¹⁹F NMR studies of the comparative electronegativity of the Ph_3E groups (E = C, Si, Ge, Sn, or Pb) in Ph_3E derivatives of tris(4-fluorophenyl)stannanethiol

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Compounds $(4-FC_6H_4)_3SnSEPh_3$ (E = C, Si, Ge, Sn, or Pb) were synthesized or generated in solution. The data on the comparative electronegativity of the Ph_3E groups were obtained from the results of ¹⁹F NMR spectroscopy. It was established that, except for E = C, the electronegativity changes in parallel with the absolute electronegativity of the central atom. Possible reasons for the deviation observed are discussed.

Key words: electronegativity, group electronegativity; carbon, silicon, germanium, tin, lead; ¹⁹F NMR spectra.

Recently, considerable attention has been given to the problems of electronegativity.¹⁻³ New atomic electronegativity scales have been suggested,⁴⁻⁶ and quantum-chemical calculations of group electronegativities have been carried out for a number of the simplest organic and organometallic groups containing Group II and III elements.^{7,8} By contrast, the data on group electronegativities of organometallic groups containing transition metal atoms and heavy main-group metal atoms are rather scarce,^{9,10} apparently, because calculations of systems containing d orbitals present difficulties, and it is necessary to take into account relativistic effects.^{6,11}

At the same time, the data on the comparative group electronegativity of organometallic groups will allow one to compare qualitatively the calculated and experimental data and to find out whether calculated electronegativities of metal atoms can predict the comparative group electronegativities of isostructural organometallic groups. These data are necessary for interpretation of the reactivities of metal-element o bonds in organometallic compounds and prediction of the effect of the group electronegativities of organometallic groups on the position of σ -metallotropic equilibria.¹² Finally, it was found recently that the use of the principle of hard and soft acids and bases requires taking into account the group electronegativities of the corresponding groups. 13, 14 This gave rise to the question of whether the comparative group electronegativities of organometallic groups remain invariant as one passes from bonds with hard ligands to bonds with soft ligands.

According to Pauling,¹⁵ atomic electronegativity is the ability of an atom in a molecule to withdraw electrons. An analogous determination should be also true for group electronegativities of organic or organometallic groups. Therefore, the following model systems are promising in studies of comparative group electronegativities of organometallic groups.

$$L_n M X M^* L_m (X = C H_2, O, S),$$

In these systems, the L_nM and L_mM^* organometallic groups compete with each other for the electron density distribution in the triad system MXM* according to their ability to withdraw the electron density. ¹⁹F NMR spectroscopy in combination with the use of an indicator organometallic group containing the 4-fluorophenyl ligand is most convenient for studying the character of the electron density distribution among the competing groups. This approach is based on results obtained previously.^{16,17} According to these results, the fluorine chemical shift in the 4-FC₆H₄QX systems is a good indicator of the change in the electron density on the fragment Q. For example, it was found that the fluorine chemical shifts of the 4-FC₆H₄ group make it possible to estimate the change in the charge on the aromatic carbon atom bonded to this group¹⁸ and reflect changes in the group electronegativities of the Ar₃Si and Ar₃Sn groups in the compounds Ar₃SiC₆H₄F-4 and Ar₃SnC₆H₄F-4.¹⁰

Recently, ¹⁹ the systems $(4-FC_6H_4)_3$ SnOMPh₃ (M = Si, Ge, Sn, or Pb) were studied by ¹⁹F NMR spectroscopy, and it was established that the group electronegativities of the Ph₃M groups decreased monotonically in the series Ph₃Si > Ph₃Ge > Ph₃Sn > Ph₃Pb. It was of interest to find out whether this order is retained when the Ph₃M groups form bonds with the S atom. In this

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connection, in this work we studied the comparative group electronegativity of the Ph_3E groups in derivatives of tris(4-fluorophenyl)stannanethiol:

E = C (1a), Si (1b), Ge (1c), Sn (1d), or Pb (1e)

Compounds 1a-c were synthesized by the reaction of $(4-FC_6H_4)_3$ SnOH (2) with Ph₃CSH (3a), Ph₃SiSH (3b), and Ph₃GeSH (3c) according to the following scheme:

$$2 + 3a - c - 1a - c + H_20$$
.

