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^{19}F NMR STUDY OF THE TRANSMISSION OF ELECTRONIC EFFECTS OF SUBSTITUENTS IN TRIARYL-4-FLUOROBENZYLSTANNANES

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The exaltation of the transmission ability (TA) of binuclear bridging groups (BBG), which contain atoms of the heavy transition metals [1-3], was first discovered by us in the case of the BBG Sn—CH_2. Previous results concerning this question have been published in [4]. In the present work, by means of ^{19}F {^{1}H} NMR the character and effectiveness of the transmission of electronic effects of substituents through the BBG Sn—CH_2, and the effect of a coordinating solvent on its TA have been studied in detail. For this purpose we have synthesized the series of triaryl-4-fluorobenzylstannanes $Ar_3SnCH_2C_6H_4F$-4 (I), Ar = 4-$MeOC_6H_4$, 4-MeC_6H_4, 3-MeC_6H_4, Ph, 4-ClC_6H_4, 3-ClC_6H_4, 4-FC_6H_4, 3-FC_6H_4, 3,4-$Cl_2C_6H_3$, and 3,5-$Cl_2C_6H_3$. For (I) and the previously synthesized mononuclear analogs $Ar_3SnC_6H_4F$-4 (II) [5] the chemical shifts of the fluorine (δF) from the internal standard PhF in $CHCl_3$ and Me_2SO were determined (Table 1). (A positive sign for δF corresponds to a shift to stronger field.)

Analysis of the experimental data obtained using $CHCl_3$, which was selected an an inert solvent, showed that for both series of compounds (I) and (II) transition from electron-donor to electron-acceptor substituents was accompanied by deactivation of the fluorine in the 4-fluorophenyl indicator group. Also the range of changes of δF (Δδ F) indicated that the substituents in (II) (Δδ F = 2.78 ppm) had a somewhat greater effect on the indicator atom than in (I) (Δδ F = 2.16 ppm). For quantitative evaluation of the difference of the TA for mononuclear and binuclear bridge systems a correlation was made of the δF values of (I) with those of the corresponding (II) compounds (Table 2). It was found that the value of the tangent of the slope angle (ρ) of the straight line which was obtained differed little from unity. Hence in the given case the introduction of an additional chain unit — the CH_2 group — to the Sn bridging atom is accompanied by only a very insignificant reduction in the TA of the system.

The specificity of the discovered phenomenon is illustrated by the results of the correlation treatment which we made of literature data for δF on the corresponding mononuclear $ArCH_2C_6H_4F$-4 (III) and binuclear $ArCH_2CH_2C_6H_4F$-4 (IV) bridging systems, the bridging groups of which consist only of C atoms [6]. As seen from the data shown (see Table 2) the introduction of an additional methylene group into the mononuclear system is accompanied by more than a threefold reduction of the effectiveness of transmission of the electronic effects, which is fully comprehensible from the viewpoint of a transition from a lesser to a greater extended system.

To explain the nature of the detected anomalously high TA of the BBG Sn—CH_2, it is necessary in our view to take account of the following facts. First, in the considered bridging

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TABLE 1. Chemical Shifts δF of (I) and (II) in $CHCl_3$ and Me_2SO from the Internal Standard PhF (ppm)

Ar	(I)		(II)	
	$CHCl_3$	Me_2SO	$CHCl_3$	Me_2SO
4-$MeOC_6H_4$	6,93	7,43	−1,13	–
4-MeC_6H_4	6,91	7,09	−1,13	−1,37
3-MeC_6H_4	7,04	–	−1,15	–
Ph	6,71	6,72	−1,52	−1,58
4-ClC_6H_4	5,64	6,21	−2,63	−2,16
3-ClC_6H_4	5,59	6,24	−3,07	−2,33
4-FC_6H_4	6,05	6,42	−2,31	−1,99
3-FC_6H_4	5,74	6,24	−2,87	−2,28
3,5-$Cl_2C_6H_3$	4,39	6,09	−4,53	–
3,4-$Cl_2C_6H_3$	4,77	6,17	−3,91	−2,49

