^{19}F NMR investigation of the polarities of the metal—oxygen bonds and the electronegativities of the Ph_nM groups in organometallic derivatives of tris(4-fluorophenyl)stannanol

D. N. Kravtsov, A. S. Peregudov, and V. M. Pachevskaya*

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 117813 Moscow, Russian Federation. Fax: +7 (095) 135 5085

A number of $Ar_3MOM^*Ph_3$ compounds containing Group IVB metals were synthesized or generated in solution. On the basis of ^{19}F NMR data for $(4\text{-}FC_6H_4)_3SnOMPh_3$ compounds, the relative polarities of the M—O bonds and relative electronegativities of the Ph_3M groups were evaluated and the latter values were found to correlate with the electronegativities of the central metal atoms. The variation of the shielding of the heavy nuclei in $Ph_3SnOMPh_3$ and $Ph_3PbOMPh_3$ does not reflect the variation in the electron density on the tin and lead atoms.

Key words: bond polarity, electronegativity, group electronegativity, silicon, germanium, tin, lead, ^{19}F NMR, ^{119}Sn NMR, ^{207}Pb NMR.

In recent years considerable attention has been paid to the problems and quantum-chemical calculations of the polarities of σ-bonds and group electronegativities.[1—7] However, these studies cover only organic compounds or heteroorganic compounds containing elements of Periods II and III. At the same time, studies dealing with organometallic compounds containing transition and heavy nontransition metals are lacking. This is apparently due to the fact that calculation of multielectron systems and systems containing d-orbitals is a difficult task and also due to the fact that for compounds of elements of Periods IV—V, relativistic effects should be taken into account.[8,9] In this connection, it seems to be of current interest to experimentally compare the electronegativities (EN) of groups containing transition or heavy nontransition metals and the polarities of bonds formed by these groups. These studies would answer the question of whether it is possible to evaluate the comparative group electronegativities (GEN) of organometallic moieties and comparative polarities of bonds formed by them using data on the EN of the central metal atoms, in particular, the spectral and absolute EN.[8,10]

It has been shown previously[11] that qualitative data on the comparative polarities of the hydrogen—element and metal—element σ-bonds and, correspondingly, on the comparative GEN of organometallic groups of the L_nM type can be obtained from a ^{19}F NMR study of model systems:

$$4\text{-}FC_6H_4QH, \qquad 4\text{-}FC_6H_4QML_n,$$

where Q is a structural fragment of the C≡C, N—R, O, OCO, or S type. The data obtained by this method agree in all cases with the results of studies of the influence of polar effects of substituents on exchange equilibria involving HX acids with the same key atoms and their organometallic derivatives:[11,12]

$$L_nMQC_6H_4F\text{-}4 + HQC_6H_4X\text{-}3(4) \rightleftharpoons HQC_6H_4F\text{-}4 + L_nMQC_6H_4X\text{-}3(4).$$

These results indicate that the variation of the chemical shift of fluorine (CSF) in the $4\text{-}FC_6H_4QX$ type systems with various natures of X is an indicator of alteration of the electron density on the Q fragment. This conclusion is consistent with the data that indicate that CSF in the $4\text{-}FC_6H_4$ group is a good indicator of the variation of the charge on the aromatic carbon atom attached to it as the nature of the aromatic system is varied.[13] Recently the indicator ability of the CSF of the $4\text{-}FC_6H_4$ group was used to study[14] the polarities of the tin—metal bonds and GEN of organometallic groups with transition metal central atoms in $(4\text{-}FC_6H_4)_3SnML_n$ compounds, the results obtained being in good agreement with the published data concerning the electron-donating ability of L_nM groups. At the same time, even for the isostructural groups $(CO)_5M$ and $C_5H_5(CO)_3M$, no parallelism between the EN of the central metal atom and the GEN of the corresponding group was found.