Because of the fact that unsymmetrical systems $Ph_3SnSPbPh_3$ are readily symmetrized upon storage in the crystalline state and in solution,²⁰ we generated compounds **1d**—e in solution by the exchange reactions:

$$(4-FC_6H_4)_3SnSSn(C_6H_4F-4)_3 + Ph_3SnSSnPh_3 \implies 4 \qquad 5a$$

$$= 2 (4-FC_6H_4)_3SnSSnPh_3$$

$$1d$$

$$4 + Ph_3PbSPbPh_3 \implies 2 (4-FC_6H_4)_3SnSPbPh_3$$

$$5b \qquad 1e$$

It was established that, as in the case of the corresponding oxygen analogs,¹⁹ the above-mentioned exchange reactions are slow within the ¹⁹F NMR time scale but proceed rather rapidly within the preparative time scale. For example, the ¹⁹F NMR spectrum of the reaction mixture of 4 with 5a or 5b has two signals. One of them belongs to initial compound 4, and the second signal belongs to the product of the exchange reaction (to 1d or 1e, respectively). The equilibrium was established in few hours. In the case of Ph₃GeSGePh₃ (5c), the corresponding exchange reaction did not occur even after heating in benzene at 65 °C for 3.5 h.

The ¹⁹F NMR spectra of solutions of **1a**—c and of solutions of the corresponding mixtures in the case of compounds **1d**—e were recorded. The fluorine chemical shifts were measured relative to PhF (external standard). Benzene, in which the initial compounds are rather readily soluble and which cannot cause polarization of the M—S bonds, was used as the solvent. The data on the fluorine chemical shifts (FCS) for the compounds under study and a number of other derivatives of tris(4-fluorophenyl)tin, namely, 4, $(4-FC_6H_4)_3SnSn(C_6H_4F-4)_3$ (6), $(4-FC_6H_4)_3SnCl$ (7a), $(4-FC_6H_4)_3SnBr$ (7b), and $(4-FC_6H_4)_3SnI$ (7c), are given in Table 1. A minus sign corresponds to a downfield shift of the signal relative to PhF and a decrease in the shielding.

The data in Table 1 demonstrate that in going from compound 6, which has a nonpolarized Sn—Sn bond, to compounds 7a-c with $Sn^{\delta-}-X^{\delta-}$ bonds, which are polarized according to the values of the absolute elec-

Table 1. Fluorine chemical shifts for solutions in benzene

| Compound | FCS, δ |
|--|----------------|
| $(4-FC_6H_4)_3SnSn(C_6H_4F-4)_3$ (6) $(4-FC_6H_4)_3SnCl$ (7a) $(4-FC_4H_4)_3SnCl$ (7b) | -2.45 -4.41 |
| $(4-FC_6H_4)_3$ SnI (7c) | -3.94 |
| $(4-FC_6H_4)_3$ SnSSn(C ₆ H ₄ F-4) ₃ (4) | -3.26 |
| $(4-FC_6H_4)_3SnSCPh_3$ (1a) | -2.63 |
| $(4-FC_6H_4)_3SnSSiPh_3$ (1b) | -2.74 |
| $(4-FC_6H_4)_3SnSSiPh_3$ (1c) | -2.60 |
| $(4-FC_6H_4)_3SnSSnPh_3$ (1d) | -2.55 |
| $(4-FC_6H_4)_3SnSPbPh_3$ (1e) | -2.13 |

tronegativities⁵ (eV) of tin and halogen atoms (Sn, 4.30; Cl, 8.30; Br, 7.59; and I, 6.76), the ¹⁹F signal shifts downfield, which is indicative of a decrease in the shielding of the fluorine atom. The degree of shielding decreases as the electronegativity (χ) of the halogen atom increases according to the following equation:

$$FCS = -0.31\chi - 1.88, r = 0.983, s = 0.06.$$

Therefore, the fluorine chemical shifts in compounds $(4-FC_6H_4)_3$ SnX adequately reflect the comparative electronegativity of the fragment X. The shielding of the fluorine atom also decreases in going from compound **6** to compound **4**, which is a consequence of polarization of the Sn-S (Sn⁵⁺-S⁵⁻) bond according to the absolute electronegativities⁵ of tin and sulfur (4.30 and 6.22 eV, respectively).

The results obtained suggest that correlations between the fluorine chemical shifts in compounds 1a-eand the group electronegativities of the Ph₃ES and Ph₃E groups can occur. As can be seen from Table 1, the shielding of fluorine in compounds 1a-e decreases in the order Pb > Sn > Ge > C > Si, which is indicative of a decrease in the group electronegativities of the Ph_nE groups in the series Si > C > Ge > Sn > Pb. The data on the comparative group electronegativity of the Ph₃Sn and Ph₃Pb groups bonded to a S atom agree with the results of studies of exchange equilibria involving the corresponding derivatives of 4-fluorothiophenol and 4-nitrothiophenol.²¹

Thus, the equilibrium of the reaction between $Ph_3PbSC_6H_4F-4$ and $Ph_3SnSC_6H_4NO_2-4$ is shifted to $Ph_3PbSC_6H_4NO_2-4$, which is a derivative of a stronger SH-acid. According to the theoretical analysis carried out previously,¹² this fact indicates that the polarity of the Pb-S bond is higher than that of the Sn-S bond.

The values of the electronegativities of the central atoms decrease in the series C > Pb > Ge > Sn > Si (2.55, 2.33, 2.01, 1.96, and 1.90, respectively²²). The absolute electronegativities⁵ are (eV) 6.27, 4.77, 4.60, 4.30, and 3.90 for C, Si, Ge, Sn, and Pb, respectively, and they decrease in the order C > Si > Ge > Sn > Pb. The values of the spectral electronegativities of the

above-mentioned elements are 2.544, 1.916, 1.994, and 1.824 for C, Si, Ge, and Sn, respectively,⁶ and they decrease in the order C > Ge > Si > Sn.

Analysis of the results obtained based on the abovementioned data on the electronegativities of the central atoms demonstrated that, except for the Ph₃C group, a number of the changes in the group electronegativities of the Ph₃E groups show the best correlation with the scale of the absolute electronegativities of the corresponding elements. It should be noted that for compounds 1b-e, as in the case of the oxygen analogs $(4-FC_6H_4)_3SnOEPh_3$,¹⁹ a correlation between the fluorine chemical shifts and the absolute electronegativities of the central atoms of the Ph₃E group was established:

FCS =
$$-0.66\chi + 0.40$$
, $r = 0.961$, $s = 0.09$.

Therefore, for four elements, the dependence of the group electronegativities of the Ph_3E groups on the absolute electronegativities of the central atoms remains unchanged when the element bonded to the Ph_3E group is replaced. Hence, although it is still an open question whether it is possible to estimate group electronegativities of isostructural groups of a molecule based on the data on the absolute electronegativities of the central atoms,²³ for four elements this parameter rather adequately reflects the change in the group electronegativities of the Ph₃E groups as a function of the nature of the central atom.

