# Primary Studies on Variation in Position of Trifluoromethyl Groups in Several Aromatic Group-14 Derivatives by $^{19}$F-NMR Spectroscopy

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Variation in the position of $CF_3$ groups in several aromatic Group-14 compounds was studied by $^{19}$F-NMR spectroscopy. In these compounds $R_nECl_{4-n}$ ($n = 1$ or 2; E = Si, Ge, or Sn; R = 2,4,6-$(CF_3)_3C_6H_2$ (=Ar), 2,6-$(CF_3)_2C_6H_3$ (=Ar′), or 2,4-$(CF_3)_2C_6H_3$ (=Ar″)), Ar, Ar′, and Ar″ are all bulky, strongly electron-withdrawing ligands. The $^{19}$F-NMR studies of the variation in position of the $CF_3$ substituents in these compounds as revealed by chemical shifts could be correlated with the electronegativities of the central elements E, and with intramolecular E–F interactions derived from single-crystal X-ray diffraction data. These interactions are considered to play an important role in the stabilization of these compounds.

**Introduction.** – The 'fluoromes' ligand 2,4,6-$(CF_3)_3C_6H_2$ (=Ar, henceforth) is well known for its stabilizing influence in the compounds of transition metals [1][2] and main-group elements [3–10]. This effect is due to the high electronegativity, combined with some M → C $\pi$ back-donation and steric demands, of the two *ortho*-positioned trifluoromethyl groups to stabilize low-valent, low-coordinate main group compounds. The 'fluoroxyl' 2,6-$(CF_3)_2C_6H_3$ (=Ar′) group, which possesses similar advantages, is used much less frequently, partly because lithiation of its precursor 1,3-bis(trifluoromethyl)benzene (Ar′H) can proceed at two different positions, leading to a mixture of Ar′ and 2,4-$(CF_3)_2C_6H_3$ (=Ar″) derivatives [11–15]. In Group 14, ArLi reacts with $ECl_4$ (E = Ge or Sn) in a 2:1 ratio to yield both $ArECl_3$ and $Ar_2ECl_2$ [14]. However, it has been found that the mixture of Ar′Li and 2,4-$(CF_3)_2C_6H_3Li$ (Ar″Li) reacts with $ECl_4$ (E = Si, Ge, or Sn) to produce either $Ar'_nECl_{4-n}$ or $Ar''_nECl_{4-n}$ ($n = 1$ or 2); the reaction does not produce the mixed-ligand compound $Ar'Ar''ECl_2$. There is a further complication in the Si derivatives, since F/Cl exchange takes place readily, particularly for Ar [1g][8][14].

Few papers report on derivatives of Group 14 (*e.g.*, Si, Ge, and Sn) with Ar, Ar′, or Ar″, especially with respect to the variation in the position of the $CF_3$ substituents. The present paper is the first to study the $CF_3$ positions in these compounds by $^{19}$F-NMR spectroscopy.

**Experimental.** – *General.* All manipulations, including NMR sample preparation, were carried out either under dry $N_2$ or *in vacuo*, by means of standard *Schlenk* procedures or a glovebox. Chemicals of the best available commercial grades were used, without further purification. $^{19}$F-NMR Spectra: *Varian-Mercury-200* spectrometer; at 188.18 MHz; chemical shifts $\delta$(F) in ppm relative to external $CFCl_3$.

*Lithiation.* By the methods of *Goodwin* [9] and *Roden* [15], ArH was directly treated with 2.5M BuLi in $Et_2O$ at $-78°$ (acetone/dry ice bath) to produce ArLi. Ar′H reacted with BuLi under the same conditions to produce a mixture Ar′Li/Ar″Li in a *ca.* 1:1 ratio [15]. **WARNING:** It is important in these reactions to keep a slight excess of the hydrocarbon (ArH or Ar′H) with respect to BuLi at all times, to avoid any attack at a $CF_3$ group and the possible explosive formation of LiF (*Scheme*).