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Therefore, it is of interest to find out what characteristic features would be observed in the case of isostructural organometallic groups containing nontransition metal key atoms. In addition, there exists a problem of the variation of relative GEN of isostructural groups as a function of the nature of the atom attached to them. Therefore, competing model systems, in which organometallic groups that are either bound directly to one another or bound to the same atom or fragment compete, regarding the electron density distribution, seem to be promising:

$L_nMM^*L_m^*$ $\quad$ $L_nMXM^*L_m^*$

($X = CH_2$, O, S).

In the present work we studied behavior of Ph_3M the type organometallic groups, containing Group IVB elements attached to an oxygen atom. Correspondingly, we used derivatives of tris(4-fluorophenyl)stannanol as model systems:

$(4\text{-}FC_6H_4)_3SnOMPh_3$

1a—d

M = Si (**a**), Ge (**b**), Sn (**c**), Pb (**d**)

Compounds **1a** and **1b** were prepared by the reactions of $(4\text{-}FC_6H_4)_3SnOH$ (**2a**) with Ph_3SiOH (**2b**) or Ph_3GeOH (**2c**) according to a known procedure:[15]

$$\mathbf{2a} + \mathbf{2b} \rightarrow \mathbf{1a} + H_2O;\ \mathbf{2a} + \mathbf{2c} \rightarrow \mathbf{1b} + H_2O.$$

Compounds **1c** and **1d** were generated in solution by the reaction of **2a** with Ph_3SnOH (**2d**) or Ph_3PbOH (**2e**). This method is based on the published ^{119}Sn NMR data,[16,17] which indicate that organotin hydroxides R_3SnOH are converted into oxides $R_3SnOSnR_3$ on dissolution in organic solvents. In its turn, the interaction of two oxides of different compositions in solution affords an asymmetrical oxide

$$R_3SnOSnR_3 + R_3^*SnOSnR_3^* \rightleftharpoons 2\ R_3SnOSnR_3^*.$$

Exchange processes in these systems were found to be slow in the ^{119}Sn NMR time scale; this allows identification of the asymmetrical compounds formed. The same could be expected for the corresponding lead derivatives.

It can be assumed that such exchange reactions would be slow in the ^{19}F NMR time scale.

In fact, we found that the ^{19}F NMR spectrum of the reaction mixture obtained in the reaction of **2a** with **2d**, **2e**, or $Ph_2SbOSbPh_2$ (**3a**) in the benzene solution exhibits two signals; one of these signals corresponds to the product of transformation of the starting **2a**, and the other one is due to a product of an exchange reaction. These data indicate that the following exchange reactions occur in the solution:

$$\underset{\mathbf{1e}}{(4\text{-}FC_6H_4)_3SnOSn(C_6H_4F\text{-}4)_3} + \underset{\mathbf{3b}}{Ph_3SnOSnPh_3} \rightleftharpoons 2\cdot\mathbf{1c}$$

$$\mathbf{1e} + \underset{\mathbf{3c}}{Ph_3PbOPbPh_3} \rightleftharpoons 2\cdot\mathbf{1d}$$

$$\mathbf{1e} + \mathbf{3a} \rightleftharpoons 2\ \underset{\mathbf{1f}}{(4\text{-}FC_6H_4)_3SnOSbPh_2},$$

and that these processes are slow on the ^{19}F NMR time scale, which makes it possible to obtain data on the CSF for compounds containing SnOSn, SnOPb, or SnOSb structural fragments.

We determined the CSF for benzene solutions of individual compounds **1a**, **1b**, and **1e** and for exchanging mixtures of compounds **1c**, **1d**, and **1f** with respect to external PhF dissolved in the same solvent at the same concentration. Benzene was chosen as the solvent, since it has sufficient dissolving ability toward the compounds under study and cannot polarize metal—oxygen bonds. The CSF for the compounds studied are listed in Table 1. The "minus" sign corresponds to a decrease in shielding and to a downfield shift of the signal with respect to that of the standard.