This dependence is not true for the Ph₃C group, which may be caused by two factors. First, when passing from Ph₃C to Ph₃Si, an additional transfer of the electron density from the S atom to the E atom can occur due to interactions between the unoccupied 3d orbitals of the Si atom and the 3p orbitals of the S atom, which contains lone electron pairs. Second, direct interaction of the π -electron systems of the aromatic rings of the (4-FC₆H₄)₃Sn and Ph₃C groups can occur. Thus, analysis of the Stewart-Briegleb structural models demonstrated that the distance between the planes of the aromatic rings of the (4-FC₆H₄)₃Sn and Ph₃C groups sharply decreases in going from 1b to 1a. As a result, a direct interaction between the π -electron systems and partial transfer of electron density to the antibonding orbitals of the 4-fluorophenyl ligand become possible. This causes an increase in the shielding of fluorine and an apparent decrease in the group electronegativity of the Ph₃C group. This question can be settled by studying derivatives of 4-fluorothiophenol of the type $Ph_3ESC_6H_4F-4$ (E = C, Si, Ge, Sn, or Pb) (8a-e) because analysis of the molecular models demonstrate that there are no contacts between the π -electron systems of the phenyl and 4-fluorothiophenoxide ligands. In addition, it was found recently¹⁰ that the fluorine chemical shifts in the compounds Ar₃SnSC₆H₄F-4 correlate with the group electronegativities of the Ar₃Sn groups. Studies of these compounds are in progress.

Experimental

The ¹⁹F NMR spectra were recorded on a Bruker WP-200 SY spectrometer; the operating frequency was 188.31 MHz for ¹⁹F (25 °C, 0.1 mol L^{-1} , a solution in benzene). Resonance conditions were stabilized relative to external D₂O. The fluorine chemical shifts were measured by the substitution method relative to external fluorobenzene in the solvent and at a concentration identical to those used for the compound studied. The error in determination of fluorine chemical shifts was no more than 0.01 ppm. The data on the fluorine chemical shifts for compound 6 were taken from Ref. 24.

Compounds 2, 32-c. 5c. and 7a were prepared according to published procedures.²⁵⁻³⁰

Synthesis of 1,1,1-triphenyl-3,3,3-tris(4-fluorophenyl)carbastanuathiane (1a). A solution of 2 (0.62 g, 1.5 mmol) in benzene (15 mL) was added to a solution of 3a (0.41 g, 1.5 mmol) in benzene (10 mL). The reaction mixture was stirred at 40-50 °C for 40 min. The solvent was evaporated on a rotary evaporator. The oil that formed was crystallized by treatment with a small amount of MeOH. The compound was recrystallized from hexane with the addition of several drops of benzene. A colorless crystalline compound was obtained (yield was 0.6 g).

Synthesis of 1,1,1-triphenyl-3,3,3-tris(4-fluorophenyl)silastannathiane (1b). A solution of 2 (0.56 g, 1.33 mmol) in benzene (10 mL) was added to a solution of 3b (0.39 g, 1.33 mmol) in benzene (10 mL). The reaction mixture was stirred at 40-50 °C for 30 min. The solvent was evaporated on a rotary evaporator. The viscous product was triturated with pentane, and crystals formed. Recrystallization from hexane gave a colorless crystalline compound (yield was 0.67 g).

Synthesis of 1,1,1-triphenyl-3,3,3-tris(4-fluorophenyl)germastannathiane (1c). A solution of 2 (1.5 g, 3.56 mmol) in benzene (20 mL) was added to a solution of 3c (1.2 g, 3.56 mmol) in benzene (15 mL). The reaction mixture was stirred at 50-60 °C for 30 min. The solvent was removed on a rotary evaporator. The oil that formed was triturated with pentane, and crystals formed. Recrystallization from hexane gave a colorless crystalline compound (yield was 1.58 g).

Synthesis of 1,1,1,3,3,3-hexakis(4-fluorophenyl)distannathiane (4). A flow of H_2S was passed through a solution of 7a (2 g, 4.55 mmol) in benzene (50 mL) containing Et_3N (1.1 mL, 7.9 mmol) for 1.5 h. Then the reaction mixture was kept at 20 °C for 30 min. The white precipitate that formed was filtered off and washed with benzene. The organic layer was washed with water and dried over Na_2SO_4 . The solvent was evaporated on a rotary evaporator. Crystallization of the residue from hexane gave colorless needle-like crystals (yield was 1.65 g).