Scheme. *Synthetic Reactions* (all performed at $-78°$)

$$\mathrm{ArH} \xrightarrow{\mathrm{BuLi,\ Et_2O}} \mathrm{ArLi} \xrightarrow{\mathrm{ECl_4,\ hexanes}} \mathrm{Ar}_n\mathrm{ECl}_{4-n}\ (\mathrm{E} = \mathrm{Ge\ or\ Sn};\ n = 1\ \mathrm{or}\ 2)$$

$$\mathrm{Ar'H} \xrightarrow{\mathrm{BuLi,\ Et_2O}} \mathrm{Ar'Li} + \mathrm{Ar''Li} \xrightarrow{\mathrm{ECl_4,\ hexanes}} \mathrm{Ar'ECl_2} + \mathrm{Ar''ECl_2}\ (\mathrm{E} = \mathrm{Si,\ Ge,\ or\ Sn})$$

$(\mathrm{Ar} = 2,4,6\text{-}(\mathrm{CF_3})_3\mathrm{C_6H_2};\ \mathrm{Ar'} = 2,6\text{-}(\mathrm{CF_3})_2\mathrm{C_6H_3};\ \mathrm{Ar''} = 2,4\text{-}(\mathrm{CF_3})_2\mathrm{C_6H_3})$

*Chloro Derivatives* **1**–**10**. All of the chloro derivatives were prepared by reacting the corresponding Group-14 tetrachloride $ECl_4$ with 2 equiv. of ArLi or a mixture Ar′Li/Ar″Li (to a total of 2 equiv.). The new compounds synthesized were: $Ar'_2SiCl_2$ **1**, $Ar''_2SiCl_2$ **2**, $ArGeCl_3$ **3**, $Ar_2GeCl_2$ **4**, $Ar'_2GeCl_2$ **5**, $Ar''_2GeCl_2$ **6**, $ArSnCl_3$ **7**, $Ar_2SnCl_2$ **8**, $Ar'_2SnCl_2$ **9**, and $Ar''_2SnCl_2$ **10** (*Fig. 1*)[1]). All products were dissolved in $Et_2O$ and the solns. placed in the refrigerator. Six of these produced well-formed colorless crystals, which were suitable for single-crystal X-ray diffraction [14]. All of these compounds were now further analyzed by $^{19}F$-NMR spectroscopy. As found by previous authors [1g][8][14], attempted synthesis of $Ar_2SiCl_2$ led to rapid F/Cl exchange, and the only product which could be isolated was $Ar_2SiF_2$. Slower exchange occurred for Ar′- and Ar″-substituted chlorosilanes [14], as shown in the *Results and Discussion* section.

**Results and Discussion.** – The results of the $^{19}F$-NMR study of **1**–**10** are listed in *Table 1*, while *Fig. 2* shows some typical $^{19}F$-NMR spectra in the $CF_3$ region. The spectra of $ArGeCl_3$ **3** and $Ar_2SnCl_2$ **8** (*Fig. 2,a* and *b*, resp.) as the main species present exhibited the expected F-atom 2:1 intensity ratio of the *o*-$CF_3$/*p*-$CF_3$ groups. The solution produced by reaction of $SnCl_4$ with the Ar′Li/Ar″Li mixture showed a *ca.* 1.8:1 ratio of $Ar'_2SnCl_2$ **9** to $Ar''_2SnCl_2$ **10** (*Fig. 2,c*). Compound **9** yielded a single resonance, having *o*-$CF_3$ groups only, while **10** gave two signals in a 1:1 intensity ratio for the *o*- and *p*-$CF_3$ groups. *Fig. 2,d*, showed that the main component $Ar''_2SiCl_2$ **2** had undergone partial Cl/F exchange to $Ar''_2SiF_2$, in the Cl/F ratio of *ca.* 4:1 (the *o*-$CF_3$ signal of $Ar''_2SiF_2$ was a *t* due to $^5J(F,F)$ coupling, and there was also a *sept.* signal at $\delta(F)$ $-133.0$ (not shown in *Fig. 2,d*) for the F-atoms bound to Si, with $^5J(F,F)$ 12.4 Hz [14]). The *p*-$CF_3$ signals of **2** and $Ar''_2SiF_2$ overlapped, hence the 1.25 relative intensity integral included both signals. The spectrum of $Ar''_2GeCl_2$ **6** (*Fig. 2,e*) again gave the expected 1:1 intensity ratio for the *o*- and *p*-$CF_3$ groups.

