^{19}F NMR study of the polarization direction and polarity of tin—hydrogen and tin—transition metal bonds in tris(4-fluorophenyl)stannane and its organometallic derivatives

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A series of $(4\text{-}FC_6H_4)_3SnML_n$ compounds containing tin—transition metal bonds were synthesized. Based on ^{19}F NMR data for these compounds, $(4\text{-}FC_6H_4)_3SnSn(C_6H_4F\text{-}4)_3$, and $(4\text{-}FC_6H_4)_3SnH$, conclusions were drawn concerning the polarization direction and relative polarity of the tin—hydrogen and tin—metal bonds in the above compounds and in the hydrides L_nMH and R_3SnH. It was found that, in the general case, the group electronegativities of the L_nM groups do not vary similarly to the electronegativities of the central metal atoms.

Key words: bond polarization, bond polarity, electronegativity, group electronegativity, metal—hydrogen bond, metal—metal bond.

At present, the following problems continue to be of current interest: the comparative effect of the nature of the key atom and the ligands bonded to it on the group electronegativity (GEN) of monovalent moieties of L_nE type (where L is a ligand and E is an element) and the extent to which the ligands affect the electronegativity (EN) of the central atom.[1,2] This fully applies, in particular, to organometallic moieties of L_nM type due to the fact that the polarity of a σ-bond affects its energy significantly.[3] In turn, the problems of energetic characteristics of metal—element σ-bonds draw attention because the thermochemistry of organometallic compounds is being developed intensely at present.[4] Usually, to estimate the effect of differences in the polarity of H—X and M—X bonds in HX-acids and their organometallic derivatives of the L_nMX type on the comparative energy of these bonds, the ENs of the central metal atoms are used as a measure of the electron requirements of the L_nM moieties,[5,6] thereby neglecting the effect of ligands.

In this connection it was of interest to compare the regularities of changes in the GENs of organometallic groups with the EN values of the central atoms and the hydrogen atoms. Qualitative data on the GENs of organometallic groups of type L_nM can be obtained by studying the polarity of M—X bonds in organometallic derivatives of L_nMX-type HX-acids. For example, it has been shown previously[7] that ^{19}F NMR spectroscopy of the model systems $4\text{-}FC_6H_4QH$ and $4\text{-}FC_6H_4QML_n$, where Q is a structural moiety of type C≡C, O, OCO, or S, is a convenient approach to the study of the relative polarity of M—X and H—X bonds. The data obtained using this approach are in good agreement with those obtained by studying the polar effects of substituent on the position of exchange equilibria involving HX-acids with the same key atom and their organometallic derivatives:[7,8]

$$L_nMQC_6H_4F\text{-}4 + HQAr \rightleftarrows HQC_6H_4F\text{-}4 + L_nMQAr$$

On the other hand, the effects observed in systems with Q = O, OCO, and S can be complicated by differences in the conformational behavior of hydrogen- and metal-containing moieties.

In view of this, to compare the electron requirements of organometallic moieties and hydrogen atom, it seemed reasonable to study compounds containing metal—metal and metal—hydrogen bonds of type

$$(4\text{-}FC_6H_4)_3MH \text{ and } (4\text{-}FC_6H_4)_3\ MM'L_n.$$

Studying such systems was also of interest because of the possibility that the GENs of organometallic moieties can depend on the nature of the key atom linked to the latter, and because experimental studies on the comparative polarity of metal—metal and metal—hydrogen bonds are rather scarce.[9]

In accordance with the above considerations, in the present work we used the ^{19}F NMR method to study the direction of polarization and the comparative polarity of tin—hydrogen and tin—metal bonds in tris(4-fluorophenyl)stannane and its organometallic derivatives

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containing monovalent groups with transition-metal central atoms:

$(4\text{-}FC_6H_4)_3SnH$; $(4\text{-}FC_6H_4)_3SnML_n$,
L_nM = $(CO)_4Co$, $(CO)_5Mn$, $(CO)_5Re$, $C_5H_5(CO)_2Fe$,
$C_5H_5(CO)_3Cr$, $C_5H_5(CO)_3Mo$, $C_5H_5(CO)_3W$.