Synthesis of 1,1,1,3,3,3-hexaphenyldistannathiane (5a). The compound was synthesized according to the procedure described above using Ph₃SnCl (2 g, 5.2 mmol). Recrystallization from hexane gave colorless crystals; yield 1.43 g (75%), m.p. 144-145 °C (cf. Ref. 31: m.p. 141-143 °C). Synthesis of 1,1,1,3,3,3-hexaphenyldiplumbathiane (5b). A

Synthesis of 1,1,1,3,3,3-hexaphenyldiplumbathiane (5b). A flow of H₂S was passed through a solution of Ph₃PbCl (2 g, 4.3 mmol) in THF (30 mL) containing Et₃N (1.1 mL, 7.9 mmol) for 0.5 h. The white precipitate that formed was filtered off. The solvent was evaporated on a rotor evaporator. The residue was twice recrystallized from light petroleum, and pale-pink crystals were obtained; yield 1.3 g (67%), m.p. 137– 139 °C (cf. Ref. 31: m.p. 139–140 °C).

Synthesis of tris(4-fluorophenyl)tin bromide (7b). 48% hydrobromic acid (0.5 mL) was added dropwise with stirring to a suspension of 2 (0.5 g, 1.2 mmol) in ether (50 mL). The

| Com- pound | Yield (%) | М.р. /°С | Found (%) Calculated | | | Molecular formula | |
|---------------|--------------|-------------|-------------------------|---------------------|----------------------------|-----------------------|--|
| | | | С | Н | S [F] | Sn | |
| la | 59 | 125-127 | <u>65.55</u> 65.41 | <u>4.37</u> 4.01 | <u>4.69</u> 4.72 | <u>17.60</u> 17.47 | C ₃₇ H ₂₇ F ₃ SSn |
| 16 | 72 | 113 | <u>62.25</u> 62.18 | <u>3.97</u> 4.04 | <u>4.50</u> 4.60 | <u>17.45</u> 17.07 | $C_{36}H_{27}F_3SSiSn$ |
| 1c | 60 | 112-113 | <u>58.34</u> 58.43 | <u>3,70</u> 3.68 | <u>4.23</u> 4.33 | <u>15.90</u> 16.01 | $C_{36}H_{27}F_3GeSSn$ |
| 4 | 86 | 138-140 | <u>51.50</u> 51.47 | <u>3.11</u> 2.88 | <u>3.76</u> 3.81 | <u>27.65</u> 28.26 | $C_{36}H_{24}F_6SSn_2$ |
| 7 b | 64 | 109 | <u>44.77</u> 44.68 | <u>2.80</u> 2.50 | [<u>11.51]</u> [11.78] | - | $C_{18}H_{12}F_3BrSn$ |
| 7e | 60 | 105 | <u>41.66</u> 40.72 | <u>2.12</u> 2.28 | [<u>10.83]</u> [10.74] | | C ₁₈ H ₁₂ F ₃ ISn |

Table 2. Characteristics of compounds 12-c, 4, and 7b,c

reaction mixture was stirred for 15 min. The ethereal solution was washed with distilled water three times and dried with MgSO₄. The solvent was removed on a rotary evaporator. The residue was twice recrystallized, and colorless crystals were obtained (yield was 0.37 g).

Synthesis of tris(4-fluorophenyl)tin iodide (7c). 57% hydroiodic acid (0.5 mL), which has been freshly distilled over red phosphorus, was added dropwise with stirring to a suspension of 2 (0.5 g, 1.2 mmol) in ether under an atmosphere of argon. The reaction mixture was stirred for 15 min. The ethereal solution was washed with an aqueous solution of $Na_2S_2O_3$ and with distilled water and dried over MgSO₄. Ether was removed on a rotary evaporator. Recrystallization of the residue from hexane gave colorless crystals (yield was 0.38 g).

The yields and melting points of the resulting compounds and the data of elemental analysis are given in Table 2.

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