

A ^{19}F NMR INVESTIGATION OF THE TRANSMISSION OF ELECTRONIC EFFECTS IN TRIARYL(4-FLUOROPHENYL)SILANES

S.I. POMBRIK *, D.N. KRAVTSOV, A.S. PEREGUDOV, E.I. FEDIN and
A.N. NESMEYANOV

Institute of Organo-Element Compounds, Academy of Sciences, Moscow (U.S.S.R.)

(Received November 2nd, 1976)

Summary

The relative ability of the silicon bridging atom to transmit electronic effects has been discussed on the basis of statistical treatment of the available literature data. To study the transmission of electronic effects in tetraarylsilanes a number of triaryl(4-fluorophenyl)silanes have been prepared. The fluorine chemical shifts relative to fluorobenzene as an internal standard have been measured for all these compounds in chloroform.

For the compounds studied, a linear relationship between the fluorine chemical shifts and the $\Sigma\sigma^0$ values of the substituted phenyl groups attached to the silicon atom has been found which proved to be better than the corresponding correlations involving the $\Sigma\sigma$ or $\Sigma\sigma^+$ values. The results obtained suggest that the transmission of electronic effects from one aromatic ring to another in tetraarylsilanes occurs mainly by an inductive mechanism. A comparison of the slope of the correlation line for triaryl(4-fluorophenyl)silanes with the corresponding value obtained previously for triaryl(4-fluorophenyl)tin compounds has shown that the transmitting ability of the Si—Car bonds is somewhat higher than that of the Sn—Car bonds.

Introduction

The problem of the relative efficiency of transmission of electronic effects through bridging groups containing Group IVB elements and in particular the Si atom, still remains unsolved despite the rather close attention with which it is being studied [1–9].

There exist three different opinions as to the efficiency of transmission of substituent electronic effects through organosilicon bridges: $\text{Si} < \text{C}$ [2,6], $\text{Si} \approx \text{C}$ [3–5,7–9] and $\text{Si} > \text{C}$ [1] which are based on the results of correlation treatment of different physico-chemical data for the corresponding model compound series. One of the major reasons underlying these differences seems to be

the insufficiently strict statistical treatment of the results obtained. For example, none of the above studies provide an accuracy of determination for the coefficients ρ of the corresponding correlation equations of the type: $y = \rho x + c$, upon which the comparative study of the transmission capacities of different bridging groups is based.

In this respect an additional statistical analysis of some of the data published [1,2,4,7] was carried out (Table 1), which showed that if the error of determination of the ρ value and the statistical criterium of equality of the two values compared [10] are taken into account, it is possible to say with 95% confidence level that according to the results of the papers [2,4,7], the bridging atoms C and Si in the respective model systems have the same transmitting capacity of electronic effects, while according to paper [1] the best conductor of electronic effects is the Si atom.

Nevertheless out of the two above conclusions the latter seems to be less convincing because it is based upon minor changes of the methyl indicator group properties which are comparable with the experimental error (the variation range of $J(^{13}\text{C}-\text{H})$ is 1.4 Hz, the accuracy of determination being ± 0.3 Hz).

Therefore, as can be seen from Table 1, the accuracy of determination for the slope of the correlation lines achieved up to date is equal to 38–40% and does not allow us to elucidate the difference between the transmission capacities of bridging atoms of the Group IV elements. However, the possibility should not be overlooked that such distinctions may appear in the investigation of the corresponding reaction series by other physico-chemical methods, which make it possible to achieve higher accuracy in determining the ρ coefficients of the correlation equation.

At present one of the most promising methods in this respect seems to be the ^{19}F NMR technique, which is widely used for studying the transmission abilities of the different bridge systems [11–14]. Earlier [15], this method was employed to characterize the efficiency of transmission of electronic effects in triaryl- (*p*-fluorophenyl)tin compounds containing the tin bridging atom, with a relative error of $\pm 5\%$ calculated for 95% significance level, which substantially exceeds the accuracy level achieved in other studies dealing with the transmission of electronic effects in organoelement compounds of Group IVB (Table 1).