This study was based on a comparison of fluorine chemical shifts (FCS) in the above compounds and the corresponding parameter for hexa(4-fluorophenyl)distannane, containing a nonpolarized metal—metal bond.

The compounds to be studied were synthesized by well-known procedures, including reduction of tris(4-fluorophenyl)tin chloride with lithium aluminum hydride and reactions of the former with sodium derivatives of carbonylhydrides and cyclopentadienylcarbonylhydrides of transition metals:

$$(4\text{-}FC_6H_4)_3SnCl + LiAlH_4 \rightarrow (4\text{-}FC_6H_4)_3SnH$$
$$(4\text{-}FC_6H_4)_3SnCl + NaCo(CO)_4 \rightarrow (4\text{-}FC_6H_4)_3SnCo(CO)_4$$
$$(4\text{-}FC_6H_4)_3SnCl + NaFe(CO)_2C_5H_5 \rightarrow$$
$$\rightarrow (4\text{-}FC_6H_4)_3SnFe(CO)_2C_5H_5.$$

Hexa(4-fluorophenyl)distannane was obtained by treatment of tris(4-fluorophenyl)stannane with tris(4-fluorophenyl)tin hydroxide:

$$(4\text{-}FC_6H_4)_3SnH + (4\text{-}FC_6H_4)_3SnOH \rightarrow$$
$$\rightarrow (4\text{-}FC_6H_4)_3SnSn(C_6H_4F\text{-}4)_3.$$

We determined FCSs for solutions of the compounds under study in benzene and compared them to those for fluorobenzene in the same solvent and at the same concentration. Benzene was used as a solvent possessing sufficient ability to dissolve the compounds of interest and as a nonpolar solvent that cannot polarize the bonds studied. The FCSs for the compounds studied are presented in Table 1. The negative sign corresponds to a decrease in shielding and a downfield shift of the signal of fluorine relative to fluorobenzene.

As noted above, conclusions concerning the direction and degree of polarization of tin—hydrogen and tin—metal bonds were made by comparing the FCSs for the corresponding compounds with that of symmetric hexa(4-fluorophenyl)distannane. This comparison shows that on going from distannane to the $(CO)_4Co$-derivative of tris(4-fluorophenyl)stannane, deshielding of fluorine occurs, which suggests the appearance of a partial positive charge on the $(4\text{-}FC_6H_4)_3Sn$ group in this compound in comparison with the symmetric compound. This implies the existence of $Sn^{\delta+}$—$Co^{\delta-}$ polarization of the tin—cobalt bond.

Table 1. Chemical shifts of fluorine (FCSs) in tris(4-fluorophenyl)stannane derivatives in benzene relative to fluorobenzene

Compound	FCS
$(4\text{-}FC_6H_4)_3SnSn(C_6H_4F\text{-}4)_3$	−2.45
$(4\text{-}FC_6H_4)_3SnH$	−1.95
$(4\text{-}FC_6H_4)_3SnCo(CO)_4$	−3.00
$(4\text{-}FC_6H_4)_3SnMn(CO)_5$	−1.46
$(4\text{-}FC_6H_4)_3SnRe(CO)_5$	−0.54
$(4\text{-}FC_6H_4)_3SnCr(CO)_3C_5H_5$	−1.32
$(4\text{-}FC_6H_4)_3SnMo(CO)_3C_5H_5$	−1.00
$(4\text{-}FC_6H_4)_3SnW(CO)_3C_5H_5$	−0.87
$(4\text{-}FC_6H_4)_3SnFe(CO)_3C_5H_5$	−0.40