*Roden* has shown that Ar′H reacts with BuLi to produce an Ar′Li/Ar″Li 1:1 mixture, which reacts with $PCl_3$ to generate Ar′Ar″PCl and $Ar''_2PCl$; these have both

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[1]) Systematic names of **1**–**10**: 1,1′-(dichlorosilylene)bis[2,6-bis(trifluoromethyl)benzene] (**1**), 1,1′-(dichlorosilylene)bis[2,4-bis(trifluoromethyl)benzene] (**2**), trichloro[2,4,6-tris(trifluoromethyl)phenyl]germane (**3**), dichlorobis[2,4,6-tris(trifluoromethyl)phenyl]germane (**4**), bis[2,6-bis(trifluoromethyl)phenyl]dichlorogermane (**5**), bis[2,4-bis(trifluoromethyl)phenyl]dichlorogermane (**6**), trichloro[2,4,6-tris(trifluoromethyl)phenyl]stannane (**7**), dichlorobis[2,4,6-tris(trifluoromethyl)phenyl]stannane (**8**), bis[2,6-bis(trifluoromethyl)phenyl]dichlorostannane (**9**), and bis[2,4-bis(trifluoromethyl)phenyl]dichlorostannane (**10**).

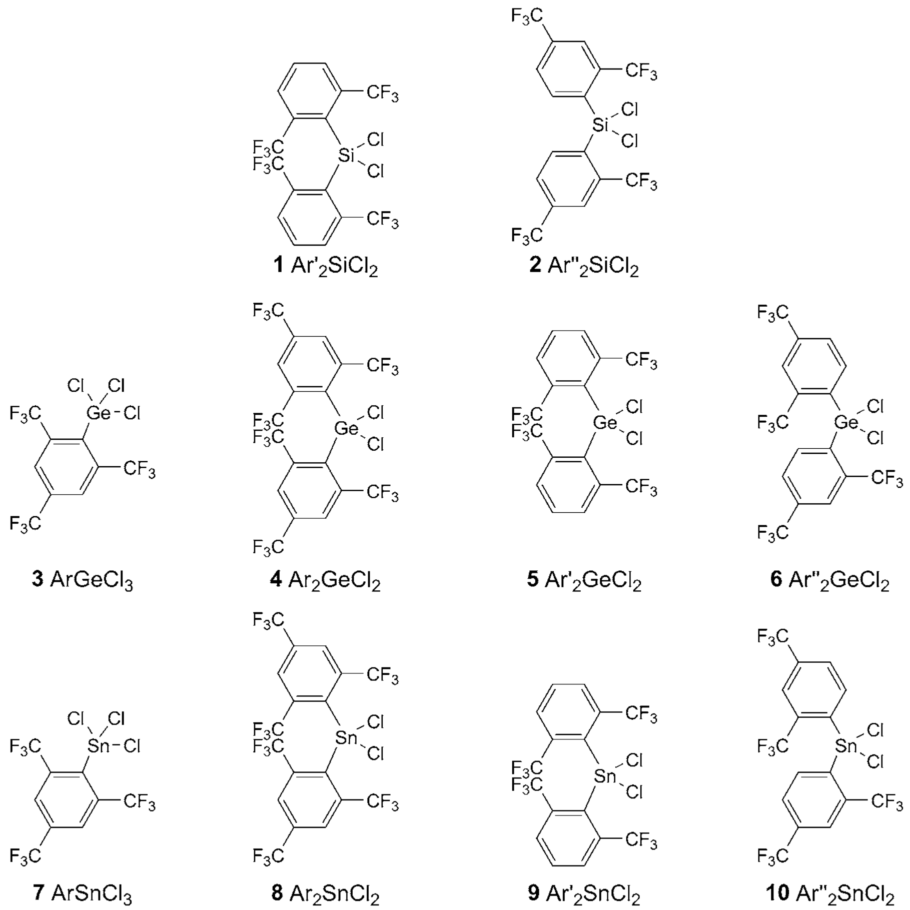

Fig. 1. *Structures of the Group-14 compounds studied*

Table 1. *$^{19}$F-NMR Chemical Shifts of Si, Ge, and Sn Compounds.* $\delta$ in ppm.