Analysis of the data presented in Table 1 shows that on going from $(4\text{-}FC_6H_4)_3SnSn(C_6H_4F\text{-}4)_3$ (**4**) to compound **1e**, the shielding of fluorine substantially decreases. This indicates that a partial positive charge arises on the tin atom and that the tin—oxygen bond is polarized as $Sn^{\delta+}—O^{\delta-}$. According to the CSF for compounds **1a—d**, the partial positive charge on the tin atom and polarization of the Sn—O bond decrease in the order **1a** > **1b** > **1c** > **1d**. This implies that polarities of the M—O bonds increase in the sequence Si < Ge < Sn < Pb and that the electron requirements and the GEN of the Ph_3M groups decrease in the sequence $Ph_3Si > Ph_3Ge > Ph_3Sn > Ph_3Pb$.

This sequence is in line with the order in which the electron-donating ability of the Et_3M groups in compounds of the Et_3MOMEt_3 type increases, *viz.*, Et_3Si < EtGe < Et_3Sn.[18]

The EN values on the primary Pauling scale[19] of the central atoms of the groups studied do not differ from

Table 1. ^{19}F chemical shifts (δ) for solutions in benzene

Compound	$\delta\ ^{19}F$
$(4\text{-}FC_6H_4)_3SnSn(C_6H_4F\text{-}4)_3$ (**4**)	−2.45
$(4\text{-}FC_6H_4)_3SnOSn(C_6H_4F\text{-}4)_3$ (**1e**)	−3.46
$(4\text{-}FC_6H_4)_3SnOSiPh_3$ (**1a**)	−3.84
$(4\text{-}FC_6H_4)_3SnOGePh_3$ (**1b**)	−3.11
$(4\text{-}FC_6H_4)_3SnOSnPh_3$ (**1c**)	−2.78
$(4\text{-}FC_6H_4)_3SnOPbPh_3$ (**1d**)	−2.14
$(4\text{-}FC_6H_4)_3SnOSbPh_2$ (**1f**)	−3.32

one another and are equal to 1.8. The EN values calculated by Allred[20] according to the Pauling procedure are the following: Si 1.90, Ge 2.01, Sn 1.96, Pb 2.33, *i.e.*, they decrease in the order Pb > Ge > Sn > Si. The absolute EN are[10] (eV): Si 4.77, Ge 4.60, Sn 4.30, Pb 3.90; they monotonically decrease in the order Si > Ge > Sn > Pb. The spectral EN for three of the elements are:[8] Si 1.916, Ge 1.994, Sn 1.824; they decrease in the order Ge > Si > Sn.

A comparison of the above sequences with the order in which the GEN of the Ph_3M groups vary found in this work, indicates that this order is in the best agreement with the scale of absolute EN of the corresponding metals. Conversely, according to the data of Table 1, the GEN of the Ph_2Sb group is smaller than that of the Ph_3Si group, despite the fact that the absolute EN of antimony is 4.85 eV, while for silicon, it is 4.77 eV. This is apparently due to the fact that these groups are not isostructural, and the Ph_2Sb group contains a smaller number of weakly electron-withdrawing aryl ligands.

At the same time, for compounds **1a—d**, we found a good correlation between the CSF and the absolute EN of the corresponding metal atoms:

$$\mathrm{CSF} = = -1.80\chi + 4.93, \quad r = 0.967.$$

These data indicate that the dependence of GEN of the Ph_3M groups on the absolute EN of the central metal atoms is not only qualitative, but also quantitative. Thus, despite the fact that the question of the legitimacy of using the difference between the absolute EN as a measure of the polarity of a bond is still an open question,[20,21] in the present case, this parameter reflects rather adequately the variation of the polarity of the M—O bond as a function of the nature of the metal.