The FCSs show that, in contrast, in all the other compounds containing tin—transition metal bonds, a partial negative charge (compared to distannane) appears on the tin atoms involved in the $(4\text{-}FC_6H_4)_3Sn$ groups, which indicates the existence of $Sn^{\delta-}$—$M^{\delta+}$ polarization of the tin—metal bonds. The polarity of these bonds increases in the series

$$(CO)_5Mn < C_5H_5(CO)_3Cr < C_5H_5(CO)_3Mo < C_5H_5(CO)_3W <$$
$$(CO)_5Re < C_5H_5(CO)_2Fe.$$

The data obtained agree with literature data[10] on partial quadrupole splitting in Mössbauer spectra of $(C_6H_5)_3SnML_n$ compounds. According to these data, the electron-donating ability of L_nM groups toward a tin atom increases in the sequence

$$Co(CO)_4 < Mn(CO)_5 < Fe(CO)_2C_5H_5.$$

These data are also consistent with the increase in the dissociative ability of metal—tin bonds in $(C_6H_5)_3SnML_n$ compounds (*cf.* Ref. 11) in the sequence

$$Fe(CO)_2C_5H_5 < Mo(CO)_3C_5H_5 < Mn(CO)_5 < Co(CO)_4$$

and with the increase in the nucleophilicity of organometallic anions toward the $(C_6H_5)_3Sn^+$ cation (*cf.* Ref. 12) in the sequence

$$^{-}Co(CO)_4 < {}^{-}Mo(CO)_3C_5H_5 < {}^{-}Mn(CO)_5 < {}^{-}Re(CO)_5 <$$
$$^{-}Fe(CO)_2C_5H_5.$$

The data obtained demonstrate that in interaction with a tin atom the GENs of organometallic moieties that contain a central transition-metal atom decrease in the sequence

$$(CO)_4Co > (CO)_5Mn > C_5H_5(CO)_3Cr > C_5H_5(CO)_3Mo >$$
$$C_5H_5(CO)_3W > (CO)_5Re > C_5H_5(CO)_2Fe.$$

On the other hand, the ENs of transition metals calculated according to Mulliken[13] have the following values (eV):

Co, 4.26; W, 4.19; Fe, 4.03; Re, 4.01;
Mo, 3.92; Cr, 3.76; Mn, 3.72,

i.e., they decrease in the sequence

$$Co > W > Fe > Re > Mo > Cr > Mn.$$

The following data are available[14] for absolute ENs (eV):

W, 4.40; Co, 4.3; Fe, 4.06; Re, 4.02; Mo, 3.9;
Cr, 3.76; Mn, 3.72,

which decrease in the sequence

$$W > Co > Fe > Re > Mo > Cr > Mn.$$

The limited number of spectral ENs for certain transition metals[15] are as follows:

Co, 1.82; Fe, 1.79; Mn, 1.74; Cr, 1.57,

and the corresponding values decrease in the sequence

$$Co > Fe > Mn > Cr.$$

Thus, no similarity of variation is observed in the general case between the GENs of organometallic groups and the ENs of transition-metal central atoms. Furthermore, even in the case of isostructural groups, opposite variation of the GENs of organometallic groups and the ENs of central metal atoms is observed, which is evident from the following sequence:

$$\text{GEN: } (CO)_5Mn > (CO)_5Re;\ C_5H_5(CO)_3Cr > C_5H_5(CO)_3Mo > C_5H_5(CO)_3W$$

$$\text{EN: } Mn < Re,\ Cr < Mo < W.$$

These data probably indicate that the interaction of ligands with metal atoms can cause inversion of the GEN of organometallic groups with respect to the EN of the corresponding metals. In particular, these data support Pearson's opinion[16] that absolute ENs cannot serve as a reliable quantitative measure of the polarity of bonds. In addition, they show that the use of the EN of a central metal atom to estimate the comparative polarity of bonds formed by monovalent or polyvalent organometallic L_nM groups (see Refs. 5, 6) might lead to incorrect conclusions in the general case.

A comparison of the FCSs for $(4\text{-}FC_6H_4)_3SnH$ and distannane shows that the tin—hydrogen bond in the former compound is polarized as $Sn^{\delta-}$—$H^{\delta+}$, *i.e.*, it has protonic polarization. Such a polarization is probably caused by the effect of the aryl groups, since calculations for the hydride of monovalent tin, SnH, attest to the hydride polarization of the metal—hydrogen bond.[17] As shown previously,[18] the effect of substituents on the electron-accepting ability of the $(XC_6H_4)_3Sn$ moieties is determined by the inductive effect and the σ^0 constants of substituted phenyl groups. The above considerations and the data obtained allow us to expect that all substituted triphenylstannanes with higher positive σ^0 constants of substituted phenyl groups[19] than σ^0 for 4-fluorophenyl should also have protonic polarization of the tin—hydrogen bond.