| Compound | | $\delta$(F) ($o$-CF$_3$) | $^4J$(Sn,F) [Hz] | $\delta$(F) ($p$-CF$_3$) |
|---|---|---|---|---|
| **1** | Ar'$_2$SiCl$_2$ | – 58.9 ($s$, 12 F) | | |
| **2** | Ar''$_2$SiCl$_2$ | – 57.9 ($s$, 6 F) | | – 64.2 ($s$, 6 F) |
| **3** | ArGeCl$_3$ | – 54.9 ($s$, 6 F) | | – 64.2 ($s$, 3 F) |
| **4** | Ar$_2$GeCl$_2$ | – 54.4 ($s$, 12 F) | | – 64.1 ($s$, 6 F) |
| **5** | Ar'$_2$GeCl$_2$ | – 53.8 ($s$, 12 F) | | |
| **6** | Ar''$_2$GeCl$_2$ | – 58.8 ($s$, 6 F) | | – 64.2 ($s$, 6 F) |
| **7** | ArSnCl$_3$ | – 55.9 (6 F)[a]) | 19 | – 63.0 ($s$, 3 F) |
| **8** | Ar$_2$SnCl$_2$ | – 57.1 (12 F)[a]) | 10 | – 64.2 ($s$, 6 F) |
| **9** | Ar'$_2$SnCl$_2$ | – 57.0 (12 F)[a]) | 10 | |
| **10** | Ar''$_2$SnCl$_2$ | – 59.1 (6 F)[b]) | | – 64.0 ($s$, 6 F) |

[a]) $s$ with Sn satellites. [b]) Sn satellites not resolved.

