast, synthetic pathways for complexes using nonstable carbenes are more constrained. One route is the deprotonation of the corresponding (and stable) imidazolium salts as introduced by Wanzlick and Öfele in 1968.[4,5] A different approach is the oxidative addition of iodo-, bromo-, and chloro-imidazolium as well as -imidazolidinium cations to zerovalent transition metals.[6] However, no fluorine derivatives were reported for this approach so far. Herein, we report the oxidative addition of bis(dialkylamino)-difluoromethylenes (acyclic **1a** and cyclic **1b** derivatives) to halides of main group elements, in particular germanium and tin. The structures of these two precursors are shown in Figure 1.

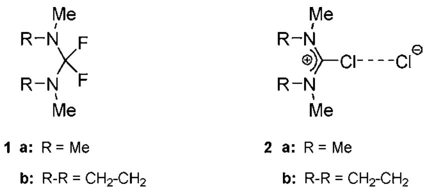
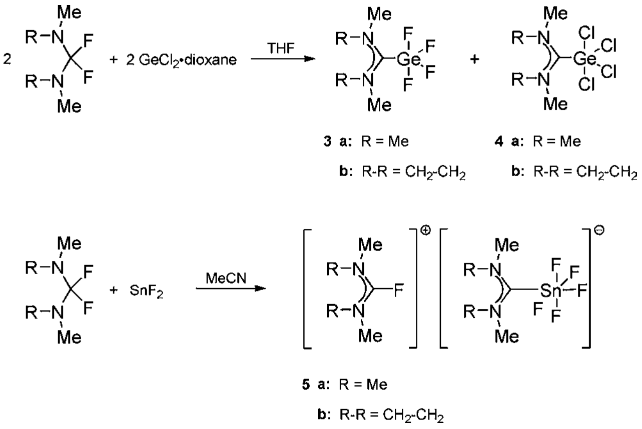


Figure 1. Carbene precursors **1a**, **1b**, **2a**, and **2b**.

Compounds **1a** and **1b** show significant differences compared to their chloro analogs **2a** and **2b** (Figure 1). The crystal structures of **1a** and **1b** are still unknown, but the ^{19}F-NMR data clearly indicates the presence of two covalent and equivalent C−F bonds.[7] This is in contrast with the 2-chloroamidinium salts, which crystal structures can be considered as linear charge−transfer complexes of carbene and chlorine.[8]

We have successfully synthesized complexes of the main group elements Ge and Sn coordinated with the bis(dimethylamino)carbene (**3a**, **4a**, **5a**) and *N,N'*-dimethylimidazolidin-2-ylidene (**3b**, **4b**, **5b**) ligands (Scheme 1). Although the acyclic carbene has not been reported so far, its cyclic analog has been previously synthesized and isolated at low temperature by Denk and co-workers.[9] These compounds are to the best of our knowledge the first examples of carbene complexes of Ge(IV)- and Sn(IV)-halides. Some examples of carbene adducts of M(II)-halides (M = Ge, Sn) have been reported in the past two decades by addition of free Arduengo-carbene to metal halides.[10,11a] Furthermore, Kuhn and co-workers prepared NHC-containing Sn(IV) complexes by addition of free NHC to R_2SnCl_2 species as well as NHC ligand transfer.[11] The only structurally characterized compound of a carbene-stabilized Ge(IV) species was synthesized by the group of Driess by oxidation of a NHC-germylene complex to NHC-germanone using N_2O.[12] All compounds were characterized in solution by multinuclear NMR-spectroscopy and single-crystal X-ray crystallography.

Scheme 1. Synthesis of Compounds 3a, 3b, 4a, 4b, 5a, 5b



The oxidative addition of an equimolar amount of **1a** to $GeCl_2$•dioxane in THF leads to the carbene-tetrafluorogermanium(IV) adduct **3a** and its corresponding chloro analog **4a**. The same addition process occurs, respectively, for **1b** in order to give **3b** and **4b**. Unlike their

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chloro counterparts, the two products **3a** and **3b** are insoluble in THF and can be easily separated and purified and were isolated as colorless solids. Only compound **3b** still coordinates an average amount of 0.6 equivalents of THF as observed in solution by the ^{1}H- and ^{13}C NMR spectroscopy. In order to get suitable crystals for single-crystal XRD, all compounds were recrystallized by diffusion of diethyl ether into an acetonitrile solution, and no THF molecule was observed by XRD for crystals of **3b** prepared with the aforementioned recrystallization step, thus suggesting loss of the coordinated THF.