In view of the series found by us in which the GEN of the Ph_3M groups decreases, *viz.*, Ph_3Si > Ph_3Ge > Ph_3Sn > Ph_3Pb, the results obtained recently[22] in a ^{207}Pb NMR study of the polarity of the Pb—M bonds in Ph_3PbMPh_3 compounds seem to be surprising. Based on the increase in the shielding of the lead atom on going from $Ph_3PbPbPh_3$ to $Ph_3PbSnPh_3$ and then to $Ph_3PbGePh_3$, it was concluded that the M—M bonds in these compounds are polarized as $Pb^{\delta-}$—$Sn^{\delta+}$ and $Pb^{\delta-}$—$Ge^{\delta+}$, which implies that the GEN of the Ph_3Pb group is greater than those of Ph_3Sn and Ph_3Ge. According to the previously reported data,[22] the shielding of the tin atom in Ph_3SnMPh_3 compounds increases in the order Ph_3Pb < Ph_3Sn < Ph_3Ge, which, by analogy, should also point to a decrease in the GEN in the series Ph_3Pb > Ph_3Sn > Ph_3Ge.

In this connection, it has been of interest to study characteristic features of the variation of the ^{119}Sn and ^{207}Pb chemical shifts in compounds **3b,d—f** and **3c,f—h**, respectively:

$Ph_3SnOMPh_3$ $Ph_3PbOMPh_3$

3b,d—f **3c,f—h**

M = Sn (**b**, **f**), Si (**d**, **g**), Ge (**e**, **h**), Pb (**f**, **c**)

For this purpose, compounds **3d—e** and **3g—h** were synthesized by the reactions of **2d** and **2e** with **2b** and **2c**, and compounds **3b**, **3c**, and **3f** were generated in a solution from **2d** or **2e**. The ^{119}Sn and ^{207}Pb chemical shifts for these compounds are listed in Table 2. The negative values correspond to upfield shifts of signals.

As follows from the data presented in Table 2, the regularities of the effects of the nature of the metal on the ^{119}Sn and ^{207}Pb chemical shifts in the compounds studied by us are the same as those in Ph_3SnMPh_3 and Ph_3PbMPh_3 compounds. In all cases, shielding of the ^{119}Sn and ^{207}Pb nuclei increases in the order Ph_3Pb < Ph_3Sn < Ph_3Ge < Ph_3Si, which should indicate, from the viewpoint of Koglin *et al.*,[22] that the GEN of the Ph_3M groups decreases in the order Ph_3Pb > Ph_3Sn > Ph_3Ge > Ph_3Si.

This conclusion is at variance with our results obtained by ^{19}F NMR spectroscopy for compounds **1a—d**. Since in the case of $L_nMQC_6H_4F$-4 compounds, the ^{19}F NMR data on the comparative polarities of the M—Q bonds are consistent with the results obtained in the study of exchange equilibria,[11,12] we believe that our results are more reliable.

Table 2. ^{119}Sn and ^{207}Pb chemical shifts for solutions in benzene

Compound	δ ^{119}Sn*	δ ^{207}Pb**
$Ph_3SnOSiPh_3$ (**3d**)	−98.4	
$Ph_3SnOGePh_3$ (**3e**)	−89.1	
$Ph_3SnOSnPh_3$ (**3b**)	−81.8	
$Ph_3SnOPbPh_3$ (**3f**)	−77.2	
$Ph_3PbOSiPh_3$ (**3g**)		−107.3
$Ph_3PbOGePh_3$ (**3h**)		−89.6
$Ph_3PbOSnPh_3$ (**3f**)		−76.2
$Ph_3PbOPbPh_3$ (**3c**)		−63.6

* Referred to external neat Me_4Sn. ** Referred to external neat Me_4Pb.

Table 3. Characteristics of compounds **1a**, **1b**, and **3e**

Compound	Yield (%)	M.p. /°C	Found/Calculated (%) C	Found/Calculated (%) H	Molecular formula
1a	81	104—106	63.69 63.62	3.82 3.97	$C_{36}H_{27}F_3OSiSn$
1b	80	98—100	59.49 59.66	3.36 3.72	$C_{36}H_{27}F_3GeOSn$
3e	85	130—131	64.45 64.47	4.55 4.47	$C_{36}H_{30}GeOSn$