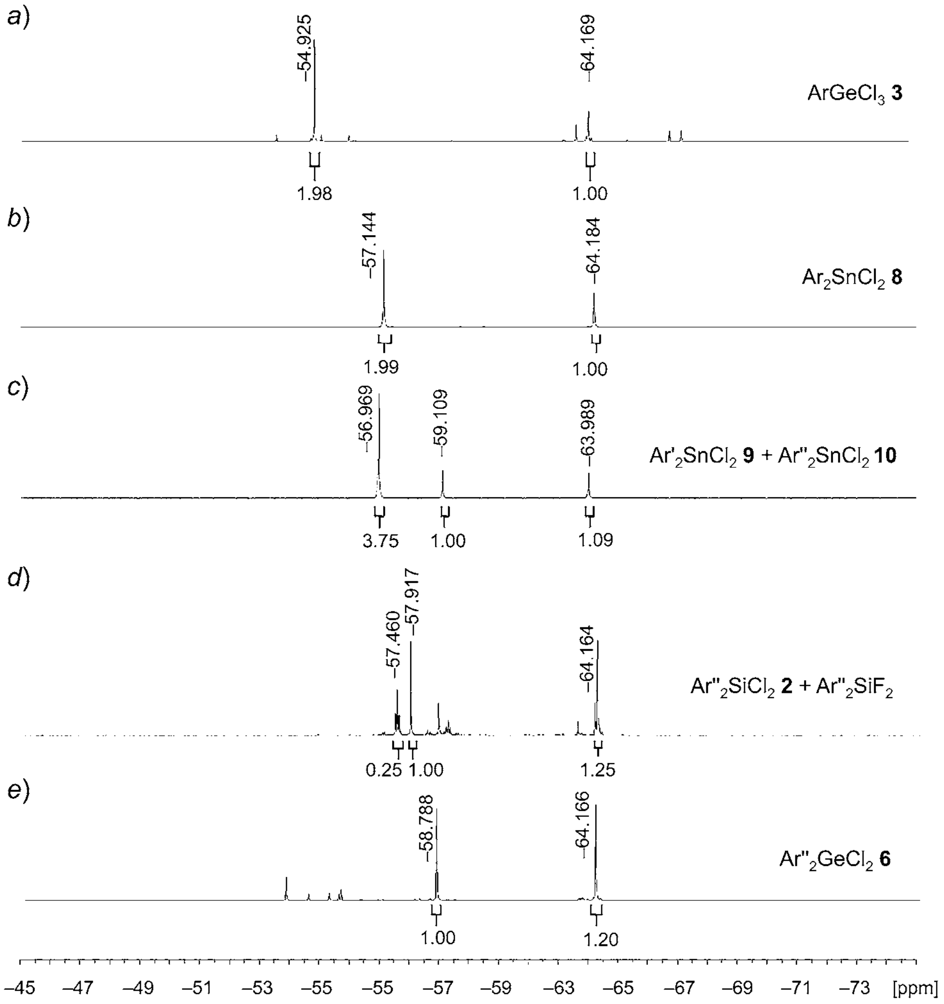

Fig. 2. *$^{19}$F-NMR Spectra of several Group-14 compounds*

been characterized by single-crystal X-ray diffraction [10][12][15]. Initially, it was thought that the structure of the predominant isomer of the diaryl-substituted germane and stannane derivatives would be $Ar'Ar''ECl_2$ (E = Ge or Sn), for steric reasons. It was found, however, that a solution of Ar'Li and Ar''Li reacting with $ECl_4$ (E = Ge or Sn) produced a mixture $Ar'_2ECl_2/Ar''_2ECl_2$ (*cf. Fig. 2,c*) and not $Ar'Ar''ECl_2$. This result is rather surprising from a steric viewpoint.

*Table 2* shows the *van der Waals* radii and electronegativities of the central element E [16], together with the shortest distances between F-atoms of the *o*-$CF_3$ groups and E for compounds where the crystal and molecular structures have been determined [14]. In all cases, these distances were considerably shorter than the sums of the *van der*

Table 2. *Bond Distance E–F of Group-14 Compounds*

| Compound | *van der Waals* radius of E [Å] | Electronegativity of E | Sum of *van der Waals* radii [Å] | Shortest E–F distance [Å] |
|---|---|---|---|---|
| **2** $Ar''_2SiCl_2$ | 2.08 (Si) | 1.89 (Si) | $1.47+2.08=3.55$ | 2.882(2) |
| **3** $ArGeCl_3$ | 2.12 (Ge) | 2.07 (Ge) | $1.47+2.12=3.59$ | 2.909(2) |
| **4** $Ar_2GeCl_2$ | 2.12 (Ge) | 2.07 (Ge) | $1.47+2.12=3.59$ | 2.757(2) |
| **6** $Ar''_2GeCl_2$ | 2.12 (Ge) | 2.07 (Ge) | $1.47+2.12=3.59$ | 2.848(2) |
| **8** $Ar_2SnCl_2$ | 2.18 (Sn) | 1.86 (Sn) | $1.47+2.18=3.65$ | 2.720(4) |
| **9** $Ar'_2SnCl_2$ | 2.18 (Sn) | 1.86 (Sn) | $1.47+2.18=3.65$ | 2.686(2) |

*Waals* radii, as shown. These results clearly indicate an additional weak ('secondary') coordination or attractive electrostatic interactions, which can play an important role in the stabilization of these compounds (*Table 2*).

The $^{19}$F-NMR chemical shifts for *p*-$CF_3$ substituents in the Si, Ge, and Sn chloro compounds with Ar, Ar′, and Ar″ were between $\delta$(F) $-64.0$ and $-64.2$, except for $ArSnCl_3$ **7** with a $\delta$(F) of $-63.0$ (*Table 1*). These results were explained by the fact that *p*-$CF_3$ groups are remote from the main-group atoms E; thus, the corresponding F-atoms did not interact with E, and their $\delta$(F) were very similar.