TABLE 2. Parameters of the Correlation Equations $y = \rho x + C$

y	x	n	$\rho \pm \Delta\rho$ *	S_ρ	S	r	C
$\delta F_{(I)}$	$\delta F_{(II)}$	10	0,79±0,04	0,02	0,10	0,997	7,90
$\delta F_{(IV)}$	$\delta F_{(III)}$	5	0,30±0,03	0,01	0,01	0,999	0,01
$\delta F_{(I)}$	σ_p^0	5	−2,99±1,05	0,33	0,125	0,982	6,53
$\delta F_{(I)}$	σ_p	5	−2,72±2,00	0,63	0,250	0,926	6,36

*Δρ was calculated for the 95% confidence level.

system (I), direct polar conjugation between the substituents on the aromatic rings attached to the Sn atom and the indicator F atom is absent, which indicates a considerably better qualitative correlation dependence between δF of (I) and the Taft inductive constants of the aromatic substituents σ_p°, compared with those for δF of (I) and the Hammett polar constants σ_p [7] (see Table 2). Second, the transition from (II) to (I) is accompanied by an increase in the angle between the vector of the dipole moment of the Ar_3Sn group and the direction of the C–F bond, as well as an increase in the spacing between the substituent and indicator. This in turn must inevitably lead to a weakening of the transmission of electronic effects in (I) compared to (II), both of the field effect [8] and the π-inductive effect [9]. Hence the detected exaltation of the TA of the BBG $Sn–CH_2$, which amounts to an insignificant reduction of the TA of (I) compared with (II), can be apparently due to the presence in (I) of an effective σ,π-conjugation of the σ-bond of $Sn–CH_2$ with the π-electrons of the aromatic ring, which substantially compensates for the weakening of the transmission of the electronic effects of the substituents due to the circumstances discussed above. This is confirmed by the large negative value of the resonance constant for the Ph_3SnCH_2 substituent ($\sigma_R^\circ = -0.21$) compared with its carbon analog Ph_3CCH_2 ($\sigma_R^\circ = -0.09$) [10].

With the object of elucidating the question of a possible effect of coordinating polar solvents on the TA of Sn and $Sn–CH_2$ bridging groups we have determined δF for (I) and (II) in Me_2SO (see Table 1). Analysis of experimental data showed that for the majority of compounds of series (I) or (II) transition from the inert solvent $CHCl_3$ to the coordinating solvent Me_2SO was accompanied by some increase in the screening of the indicator atom F, this tendency being more clearly expressed for compounds containing electron-donor substituents. Hence both for (I) and for (II) a specific solvation by molecules of the coordinating solvent probably occurs, which leads to an increase in the electron-donor ability of the AR_3SnCH_2 and Ar_3Sn groups correspondingly. Also from Table 1 it follows that transition from $CHCl_3$ to the polar and coordinating solvent Me_2SO results in a reduction in the efficiency of the transmission of electronic effects of the substituents in both systems. Here, starting from a comparison of the ranges of ΔδF variation, the "suppression" effect on the electron conduction in Me_2SO for mononuclear (II) ($\Delta\delta F_{Me_2SO}/\Delta\delta F_{CHCl_3} = 0.62$) and binuclear (I) ($\Delta\delta F_{Me_2SO}/\Delta\delta F_{CHCl_3} = 0.59$) of the bridging systems is practically the same.

In further work, to provide greater detail of the experimental results a study will be made of the effect of coordinating solvents on the effectiveness of transmission of the electronic effects of substituents in the carbon analogs of the studied organotin compounds.

TABLE 3. Characteristics of Tetraarylstannanes, Triarylstannyl Chlorides, and Triaryl-4-fluorobenzylstannanes