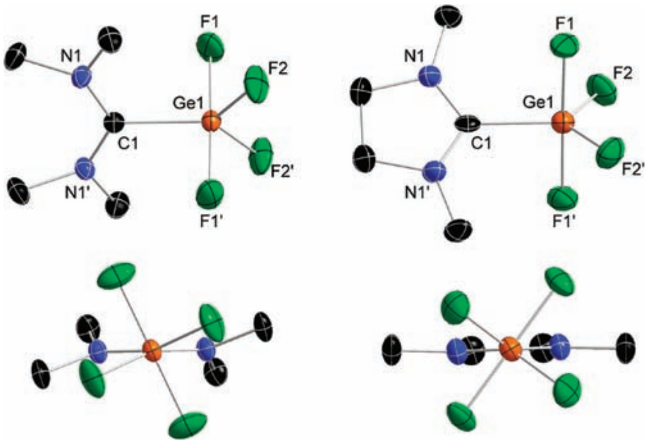
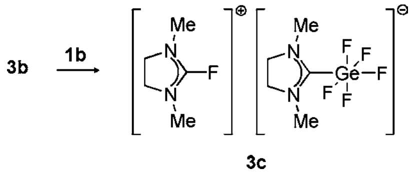


Figure 2. Top: Solid state molecular structure of **3a** (left) and **3b** (right) with the thermal ellipsoids set at 50% probability level (H atoms are omitted for clarity). Selected bond lengths [pm] and angles [deg] for **3a**: Ge1−C1 201.1(2), Ge1−F1 178.2(2), Ge1−F2 172.37(12), N1−C1−N1′ 122.2(2), F1−Ge1−F1′ 178.47(6), F2−Ge1−F2′ 110.63(9). For **3b**: Ge1−C1: 198.1(4), Ge1−F1 178.1(2), Ge1−F2 172.9(2), N1−C1−N1′ 111.8(4), F1−Ge1−F1′ 178.87(13), and F2−Ge−F2′ 117.73(16). Bottom: View along the Ge1−C1 bond.

Complexes **3a** and **3b** crystallize in the monoclinic space group C_2/c. The germanium centers in both compounds are in an idealized trigonal bipyramidal environment, with the angular sum for the equatorial ligands being about 360° and the angles between the axial fluorine substituents about 180°. The carbon−germanium bond length is considerably longer for the acyclic carbene complex **3a** (201.1(2) pm) than for the cyclic **3b** (198.1(4) pm). The germanium−fluorine bond lengths are however not affected by the nature of the carbene ligand, whereas only the equatorial F2−Ge−F2′ angle is larger for the cyclic analog **3b** due to the shorter carbon−germanium bond. In solution, broad singlets in the ^{19}F-NMR were detected for both compound (−115.76 ppm for **3a** and −116.79 ppm for **3b**), which remain as singlets even at −100 °C, showing that the pseudorotation process does not slow down at this temperature. To the best of our knowledge, no ^{19}F-NMR data for pentacoordinated GeF_4 has been reported. Previously reported *cis*- and *trans*-[GeF_4L_2] neutral complexes showed signals between −78 and −179 ppm, which is comparable to the ppm range of **3a** and **3b**.[13]

Complex **3b** gives, in the presence of an excess amount of **1b**, the salt **3c** (Scheme 2), which structure is shown in Figure 3. The geometry at the germanium center changes from trigonal bipyramidal to octahedral alongside a drastic increase in the carbon−germanium bond length. In the case of acyclic carbene complex **3a**, addition of **1a** leads to unidentified decomposed products.

Scheme 2. Formation of 3c



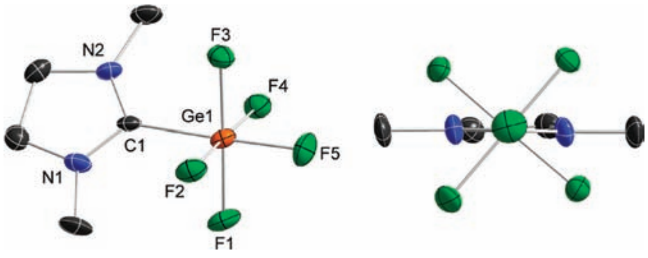


Figure 3. Left: Solid state molecular structure of the anionic unit of **3c** with the thermal ellipsoids set at 50% probability level (H atoms and the cation are omitted for clarity). Selected bond lengths [pm] and angles [deg]: Ge1−C1 205.7(5), Ge1−$F5_{trans}$ 178.8(3), average Ge−F_{cis} 180.4(3), and N1−C1−N2 108.4(4). Right: View along the Ge1−C1 bond.