A comparison of the electronic characteristics of the hydrogen atom and the $(CO)_4Co$ group with those of the $(4\text{-}FC_6H_4)_3Sn$ group shows that the metal—hydrogen bond in the carbonylhydride $HCo(CO)_4$ also has protonic polarization. This conclusion does not agree with IR and photoelectron spectroscopy data,[20,21] but it agrees with quantum-chemical calculations of population analysis according to Levdin.[22] Thus, the results obtained indicate that, contrary to an earlier opinion,[5] metal—hydrogen bonds do not necessarily have hydride polarization.

Experimental

$^{19}F-\{^1H\}$ NMR spectra were recorded on a Bruker WP-200SY spectrometer with a working frequency of 188.31 MHz for fluorine. FCSs were determined by the substitution method relative to a 0.2 *M* solution of fluorobenzene in benzene. The "—" sign corresponds to downfield shifts of the fluorine signal. The FCSs were determined to within ±0.05 ppm. Resonance conditions were stabilized by the deuterium signal from D_2O placed between the walls of a 5 mm tube and a 4 mm enclosure containing a solution of the sample or the standard. The signal of fluorine in tris(4-fluorophenyl)stannane and its organometallic derivatives was sufficiently narrow for the majority of the compounds studied and was accompanied by one set of satellites caused by spin-spin interaction of ^{19}F nuclei with $^{117(119)}Sn$ nuclei with a $^5J(F,Sn)$ coupling constant of about 10 Hz. In the case of $(4\text{-}FC_6H_4)_3SnCo(CO)_4$, the fluorine signal was markedly broadened, and the above satellites were not detected.

Tris(4-fluorophenyl)tin chloride,[23] tris(4-fluorophenyl)stannane,[23] and tris(4-fluorophenyl)tin hydroxide[24] were obtained by the reported procedures.

(Chromiumtricarbonyl-π-cyclopentadienyl)tris(4-fluorophenyl)stannane. A solution of $C_5H_5(CO)_3CrNa$ in THF was generated by treatment of $[C_5H_5(CO)_3Cr]_2Hg$ [25] (1 g, 1.6 mmol) with sodium amalgam (obtained from 0.38 g Na and 40 g Hg) in dry THF (30 mL) under argon. The solution was stirred for 1.5 h and added to a solution of $(4\text{-}FC_6H_4)_3SnCl$ (1.3 g, 3 mmol) in dry THF (30 mL). The reaction mixture was stirred for 2 h at ~20 °C. The solvent was distilled off on a rotary evaporator to give 1.3 g (65 %) of green crystals. Repeated crystallization from a benzene—heptane mixture (1 : 1) gave a yellowish-orange compound, m.p. 176—178 °C. Found (%): C, 51.90; H, 2.81; F, 9.83; Cr, 8.69; Sn, 20.04. $C_{26}H_{17}CrF_3O_3Sn$. Calculated (%): C, 51.60; H, 2.83; F, 9.42; Cr, 8.59; Sn, 19.61.

(Molybdenumtricarbonyl-π-cyclopentadienyl)tris(4-fluorophenyl)stannane. Dry THF (30 mL) was added to sodium amalgam obtained from 0.5 g Na and 50 g Hg, and then $[C_5H_5(CO)_3Mo]_2$ (1 g, 2 mmol) was added under argon. The reaction mixture was stirred for 30 min at ~20 °C. The resulting solution of $C_5H_5(CO)_3MoNa$ in THF was cannulated into a reaction flask, and a solution of $(4\text{-}FC_6H_4)_3SnCl$ (1.5 g, 3.4 mmol) in THF (50 mL) was added dropwise. The reaction mixture was stirred for 1.5 h at ~20 °C. The mixture was filtered, the solvent was removed, and the residue was dissolved in benzene and chromatographed on Al_2O_3. The product was eluted from the column with a benzene—petroleum ether mixture (1 : 1) and crystallized from a toluene—pentane mixture (1 : 2) to give 1.3 g (60 %) of a colorless compound, m.p. 171—172 °C. Found (%): C, 48.13; H, 2.40; F, 8.56; Mo, 14.96; Sn, 17.69. $C_{26}H_{17}F_3MoO_3Sn$. Calculated (%): C, 48.11; H, 2.64; F, 8.78; Mo, 14.79; Sn, 18.28.