This gave us a reason to hope that the above mentioned method might be successfully employed for a more accurate quantitative comparison of trans-

TABLE 1
PARAMETERS OF CORRELATION EQUATIONS ($y = \rho x + c$)

System	x	y	ρ	S_ρ^a	$\Delta\rho^b$	$\Delta\rho\%$ ^c	Ref.
$\text{ArSi}(\text{CH}_3)_3$	σ	$\delta^{13}\text{C}$	3.83	0.64	1.47	39	2
$\text{ArC}(\text{CH}_3)_3$	σ	$\delta^{13}\text{C}$	4.56	0.70	1.72	39	4
$\text{ArSi}(\text{CH}_3)_3$	σ	$J(^{13}\text{C}-\text{H})$	2.89	0.46	1.12	38	1
$\text{ArC}(\text{CH}_3)_3$	σ	$J(^{13}\text{C}-\text{H})$	1.03	0.45	0.41	40	4
$\text{ArSi}(\text{CH}_3)_2\text{H}$	σ	$J(^{13}\text{C}-\text{H})$	1.04	0.19	0.47	45	7

^a S_ρ = Standard error of the coefficient ρ . ^b $\Delta\rho$ = absolute error of the coefficient ρ for 95% confidence level. ^c $\Delta\rho\%$ = relative error of the coefficient ρ for 95% confidence level.

mission capacities of the bridging C, Si, Ge, Sn and Pb atoms and element—aromatic carbon bonds. In this connection the present paper deals with a study of the nature and efficiency of transmission of electronic effects through the bridging silicon atom in the framework of the ^{19}F NMR method.

Results and discussion

In order to solve the problem indicated, a number of model compounds of the type $\text{Ar}_3\text{SiC}_6\text{H}_4\text{F-4}$, where $\text{Ar} = 4\text{-(CH}_3)_2\text{NC}_6\text{H}_4$, $4\text{-CH}_3\text{OC}_6\text{H}_4$, $4\text{-CH}_3\text{C}_6\text{H}_4$, $3\text{-CH}_3\text{C}_6\text{H}_4$, C_6H_5 , $4\text{-FC}_6\text{H}_4$, $3\text{-FC}_6\text{H}_4$, $4\text{-ClC}_6\text{H}_4$, $3\text{-ClC}_6\text{H}_4$, $3,4\text{-Cl}_2\text{C}_6\text{H}_3$ or $3,4,5\text{-Cl}_3\text{C}_6\text{H}_2$ were prepared and their fluorine chemical shifts relative to fluorobenzene as an internal standard have been determined in 0.2 *M* solutions in chloroform (Table 2).

The results obtained clearly show that the fluorine chemical shifts associated with the *p*-fluorophenyl group depend substantially upon the nature of the aryl substituent attached to the metal atom, the overall range of ^{19}F chemical shifts in the system studied being approximately equal to 5.6 ppm.

In order to determine the nature of transmission of electronic effects through the bridging silicon atom we carried out the correlation of fluorine chemical shifts with polar constants of substituents in aromatic rings, for which values σ^0 [16], σ [17] and σ^+ [18], were chosen characterizing respectively either absence (σ^0) or presence of the direct polar conjugation of the substituents in the aromatic ring with an indication center of either ordinary (σ), or strongly electronaccepting (σ^+) character (Table 3).

From the parameters of the obtained correlation equations it follows that in passing $\Sigma\sigma^0$ to $\Sigma\sigma$ or $\Sigma\sigma^+$ the quality of the correlation relationship substantially worsens e.g. the description of the behaviour of the bridging groups in question, the Taft inductive constants of the aryl groups should be considered as most suitable (Fig. 1), and therefore the transmission of electronic effects through the Si—Car bonds as in the case of the Sn—Car bonds [16], proceeds mainly by an inductive mechanism. The data for the dual parameter correlation (Table 4) of the fluorine chemical shifts with inductive and resonance constants of the substituents led also to a similar conclusion.