The carbene complexes of tetrachlorogermanium(IV), **4a** and **4b**, are isostructural with their analogs **3a** and **3b**. The expected weaker Lewis acid−base interaction between the carbene ligand and $GeCl_4$ compared to GeF_4 is reflected by a small increase in the carbon−germanium bond length. The angles between the two axial chloride atoms are 171.97(2)° for **4a** and 175.20(7)° **4b**, showing distortion from an idealized trigonal bipyramidal environment of the germanium centers. Nevertheless, the equatorial angular sum is still about 360° for both **4a** and **4b** (for further structural parameters, see the Supporting Information).

Addition of **1a** or **1b** to a suspension of SnF_2 in acetonitrile leads to a clear solution of salts **5a** or **5b** containing hexacoordinated tin(IV). In contrast to **3a** or **3b**, the respective neutral tin analogs could not be obtained. This is due to the fact that tetrafluorotin(IV) is a stronger Lewis acid, which is able to abstract an additional fluoride from **1a** or **1b** (Figure 4) with 2-fluoroamidinium acting as countercation (Scheme 1). The isolated products are colorless and highly hygroscopic salts. Compound **5a** crystallizes in the triclinic space group *P*-1 and **5b** in the monoclinic space group $P2_1/n$. In both salts, the tin center is in an idealized octahedral environment. The most significant difference is the carbon−tin bond length in **5a** (229.0(3) pm) and in **5b** (225.6(4) pm), and the *trans*-fluorine−tin bond length decreases from the acyclic **5a** (197.2(2) pm) to the cyclic **5b** (195.5(3) pm) complex. The average length of the four *cis*-fluorine−tin bonds is only slightly affected by the nature of the carbene ligand (197.6(2) pm (**5a**) and 197.3(3) pm (**5b**)).

The ^{19}F-NMR spectra for both salts exhibit a doublet for the *cis*-fluorine atoms at −132.58 ppm (**5a**) and −138.14 ppm (**5b**) and a quintet for the *trans*-fluorine atoms at −155.81 ppm (**5a**) and −157.58 ppm (**5b**), as well as a singlet for the respective cations at −46.34 ppm and −90.72 ppm. The ^{119}Sn signals for both compounds appear as doublet of quintets at −749.75 ppm for **5a** ($^{1}J_{SnF(cis)}$ = 2160 Hz, $^{1}J_{SnF(trans)}$ = 1490 Hz) and at −741.97 ppm for (**5b**) ($^{1}J_{SnF(cis)}$ = 1980 Hz, $^{1}J_{SnF(trans)}$ = 1530 Hz) and are within the range of neutral hexacoordinated

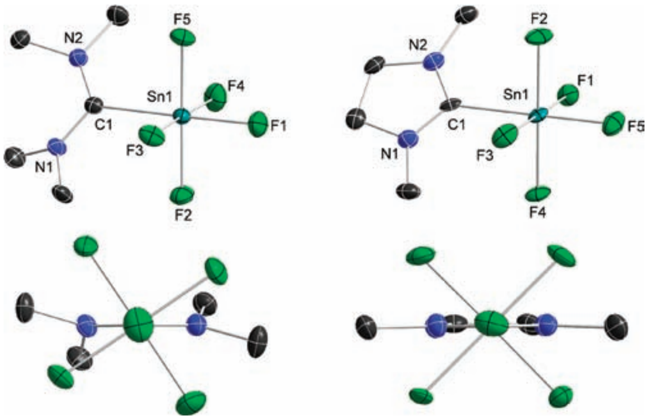


Figure 4. Top: Solid state molecular structure of the anionic units of **5a** (left) and **5b** (right) with the thermal ellipsoids set at 50% probability level (H atoms and cations are omitted for clarity). Selected bond lengths [pm] and angles [deg] for **5a**: Sn1−C1 229.0(3), Sn1−F1$_{trans}$ 197.2(2), average Sn1−F$_{cis}$ 197.6(2), and N1−C1−N2 118.0(3); **5b**: Sn1−C1 225.6(4), Sn1−F5$_{trans}$ 195.5(3), average Sn−F$_{cis}$ 197.3(3), and N1−C1−N2 109.8(4). Bottom: View along the Sn1−C1 bond.

tin(IV)-fluorides of the type *cis*- and *trans*-[SnF_4L_2], as well as for dianionic complexes of the type [$RSnF_5$] (R = Me, Bu).[14]

In 2009, Roesky and co-workers reported a NHC-SiF_4 complex with the carbene ligand at the axial position.[15] All fluorine atoms of the complex appear as one singlet in the ^{19}F-NMR spectrum even at −78 °C, which is in accordance with compounds **3a** and **3b**. There is however no reference to an anionic form, which has only been observed so far for compounds **3c**, **5a**, and **5b**.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details for the synthesis of compounds **3a**, **3b**, **3c**, **4a**, **4b**, **5a**, and **5b**, and X-ray crystallographic (CIF) and NMR-spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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