Compound	Yield, %	mp, °C	Found/Calculated, %		
			C	H	Sn
$(3\text{-}ClC_6H_4)_4Sn$	90	101–102 (ethanol)	50,86 / 51,00	2,81 / 2,85	20,80 / 21,00
$(3,5\text{-}Cl_2C_6H_3)_4Sn$	40	167–168 (heptane)	41,25 / 41,00	1,89 / 1,72	16,56 / 16,88
$(3,4\text{-}Cl_2C_6H_3)_4Sn$	45	165–167 (octane)	41,32 / 41,00	1,91 / 1,72	– / 16,88
$(3,4,5\text{-}Cl_3C_6H_2)_4Sn$	81	270–271 DMFA	34,31 / 34,27	0,99 / 1,00	14,31 / 14,11
$(3\text{-}FC_6H_4)_4Sn$	70	182–183 (octane)	57,95 / 57,76	3,12 / 3,23	23,57 / 23,78
$(3\text{-}ClC_6H_4)_3SnCl$	40	78–79 (hexane)	44,21 / 44,21	2,49 / 2,47	24,32 / 24,27
$(3,5\text{-}Cl_2C_6H_3)_3SnCl$	60	108–110 (hexane)	36,65 / 36,49	1,61 / 1,53	– / 20,03
$(3,4\text{-}Cl_2C_6H_3)_3SnCl$	40	115–116 (heptane)	36,94 / 36,49	1,79 / 1,53	– / 20,03
$(3,4,5\text{-}Cl_3C_6H_2)_3SnCl$	12	200-201 (octane)	31,25 / 31,06	1,33 / 0,87	17,46 / 17,06
$(3\text{-}FC_6H_4)_3SnCl$	62	36–37 (pentane)	49,02 / 49,19	2,54 / 2,75	26,73 / 27,01
$(4\text{-}CH_3OC_6H_4)_3SnCH_2C_6H_4F\text{-}4$	40	Oil	59,94 / 60,12	4,84 / 4,87	– / 21,22
$(4\text{-}CH_3C_6H_4)_3SnCH_2C_6H_4F\text{-}4$	40	64–65 (methanol)	67,08 / 67,09	5,32 / 5,43	23,67 / 23,68
$(3\text{-}CH_3C_6H_4)_3SnCH_2C_6H_4F\text{-}4$	30	Oil	67,20 / 67,09	5,45 / 5,43	– / 23,68
$(4\text{-}ClC_6H_4)_3SnCH_2C_6H_4F\text{-}4$	60	75–78 (hexane)	53,25 / 53,34	3,48 / 3,25	20,86 / 21,10
$(4\text{-}FC_6H_4)_3SnCH_2C_6H_4F\text{-}4$	90	65–66 (methanol)	58,92 / 58,52	3,50 / 3,54	22,69 / 23,13
$(3\text{-}ClC_6H_4)_3SnCH_2C_6H_4F\text{-}4$	54	75–76 (methanol)	52,97 / 53,34	3,22 / 3,23	21,37 / 21,10
$(3\text{-}FC_6H_4)_3SnCH_2C_6H_4F\text{-}4$	74	70–71 (methanol)	58,62 / 58,52	3,32 / 3,54	23,10 / 23,13
$(3,4\text{-}Cl_2C_6H_3)_3SnCH_2C_6H_4F\text{-}4$	22	70–73 (hexane)	44,93 / 45,08	2,24 / 2,29	17,90 / 17,82
$(3,5\text{-}Cl_2C_6H_3)_3SnCH_2C_6H_4F\text{-}4$	43	119–121 (hexane)	45,09 / 45,08	2,16 / 2,29	– / 17,82
$(3\text{-}FC_6H_4)_3SnC_6H_4F\text{-}4$	52	98–99 (hexane)	57,56 / 57,75	3,23 / 3,23	23,82 / 23,78

EXPERIMENTAL

The ^{19}F $\{^1H\}$ NMR spectra were recorded on a RYa-2309 spectrometer (84.56 MHz) at 25° and at concentrations not exceeding 0.4 M. The solvents were purified by standard procedures and distilled in a current of argon. The accuracy of determining δF was ±0.01 ppm.

The symmetrical aryl derivatives of Sn were synthesized by reacting the arylmagnesium bromide with $SnCl_4$. 4-Fluorobenzyl derivatives of triaryltin were synthesized by reaction of 4-fluorobenzylmagnesium chloride with the corresponding triarylchlorostannanes, which were prepared by the Kocheshkov method of cleaving tetraarylstannanes by the action of $SnCl_4$. We did not succeed in synthesizing tris(3,4,5-trichlorophenyl)-4-fluorobenzylstannane, since during reaction of the Grignard reagent with the corresponding chloride a quantitative symmetrization of the latter was observed. Tris(3-fluorophenyl)-4-fluorophenylstannane was synthesized by the reaction of 4-fluorophenylmagnesium bromide with the chloride of tris-(3-fluorophenyl)tin.