TABLE 2

^{19}F CHEMICAL SHIFTS FOR TRIARYL(4-FLUOROPHENYL)SILANES IN CHLOROFORM RELATIVE TO INTERNAL FLUOROBENZENE

Compound	$\delta^{19}\text{F}$ (ppm)
$[4\text{-(CH}_3)_2\text{NC}_6\text{H}_4]_3\text{SiC}_6\text{H}_4\text{F-4}$	−0.8
$[4\text{-CH}_3\text{OC}_6\text{H}_4]_3\text{SiC}_6\text{H}_4\text{F-4}$	−1.8
$[4\text{-CH}_3\text{C}_6\text{H}_4]_3\text{SiC}_6\text{H}_4\text{F-4}$	−1.7
$[3\text{-CH}_3\text{C}_6\text{H}_4]_3\text{SiC}_6\text{H}_4\text{F-4}$	−1.8
$(\text{C}_6\text{H}_5)_3\text{SiC}_6\text{H}_4\text{F-4}$	−2.3
$[4\text{-FC}_6\text{H}_4]_3\text{SiC}_6\text{H}_4\text{F-4}$	−3.1
$[4\text{-ClC}_6\text{H}_4]_3\text{SiC}_6\text{H}_4\text{F-4}$	−3.5
$[3\text{-FC}_6\text{H}_4]_3\text{SiC}_6\text{H}_4\text{F-4}$	−3.7
$[3\text{-ClC}_6\text{H}_4]_3\text{SiC}_6\text{H}_4\text{F-4}$	−4.0
$[3,4\text{-Cl}_2\text{C}_6\text{H}_3]_3\text{SiC}_6\text{H}_4\text{F-4}$	−5.0
$[3,4,5\text{-Cl}_3\text{C}_6\text{H}_2]_3\text{SiC}_6\text{H}_4\text{F-4}$	−6.4

TABLE 3

PARAMETERS OF CORRELATION EQUATIONS ($y = \rho x + c$)

System	x	y	ρ	S_{ρ}^a	$\Delta\rho^b$	$\Delta\rho\%$ ^c	S_c^d	C	S	r^e	n ^f
4-FC ₆ H ₄ SiAr ₃	$\Sigma\sigma^0$	δ_F	-4.02	0.12	0.27	7	0.05	-2.38	0.155	0.996	11
4-FC ₆ H ₄ SiAr ₃	$\Sigma\sigma$	δ_F	-3.67	0.22	0.49	13	0.09	-2.61	0.300	0.981	11
4-FC ₆ H ₄ SiAr ₃	$\Sigma\sigma^+$	δ_F	-2.03	0.39	0.87	43	0.26	-3.22	0.866	0.834	11
4-FC ₆ H ₄ SnAr ₃ (I)	$\delta_F(I)$	$\delta_F(II)$	1.12	0.01	0.03	3	0.04	-0.55	0.067	0.999	10
4-FC ₆ H ₄ SiAr ₃ (II)											
4-FC ₆ H ₄ SnAr ₃ [15]	$\Sigma\sigma^0$	δ_F	-3.65	0.09	0.19	5	0.04	-1.05	0.122	0.997	12

^a S_{ρ} = standard error of the coefficient ρ , ^b $\Delta\rho$ = absolute error of the coefficient ρ for 95% confidence level, ^c $\Delta\rho\%$ = relative error of the coefficient ρ for 95% confidence level, ^d S_c = standard error of the coefficient C, ^e r = correlation coefficient, ^f n = number of compounds in the system.

TABLE 4

PARAMETERS OF CORRELATION EQUATIONS $\delta\rho = \rho_I\rho_I + \rho_R X + C$

$\delta^{19}F$	n	x	$-\rho_I$	$-\rho_R$	$\lambda = \rho_R/\rho_I$	$S_{\rho_I}^a$	$S_{\rho_R}^b$	C	S^c	R^d
(4-XC ₆ H ₄) ₃ SiC ₆ H ₄ F-4	6	σ_R^0	4.16	3.51	0.84	0.14	0.17	-2.30	0.09	0.997
(4-XC ₆ H ₄) ₃ SiC ₆ H ₄ F-4	6	σ_R^+	3.71	2.08	0.56	0.19	0.14	-2.20	0.14	0.994
(4-XC ₆ H ₄) ₃ SiC ₆ H ₄ F-4	6	σ_R^+	3.17	0.99	0.31	0.35	0.13	-2.20	0.32	0.978
(4-XC ₆ H ₄) ₃ SnC ₆ H ₄ F-4	6	σ_R^0	3.75	3.23	0.86	0.10	0.12	-1.59	0.07	0.998
(4-XC ₆ H ₄) ₃ SnC ₆ H ₄ F-4	6	σ_R^+	3.31	1.51	0.58	0.03	0.10	-1.51	0.08	0.997
(4-XC ₆ H ₄) ₃ SnC ₆ H ₄ F-4	6	σ_R^+	2.81	0.93	0.33	0.08	0.21	-1.51	0.16	0.990

^a S_{ρ_I} = standard error of the coefficient ρ_I , ^b S_{ρ_R} = standard error of the coefficient ρ_R , ^c S = standard deviation of the points from the plane, ^d R = general correlation coefficient.