(Tungstentricarbonyl-π-cyclopentadienyl)tris(4-fluorophenyl)stannane. Dry THF (50 mL) and $[C_5H_5(CO)_3W]_2$ (1 g, 1.5 mmol) were added under argon to sodium amalgam obtained from 0.35 g Na and 35 g Hg. The resulting solution of $C_5H_5(CO)_3WNa$ was stirred for 30 min, and then cannulated with filtration into a reaction flask, and a solution of $(4\text{-}FC_6H_4)_3SnCl$ (1.3 g, 3 mmol) in dry THF (30 mL) was added dropwise. The reaction mixture was stirred for 1 h at ~20 °C, the solvent was removed *in vacuo*, and the residue was extracted with benzene and chromatographed on Al_2O_3. The product was eluted with benzene and crystallized from a benzene—heptane mixture (1 : 1) to give 0.80 g (37 %) of a colorless compound, m.p. 182—183 °C. Found (%): C, 43.15; H, 2.36; F, 8.07; $C_{26}H_{17}F_3O_3SnW$. Calculated (%): C, 42.37; H, 2.32; F, 7.73.

(Irondicarbonyl-π-cyclopentadienyl)tris(4-fluorophenyl)stannane. A solution of $C_5H_5(CO)_2FeNa$ in THF was generated by treatment of a solution of $[C_5H_5(CO)_2Fe]_2$ (1 g, 3 mmol) in dry THF (100 mL) with sodium amalgam (obtained from 0.3 g Na and 30 g Hg) under argon. The solution was stirred for 1 h at ~20 °C, the mercury was separated, and the solution was cannulated using argon pressure into a reaction flask containing a solution of $(4\text{-}FC_6H_4)_3SnCl$ (2.66 g, 6 mmol) in THF (60 mL). The reaction mixture was stirred for 2 h at ~20 °C. The solvent was distilled off on a rotary evaporator, the residue was extracted with benzene, and the solution in benzene was chromatographed on Al_2O_3. The product was eluted from the column with a hexane—benzene mixture (2 : 1), the solvent was removed, and the product was recrystallized from hexane to give 1.17 g (52 %) of a yellow compound, m.p. 133 °C. Found (%): C, 51.60; H, 2.81; F, 9.76; Sn, 20.23. $C_{25}H_{17}F_3FeO_3Sn$. Calculated (%): C, 51.69; H, 2.95; F, 9.80; Sn, 20.40.

(Manganesepentacarbonyl-π-cyclopentadienyl)tris(4-fluorophenyl)stannane. A solution of $NaMn(CO)_5$ in THF was generated by treatment of a solution of $Mn_2(CO)_{10}$ (1 g, 2.5 mmol) in dry THF (100 mL) with sodium amalgam (obtained from 0.25 g Na and 25 g Hg) under argon. The solution was stirred at ~20 °C for 30 min and cannulated under argon into a reaction flask. A solution of $(4\text{-}FC_6H_4)_3SnCl$ (2.25 g, 5 mmol) in THF (50 mL) was then added dropwise with stirring to the above solution, the reaction mixture was stirred at ~20 °C, the solvent was distilled off to leave half of the original volume, and the solution was poured into a water—ice mixture. The precipitate that formed was filtered off, dried, and repeatedly extracted with boiling hexane. The combined extracts were concentrated to a small volume and cooled. The crystals that formed were filtered off and crystallized twice from hexane to give 1.6 g (52 %) of colorless crystals, m.p. 128—129 °C. Found (%): C, 46.02; H, 1.97: F, 9.28; Sn, 19.49. $C_{23}H_{12}F_3MnO_5Sn$. Calculated (%): C, 46.23; H, 2.02; F, 9.52; Sn, 19.81.