The purity of the studied compounds was monitored by means of the ^{19}F NMR spectra and by TLC on Al_2O_3. The constants and analytical data of compounds not previously described are given in Table 3. Typical examples of the syntheses are given below.

Tetrakis(3-chlorophenyl)stannane. To a solution of 3-chlorophenylmagnesium bromide in 250 ml of abs. ether, prepared from 76.4 g (0.4 mole) 3-chlorobromobenzene and 9.6 g (0.41 g-atom) Mg under an argon atmosphere, was added, with stirring and cooling with ice, a solution of 20.9 g (0.08 mole) $SnCl_4$ in 100 ml abs. benzene. A copious light-yellow precipitate separated out. The reaction mixture was held at the boiling point for 3 h, stood overnight and treated with dilute HCl, the organic solvent layer dried with $CaCl_2$, and the solvent removed under vacuum. After recrystallizing the residue from ethanol, 47 g (90%) of a colorless crystalline substance, mp 101-102°, was obtained.

Tetrakis(3,4,5-trichlorophenyl)stannane. To a solution of 3,4,5-trichlorophenylmagnesium bromide, prepared from 80 g (0.31 mole) 3,4,5-trichlorobromobenzene and 7.7 g (0.32 g-atom) Mg in 300 ml abs. ether, with strong stirring and cooling with ice under an argon atmosphere, was added a solution of 20.9 g (0.08 mole) $SnCl_4$ in 100 ml abs. benzene. The reaction mixture was held at the boiling point for 6 h, treated with dil. HCl, filtered and the precipitate washed with ether. After recrystallization from DMFA, 55 g (81%) of a white, lustrous, finely crystalline substance, mp 270° was obtained.

Tris(3,4,5-Trichlorophenyl)stannyl Chloride. A mixture of 4.2 g (5 mmole) tetra(3,4,5-trichlorophenyl)stannane and 0.52 g (2 mmole) $SnCl_4$ was heated in a sealed ampul for 7 h at 270°, cooled to ~20° and left overnight. The resinous dark-brown mass was treated with 300 ml ether, filtered, the ether removed under vacuum, and the residue recrystallized three times from octane with addition of activated carbon. The product obtained was 0.7 g (12%) of colorless, acicular, lustrous crystals with mp 200-201°.

Tris(4-anisyl)-4-fluorobenzylstannane. To a solution of 4-fluorobenzylmagnesium chloride, prepared from 2.17 g (14 mmole) 4-fluorobenzyl chloride and 0.34 g (14 mg-atom) magnesium in 50 ml abs. ether under an argon atmosphere, was added a solution of 4.8 g (10 mmole) tris(4-anisyl)stannyl chloride in 25 ml abs. ether. A copious white precipitate separated out. The reaction mixture was held at boiling point on a water bath for 2 h, cooled, treated with a saturated solution of NH_4Cl, the organic solvent layer separated, the residue extracted with ether, the combined ether extracts dried over Na_2SO_4, and the solvent removed under vacuum. The residue, which was a viscous yellow oil, was purified by chromatography in a thin layer of Al_2O_3 (eluent — light petroleum:acetone = 10:1, R_f 0.6). The product was 2.3 g (40%) of light-yellow transparent oil. Tris(4-tolyl)-4-fluorobenzylstannane was obtained analogously (eluent — light petroleum:acetone = 10:1, R_f 0.6).

Tris(3,5-dichlorophenyl)-4-fluorobenzylstannane. To a solution of 4-fluorobenzyl magnesium chloride [from 0.9 g (6 mmole) 4-fluorobenzyl chloride and 0.14 g (6 mg-atom) Mg] in 25 ml abs. ether was added a solution of 1.9 g (3 mmole) tris(3,5-dichlorophenyl)stannyl chloride in 25 ml abs. benzene. The reaction mixture was heated at the boiling point for 4 h, treated with a saturated aqueous solution of NH_4Cl, the organic layer separated, washed with an aqueous solution of KF, dried with Na_2SO_4, the ether removed, the residue treated with boiling methanol and the yellow precipitate filtered off. After recrystallization from hexane, 0.9 g (43%) of a light-yellow crystalline substance, mp 119-121°, was obtained.