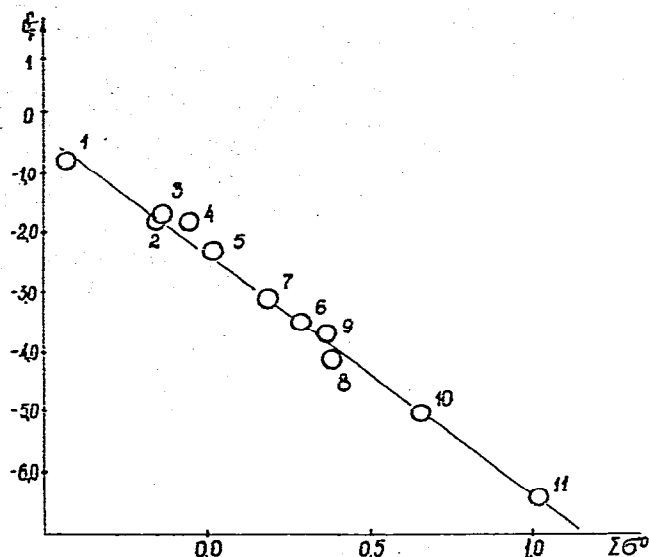


Fig. 1. Plot of ^{19}F chemical shifts for $4\text{-FC}_6\text{H}_4\text{SiAr}_3$ in chloroform versus the $\Sigma\sigma^0$ values for the substituted phenyl groups attached to the silicon atom: 1, $4\text{-(CH}_3)_2\text{NC}_6\text{H}_4$; 2, $4\text{-CH}_3\text{OC}_6\text{H}_4$; 3, $4\text{-CH}_3\text{C}_6\text{H}_4$; 4, $3\text{-CH}_3\text{C}_6\text{H}_4$; 5, C_6H_5 ; 6, $4\text{-ClC}_6\text{H}_4$; 7, $4\text{-FC}_6\text{H}_4$; 8, $3\text{-ClC}_6\text{H}_4$; 9, $3\text{-FC}_6\text{H}_4$; 10, $3,4\text{-Cl}_2\text{C}_6\text{H}_3$; 11, $3,4,5\text{-Cl}_3\text{C}_6\text{H}_2$.

These data show that the best results for both $\text{Ar}_3\text{SiC}_6\text{H}_4\text{F-4}$ type compounds and their organotin analogues are obtained by using the σ_R^0 and σ_I polar constants.

Moreover the comparative study of the values ρ (Table 3) for the respective correlation relationships $\delta^{19}\text{F}(\text{Ar}_3\text{SiC}_6\text{H}_4\text{F-4})-\sigma^0$ and $\delta^{19}\text{F}(\text{Ar}_3\text{SnC}_6\text{H}_4\text{F-4})-\sigma^0$ carried out with the aid of statistical equality criterium [10] shows that for a 95% significance level the transmission of the electronic effects of substituents in the aromatic groups to the indicator fluorine atom proceeds somewhat more effectively through the bridging silicon atom. Slightly better transmitting properties of the Si atom as compared to the Sn atom are shown also by the slope of the correlation line establishing the connection between the chemical shifts of fluorine in triaryl-(*p*-fluorophenyl)silanes and in the corresponding triaryl-(*p*-fluorophenyl)tin compounds, the value of which exceeds 1.

In the light of the data about the inductive nature of transmission of electronic effects through the bridging atoms of Si and Sn, the greater transmitting capacity of Si may be most probably explained by the presence, in the tetraarylsilanes, of a slight separate resonance $d_\pi-p_\pi$ interaction between the vacant d -orbitals of Si and the π -electronic systems of the adjacent aromatic rings. This arises due to the specific geometry of the d -orbitals [19] and which results in the lack of through-conjugation from one aromatic ring to another.