The anomalous effects of the nature of the metal on the shielding of the ^{119}Sn nuclei in Ph_3SnMPh_3 and $Ph_3SnOMPh_3$ compounds and on the shielding of the ^{207}Pb nuclei in Ph_3PbMPh_3 and $Ph_3PbOMPh_3$ may be due to the fact that structural changes in these compounds occur in the immediate neighborhood of the indicator nucleus. Therefore, the shielding of the ^{119}Sn and ^{207}Pb nuclei may be determined not only by the orbital contributions from the Sn—M, Sn—O, Pb—M, and Pb—O bonds, reflecting the direction and the degree of their polarization, but also by the orbital contributions from the unshared electron pairs located in the p-, d-, and f-orbitals of the metal M, which may exert a deshielding effect. In fact, IGLO calculations indicate[23] that the overall orbital contribution of the three unshared electron pairs to the proton chemical shift in the HF molecule is 15.45 ppm, which is greater than the orbital contribution of the H—F bond equal to 12.70 ppm. In conformity with this, it may be assumed that in Ph_3SnMPh_3, Ph_3PbMPh_3, $Ph_3SnOMPh_3$, and $Ph_3PbOMPh_3$ type compounds the increase in the deshielding effect of the orbitals of the unshared electron pairs of the metal on going from Si to Pb dominates over the shielding effect of the orbitals of the Sn—M, Pb—M, Sn—O, and Pb—O bonds caused by the decrease in the GEN of the Ph_3M groups. An ultimate solution of this problems requires IGLO calculations of the contributions of the unshared electron pairs of metals to the shielding of the ^{119}Sn and ^{207}Pb nuclei in the systems containing SnM, PbM, SnOM, and PbOM fragments. However, these calculations should take into account relativistic effects.[23] In this connection, at present, an ^{19}F NMR study of compounds of the $(4\text{-}FC_6H_4)_3SnMPh_3$ type is of interest.

Experimental

^{19}F, ^{119}Sn, and ^{207}Pb NMR spectra were recorded on a Bruker WP-200 SY spectrometer operating at 188.3, 74.63, and 41.813 MHz, respectively, at 25 °C with 0.05—0.1 mol L^{-1} solutions in benzene. The resonance conditions were stabilized using external D_2O. The CSF were measured by the method of substitution with respect to the signal of the external fluorobenzene in the same solvent and at the same concentration as the compound studied. The "+" sign corresponds to an upfield shift of the signal with respect to the standard. The errors in the determination of the CSF did not exceed ±0.01 ppm. The ^{119}Sn chemical shifts were measured by the method of substitution with respect to neat Me_4Sn with an accuracy of ±0.1 ppm, and the ^{207}Pb chemical shifts were determined by the method of substitution with respect to Ph_3PbCl in $CDCl_3$ and were then calculated for Me_4Pb using a value of 33.0 ppm taken from the literature.[24]

Compounds **1c**, **1d**, **1f**, and **3f** were generated in solution by mixing solutions of the starting **2a** or **2d** in anhydrous benzene with solutions of **2d**, **2c**, and **3a** in the same solvent. The known compounds **2a**, **2b**, **2c**, **2d**, and **3a** were prepared by reported procedures.[25—29] The known compounds **3d**, **3g**, and **3h** (see Ref. 15) and compounds **1a—b** and **3e** not described in the literature were synthesized by the treatment of **2a**, **2d**, or **2e** with **2b** or **2c** (see Ref. 15).

Synthesis of 1,1,1-triphenyl-3,3,3-tris(4-fluorophenyl)-germastannoxane (1b). A solution of **2a** (0.84 g, 2 mmol) in 30 mL of anhydrous benzene was added to a solution of **2c** (0.64 g, 2 mmol) in 10 mL of the same solvent. The mixture was boiled for 10 min with a Dean—Stark distillation head. Removal of the benzene *in vacuo* gave an oil, which crystallized on the addition of hexane. Recrystallization from hexane gave 1.16 g (80 %) of a colorless crystalline solid, m.p. 98—100 °C.

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