(Rheniumpentacarbonyl-π-cyclopentadienyl)tris(4-fluorophenyl)stannane. A solution of $NaRe(CO)_5$ in THF was generated by treatment of a solution of $Re_2(CO)_{10}$ (1 g, 1.5 mmol) in dry THF (150 mL) with sodium amalgam (obtained from 0.6 g Na and 60 g Hg) under argon. The resulting solution was stirred for 1 h and cannulated with argon into a reaction flask already containing $(4\text{-}FC_6H_4)_3SnCl$ (1.35 g, 3 mmol) in THF (30 mL). The reaction mixture was stirred for 1.5 h at ~20 °C, the solvent was removed on a rotary evaporator, the residue was extracted with benzene, and the benzene solution was chromatographed on Al_2O_3. The product was eluted from the column with hexane and recrystallized from hexane to give 1.0 g (60 %) of a colorless compound, m.p. 137—139 °C. Found (%): C, 38.14; H, 1.65; F, 8.00; Sn, 16.6. $C_{23}H_{12}F_3O_5ReSn$. Calculated (%): C, 37.83; H, 1.66; F, 7.80; Sn, 16.25.

(Cobalttetracarbonyl-π-cyclopentadienyl)tris(4-fluorophenyl)stannane. A solution of $NaCo(CO)_4$ in THF was generated by treatment of a solution of $Co_2(CO)_8$ (1 g, 3 mmol) in dry THF (30 mL) with sodium amalgam (obtained from 0.65 g Na and 65 g Hg) under argon. The resulting solution was stirred for 1.5 h at ~20 °C and then cannulated with argon into a reaction flask already containing $(4\text{-}FC_6H_4)_3SnCl$ (2.56 g, 6 mmol) in THF (50 mL). The reaction mixture was stirred for 2 h at ~20 °C, the solvent was removed, and the residue was extracted with benzene and chromatographed on Al_2O_3. The product was eluted from the column with a benzene—hexane mixture (1 : 1) and recrystallized from a benzene—hexane mixture (1 : 2) to give a yellow compound, m.p. 113—114 °C. Yield 1.7 g (51 %). Found (%): C, 45.94; H, 2.10; F, 9.92. $C_{22}H_{12}CoF_3O_4Sn$. Calculated (%): C, 46.26; H, 2.04; F, 9.81.

Hexakis(4-fluorophenyl)distannane. A reaction flask equipped with a stirrer, a reflux condenser, and a dropping funnel was charged under argon with dry ether (25 mL), and then $LiAlH_4$ (0.15 g, 4 mmol) was added. A solution of $(4\text{-}FC_6H_4)_3SnCl$ (1 g, 2.3 mmol) in ether (30 mL) was added, and the reaction mixture was stirred for 20 min at ~20 °C and then for 2.5 h at the b.p. of ether. The reaction mixture was cooled, and hydroquinone (0.05 g) and H_2O (5 mL) were added to it. The aluminum hydroxide formed was dissolved by adding 20% sodium-potassium tartrate. The organic layer was separated and dried with Na_2SO_4, and then the ether was removed. The residue was dissolved in benzene (20 mL), and $(4\text{-}FC_6H_4)_3SnOH$ (0.95 g, 2.3 mmol) in benzene (25 mL) was added to the solution. The reaction mixture was stirred at the b.p. for 15 min. The benzene was distilled off on a rotary evaporator, and the residue was crystallized from a hexane—benzene mixture (3 : 1) to give 1 g (55 %) of colorless crystals, m.p. 219—220 °C (Ref. 23: m.p. 221—223 °C). Found (%): C, 53.51; H, 2.98; F, 13.72; Sn, 29.32. $C_{36}H_{24}F_6Sn_2$. Calculated (%): C, 53.51; H, 2.99; F, 14.10; Sn, 29.38.

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