To verify the correctness of the suggested hypothesis we have determined, by means of the fluorine chemical shifts in *m*- and *p*-fluorophenyltriphenylsilanes (δ_p -1.8 ppm, δ_m -0.2 ppm) on the basis of the corresponding Taft equations [20,21], the values of the inductive (σ_I 0.11) and conjugative (σ_R^0 0.07) constants of the Ph_3Si group which show that the mentioned group is a weak electron-

TABLE 5
ANALYTICAL DATA AND PHYSICAL PROPERTIES OF TRIARYL(4-FLUOROPHENYL)SILANES

Compound	Yield (%)	B.p. (°C/mmHg)	M.p. (°C)	Analysis found (calcd.) (%)		
				C	H	Si
(4-CH ₃) ₂ NC ₆ H ₄) ₃ SiC ₆ H ₄ F-4	40	—	144–146 (petroleum ether)	74.67 (74.51)	7.35 (7.08)	5.42 (5.80)
(4-CH ₃ OC ₆ H ₄) ₃ SiC ₆ H ₄ F-4	70	270/2	—	72.43 (72.79)	5.70 (5.61)	
(4-CH ₃ C ₆ H ₄) ₃ SiC ₆ H ₄ F-4	40	—	195–197 (petroleum ether)	81.75 (81.75)	6.32 (6.35)	7.07 (7.07)
(3-CH ₃ C ₆ H ₄) ₃ SiC ₆ H ₄ F-4	64	—	106–108 (ethanol)	81.65 (81.75)	6.31 (6.35)	7.07 (7.07)
(C ₆ H ₅) ₃ SiC ₆ H ₄ F-4	50	—	181–182 (propanol)	81.54 (81.36)	5.50 (5.40)	7.85 (7.92)
(4-FC ₆ H ₄) ₃ SiC ₆ H ₄ F-4	65	—	131–132 (methanol)	70.56 (70.77)	4.22 (3.95)	6.52 (6.87)
(4-ClC ₆ H ₄) ₃ SiC ₆ H ₄ F-4	50	—	142–144 (propanol)	62.60 (62.94)	3.60 (3.52)	6.00 (6.13)
(3-ClC ₆ H ₄) ₃ SiC ₆ H ₄ F-4	40	205–207/2	102–103 (ethanol)	62.91 (62.94)	3.68 (3.52)	6.11 (6.13)
(3-FC ₆ H ₄) ₃ SiC ₆ H ₄ F-4	40	—	141–143 (ethanol)	70.50 (70.57)	4.00 (3.95)	6.71 (6.87)
(3,4-Cl ₂ C ₆ H ₃) ₃ SiC ₆ H ₄ F-4	80	—	139–141 (propanol)	51.44 (51.34)	2.16 (2.33)	4.70 (5.00)
(3,4,5-Cl ₃ C ₆ H ₂) ₃ SiC ₆ H ₄ F-4	89	—	178–179 (propanol)	43.07 (43.35)	1.47 (1.51)	3.75 (4.22)

accepting substituent. Moreover, as the comparison of the σ_R^0 values for the Ph_3Si and Ph_3Sn [24] groups shows; the contribution of the resonance constituent to the interactions in the Si—Car bond is slightly greater than in the Sn—Car bond.

The results obtained in the present study make it possible to say that, in particular, model systems of the $\text{Ar}_3\text{MC}_6\text{H}_4\text{F-4}$ type can be successfully used for a more accurate quantitative comparison of the transmission capacity of all the Group IVB bridging elements and of the corresponding element—aromatic carbon bonds. This is due to the fact that these systems have some advantages over other possible systems. Thus, if a reasonable assumption is made concerning the equality of the mean deviation of points from the regression line for the correlation equations with an equal number of points relating to $\text{Ar}_3\text{MC}_6\text{H}_4\text{F-4}$ and $\text{Ar}_2\text{MR}_2\text{C}_6\text{H}_4\text{F-4}$ systems, it is possible to demonstrate that the relative error of the coefficient ρ for the former series of compounds will be approximately three times smaller than that for the latter.

Experimental

General

The ^{19}F NMR spectra were recorded at 34°C on a Hitachi Perkin—Elmer R-20 spectrometer operating at 56.4 MHz. All measurements were performed in a solution of concentration not greater than 0.2 mol l^{-1} . The use of the substitution method for the determination of fluorine chemical shifts has been described elsewhere [23]. The experimental error in the estimation of the fluorine chemical shifts was not greater than $\delta \pm 0.1 \text{ ppm}$. Chloroform was purified by a conventional method and distilled over phosphorous pentoxide.