A much larger shift range was found for the *o*-$CF_3$ groups, from $\delta$(F) $-53.8$ to $-59.1$ (*Table 1*), due at least in part to the intramolecular F–E interactions mentioned above. The atoms E also differ in covalent radius and electronegativity (*Table 2*), which can affect the chemical shifts. As shown in *Table 1*, the $\delta$(F) value was always more negative for the *o*-$CF_3$ groups where E = Sn than for the analogous compound where E = Ge, consistent with their relative electronegativities [16]. Fewer values for Si compounds could be compared because of the rapid F/Cl exchange found in Ar systems. Hence, $Ar_2SiCl_2$ was not observed, although it may well be formed as a reactive intermediate [1g] [8] [14]. The F-atoms of the *o*-$CF_3$ groups of $Ar'_2SiCl_2$ **1** had a more negative shift than those of either $Ar'_2GeCl_2$ **5** or $Ar'_2SnCl_2$ **9**. Ge is generally regarded as being more electronegative than Sn or Si, which have comparable electronegativities (*Table 2*); so the less negative shifts in Ge compounds probably reflected this, while the results for Si and Sn compounds were very similar where data were available. The exception to this generally good correlation appeared to be $Ar''_2GeCl_2$ **6**, which had a more negative $\delta$(F) for the *o*-$CF_3$ groups than any of the other germanium compounds. Both $ArGeCl_3$ **3** and $Ar''_2GeCl_2$ **6** have only six F-atoms of the *o*-$CF_3$ groups; however $Ar_2GeCl_2$ **4** and $Ar'_2GeCl_2$ **5** have twelve such F-atoms; so, in $ArGeCl_3$ **3** and $Ar''_2GeCl_2$ **6**, there are fewer possible weak interactions of the type discussed previously. In a similar way, $Ar''_2SnCl_2$ **10** had a more negative shift than $Ar'_2SnCl_2$ **9**, although the reverse pattern appeared to hold for Si compounds **1** and **2**, where the values were not very different (*Table 1*). Small $^4J$(Sn,F) couplings were observed in compounds **7**, **8**, and **9** (*Table 1*), though it was not possible to distinguish the separate $^{117}$Sn–$^{19}$F and $^{119}$Sn–$^{19}$F satellites. These values were entirely compatible with the number of bonds involved.

$^{19}$F-NMR Spectroscopy is clearly valuable as a means of identifying the products formed in these reactions, particularly those from the Ar′Li/Ar″Li mixture. In the disubstituted compounds $R^1R^2ECl_2$, *e.g.*, if $R^1 = R^2 =$ Ar′, only a single signal from twelve F-atoms of $o$-$CF_3$ groups should be seen. If $R^1 = R^2 = Ar''$, then two equally intense signals should be apparent, one from six F-atoms of $o$-$CF_3$ groups at higher frequency and one from six F-atoms of $p$-$CF_3$ groups at lower frequency. In the event of formation of the mixed species $Ar'Ar''ECl_2$, there should be two separate signals for the F-atoms of $o$-$CF_3$ groups in a 2 : 1 intensity ratio, and one signal of intensity 1 for the F-atoms of the $p$-$CF_3$ group. As stated above, such a species was not detected in the present work. More complex mixtures of possible products can be similarly analyzed.

**Conclusions.** – The variation in $^{19}$F-NMR chemical shifts for some Group-14 aryl-substituted chloro derivatives $R_nECl_{4-n}$ ($R = 2,4,6\text{-}(CF_3)_3C_6H_2$ (= Ar), $2,6\text{-}(CF_3)_2C_6H_3$ (= Ar′), or $2,4\text{-}(CF_3)_2C_6H_3$ (= Ar″); E = Si, Ge, or Sn; $n = 1$ or 2) was studied for the first time. While the $\delta$(F) for $p$-$CF_3$ groups remained essentially constant, those for the $o$-$CF_3$ groups showed interesting variations, which could be correlated with the number of weak E–F interactions found in the solid state, and with the electronegativities of the Group-14 elements. $^{19}$F-NMR spectroscopy was particularly valuable for identifying the components of mixtures of species in solution. We hope to extend this approach to other groups of the Periodic Table in the near future.

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