Tris(3-fluorophenyl)-4-fluorophenylstannane. To a solution of 3-fluorophenylmagnesium bromide, prepared from 5.25 g (30 mmole) 3-fluorobromobenzene and 0.72 g (30 mg-atom) Mg in 30 ml abs. ether under an argon atmosphere, was added, with cooling, a solution of 2.56 g (8 mmole) 4-fluorophenyltrichlorostannane in 30 ml abs. toluene. The ether was distilled off and the remainder heated 3 h at 90°. After treating the reaction mixture with dilute HCl, the organic layer was dried with $CaCl_2$, and evaporated under vacuum. Crystallization of the residue from MeOH afforded 1.9 g (52%) of white lustrous crystals, mp 98-99°.

CONCLUSIONS

It has been established that there is no significant difference in the transmission ability of the binuclear bridging group $Sn—CH_2$ and the bridging atom Sn. The effectiveness of the transmission of electronic effects of substituents through the tin-containing bridging groups $Sn—CH_2$ and Sn is considerably reduced in a coordinating solvent medium, while for both bridges the "suppression" of the electronic conduction effect is approximately the same.

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REACTION OF TRIETHYLSILYLMETHYLAMINE AND SOME SECONDARY ORGANOSILICON AMINES WITH FORMALDEHYDE AND SULFUR

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The reaction of 3-alkyl- and 3-alkoxysilylpropylamines $R_3Si(CH_2)_3NH_2$ (I) with CH_2O and elemental sulfur [1, 2], and with thiourea in the presence of $(NH_4)_2SO_4$ [2], has been investigated by means of the easily available N,N'-bis(3-trialkylsilyl)- and N,N'-bis(3-trialkoxysilylpropyl)thiourea.

In this investigation we studied the reaction of sulfur and CH_2O (or paraformaldehyde) with triethylsilylmethylamine (II) and with $[Et_3Si(CH_2)_n]_2NH$ (where n = 1 or 3). In aqueous ethanol the main reaction product of II with CH_2O and sulfur is triethylsilylmethyl isothiocyanate (III). Also formed are (triethylsilymethyl)formamide (IV) and (triethylsilylmethyl)thioformamide (V). It can be suggested that in contrast to amines I, the aldimine $Et_3SiCH_2N{=}CH_2$ (VI) that is formed in one of the intermediate steps of this reaction is not converted to a trimer, and the process proceeds by the scheme

$$\underset{(II)}{Et_3SiCH_2NH_2} + CH_2O \rightarrow [Et_3SiCH_2NHCH_2OH] \rightarrow \begin{cases} \xrightarrow[-H_2S]{S} Et_3SiCH_2NHCHO \quad (IV) \\ \xrightarrow[-H_2O]{S} Et_3SiCH_2NHCHS \quad (V) \\ \xrightarrow[-H_2O]{} \underset{(VI)}{[Et_3SiCH_2N{=}CH_2]} \xrightarrow[-H_2S]{S} \underset{(III)}{Et_3SiCH_2NCS} \end{cases}$$

The trimer of aldimine VI, 1,3,5-tris(triethylsilylmethyl)hexahydrotriazine, also could not be obtained by the reaction of II with paraformaldehyde and sulfur under the conditions of [2]. In this case the formation of N,N'-bis(triethylsilylmethyl)thiourea (VII) along with isothiocyanate III, formamide IV, and thioformamide V is explainable, by analogy with [3], by the reaction of aldimine VI with the starting amine II and sulfur:

$$(VI) + (II) \xrightarrow[-H_2S]{S} \underset{(VII)}{(Et_3SiCH_2NH)_2C{=}S}$$

or by the reaction of amine II with isothiocyanate III.

Compounds III-V are formed as a mixture that is hard to separate by ordinary methods, and its composition was determined by PMR. Using preparative GLC, only a 4:1 mixture of III and IV could be separated from the reaction product. The individual substance VII was obtained by the reaction of amine II with thiourea in the presence of a catalytic amount of $(NH_4)_2SO_4$:

$$2(II) + NH_2C(S)NH_2 \xrightarrow[-2NH_3]{(NH_4)_2SO_4} (VII)$$

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