Triphenyl-4-fluorophenylsilane and triphenyl-3-fluorophenylsilane [24] were prepared by treating triphenylchlorosilane with either 4-fluorophenyl- [25] or 3-fluorophenyllithium [24]. The other unsymmetric triaryl(4-fluorophenyl)silanes studied in the present communication were synthesized by the action of the corresponding organolithium compounds upon 4-fluorophenyl-trichlorosilane [26], which was prepared by treating silicon tetrachloride with 4-4-fluorophenylmagnesium bromide. Some typical examples of the preparation of the triaryl(4-fluorophenyl)silanes are given below. Analytical data and physical properties of prepared compounds are presented in Table 5.

Triphenyl-4-fluorophenylsilane

To a rapidly stirred solution of *n*-butyllithium in 50 ml of dry diethyl ether, prepared from 4.6 (0.05 ml) of butyl chloride and 0.85 g (0.12 g atom) of lithium, was slowly added a solution of 6.7 g (0.038 mol) of 4-bromofluorobenzene in 30 ml of the same solvent under nitrogen while maintaining the temperature below -50°C . After stirring at -50°C for 1 h a solution of 2.94 g (0.01 mol) of triphenylchlorosilane in 30 ml of dry ether was added to the prepared solution of 4-fluorophenyllithium. After stirring at room temperature for 8 h and refluxing for 2 h, the reaction mixture was decomposed with a saturated aqueous solution of NH_4Cl . The ether layer was separated, dried over CaCl_2 and the solvent removed. The residual brown oil was treated by ice

acetic acid, washed with petroleum ether and recrystallized from propanol. 1.7 g of a colourless crystalline substance were obtained after sublimation.

4-Fluorophenyltrichlorosilane

To a solution of 4-fluorophenylmagnesium bromide, obtained from 50.7 g (0.29 mol) of 4-bromofluorobenzene and 7.2 g (0.3 mol) of magnesium turnings in 250 ml of dry ether under dry argon was slowly added a solution of 47 g (0.27 mol) of silicon tetrachloride in 100 ml of the same solvent with stirring and cooling in an ice bath. After refluxing for 5 h, the reaction mixture was cooled and the resulting solid was filtered and washed with dry ether under argon. All ether filtrates were combined, the solvent removed and the residue distilled under reduced pressure and in dry inert atmosphere yielding 33.4 g of colourless liquid with b.p. 86–88°C/17 mmHg (lit. [26] b.p. 194.5–196.5°C/738 mmHg).

Tris(3,4,5-trichlorophenyl)(4-fluorophenyl)silane

A solution of 9.38 g (0.036 mol) of 3,4,5-trichlorobromobenzene in 50 ml of dry ether was added slowly under dry argon to a stirred solution of *n*-butyllithium in dry ether prepared from 4.6 g (0.05 mol) of butyl chloride and 0.85 g (0.12 g atom) of lithium in 50 ml of ether at –70°C. After stirring at –70°C for 1 h, a solution of 2.1 g (0.09 mol) of 4-fluorophenyltrichlorosilane in 30 ml of dry ether was added to the prepared solution of 3,4,5-trichlorophenyllithium. Then the reaction mixture was stirred at room temperature for 3 h, refluxed for 1 h, cooled and decomposed with a saturated aqueous of NH_4Cl . The ether layer was separated, dried over CaCl_2 and the solvent removed. Two crystallizations of the residual brown oil from propanol gave 5.9 g of a crystalline substance.

Tris(4-chlorophenyl)(4-fluorophenyl)silane, tris(3-chlorophenyl)(4-fluorophenyl)silane, tetra(4-fluorophenyl)silane, tris(3-fluorophenyl)(4-fluorophenyl)silane and tris(3,4-dichlorophenyl)(4-fluorophenyl)silane were prepared in a similar manner.

Tris(4-dimethylaminophenyl)(4-fluorophenyl)silane

To a solution of 4-dimethylaminophenyllithium, prepared from 6.4 g (0.032 mol) of 4-bromodimethylaniline and 0.51 g (0.064 g atom) of lithium in 50 ml of dry ether, was added a solution of 2.3 g (0.01 mol) of 4-fluorophenyltrichlorosilane in 30 ml of the same solvent with cooling and under argon. After refluxing for 3 h, the reaction mixture was decomposed with a saturated aqueous solution of NH_4Cl . The ether layer was separated, dried over Na_2SO_4 and the solvent removed. 1.6 g of a white crystalline substance were obtained after two crystallizations from petroleum ether under argon.

Tris(4-methoxyphenyl)(4-fluorophenyl)silane, tris(4-methylphenyl)(4-fluorophenyl)silane and tris(3-methylphenyl)(4-fluorophenyl)silane were prepared in a similar manner.

References

- 1 M.E. Freeburger and L. Spialter, J. Amer. Chem. Soc., 93 (1971) 1894.
- 2 R.E. Hess, C.K. Haas, B.A. Kaduk, C.D. Schaeffer and C.H. Yoder, Inorg. Chim. Acta, 5 (1971) 161.

- 3 C.H. Yoder, R.H. Tuck and R.E. Hess, *J. Amer. Chem. Soc.*, 91 (1969) 539.
- 4 C.D. Schaeffer, J.J. Zuckerman and C.H. Yoder, *J. Organometal. Chem.*, 80 (1974) 29.
- 5 N.S. Nametkin, V.D. Tyurin, S.P. Gubin and S.A. Smirnova, *Dokl. Akad. Nauk SSSR*, 186 (1969) 104.
- 6 M.G. Voronkov, V.P. Feshin, V.F. Mironov, S.A. Mikhailyants and G.K. Gar, *Zh. Obshh. Khim.*, 41 (1971) 2211.
- 7 Y. Nagai, M.A. Ohtsuki, T. Nakano and H. Watanabe, *J. Organometal. Chem.*, 35 (1972) 81.
- 8 H. Sakurai and M. Ohtsuru, *J. Organometal. Chem.*, 13 (1968) 81.
- 9 L.F.R. Jaggart and A. Pidcock, *J. Organometal. Chem.*, 16 (1969) 324.
- 10 S.A. Aivazyam, *Statistical investigation of relationships*, Moscow, Metallurgiya, 1968.
- 11 R.W. Taft, S. Ehrenson and S.K. Dayal, *J. Amer. Chem. Soc.*, 94 (1972) 9113.
- 12 P.J. Mitchell and L. Phillips, *J. Chem. Soc., Perkin Trans. 2*, (1974) 109.
- 13 I.R. Ager, L. Phillips and S.J. Roberts, *J. Chem. Soc., Perkin Trans 2*, (1972) 1988.
- 14 R.G. Pews, *J. Chem. Soc. Chem. Commun.*, (1971) 458.
- 15 D.N. Kravtsov, B.A. Kvasov, T.S. Khazanova and E.I. Fedin, *J. Organometal. Chem.*, 61 (1973) 219.
- 16 R.P. Wells, S.E. Ehrenson and R.W. Taft, *Progr. Phys., Org. Chem.*, 6 (1968) 147.
- 17 H.H. Jaffe, *Chem. Rev.*, 53 (1953) 191.
- 18 H.C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, 80 (1958) 4979.
- 19 H.H. Jaffe, *J. Phys. Chem.*, 58 (1954) 185.
- 20 R.W. Taft, E. Price, I.R. Fox, I.C. Lewis, K.K. Andersen and C.T. Davis, *J. Amer. Chem. Soc.*, 85 (1963) 709.
- 21 R.W. Taft, E. Price, I.R. Fox, I.C. Lewis, K.K. Andersen and C.T. Davis, *J. Amer. Chem. Soc.*, 85 (1963) 3146.
- 22 A.N. Nesmeyanov, D.N. Kravtsov, B.A. Kvasov, E.I. Fedin and T.S. Khazanova, *Dokl. Akad. Nauk SSSR*, 199, 5 (1971) 1078.
- 23 A.N. Nesmeyanov, D.N. Kravtsov, E.I. Fedin, B.A. Kvasov, V.M. Pachevskaya and L.S. Golovchenko, *Dokl. Akad. Nauk SSSR*, 183 (1968) 1098.
- 24 H. Gilman, R. Gorsich and B.J. Gay, *J. Org. Chem.*, 27 (1962) 1023.
- 25 R.I. Morgan, P. Tannhauser, R.I. Pratt, T.C. Meyers and V.I. Ewod, *J. Amer. Chem. Soc.*, 77 (1955) 5658.
- 26 V. Chvalovsky and V. Bazant, *Collect. Czech. Chem. Commun.*, 16 (1951) 580.