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A ^{19}F NMR STUDY OF THE TRANSMISSION OF ELECTRONIC EFFECTS IN TRIARYLANTIMONY AND TRIARYLBISMUTH COMPOUNDS. A COMPARISON WITH THE NITROGEN- AND CARBON-CONTAINING ANALOGUES

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Summary

A ^{19}F NMR study of the transmission of electronic effects has been made for the systems $\text{Ar}_2\text{EC}_6\text{H}_4\text{F}-4$ ($\text{E} = \text{Sb}, \text{Bi}, \text{CH}, \text{N}$). The fluorine chemical shifts obtained are correlated with the polar constants ($\Sigma\sigma^0$ and $\Sigma\sigma$) of the substituents, suggesting that electronic effects are transmitted through the $\text{Sb}-\text{C}_{\text{ar}}$, $\text{Bi}-\text{C}_{\text{ar}}$ and $\text{C}-\text{C}_{\text{ar}}$ bonds predominantly by an inductive mechanism, whereas the transmission through the $\text{N}-\text{C}_{\text{ar}}$ bonds is contributed to significantly by classical resonance effects due to competitive conjugation of the lone pair with the aromatic rings, and the substituents therein. A dual parameter correlation of the fluorine chemical shifts with the inductive (σ_{I}) and resonance (σ_{R}^0 and σ_{R}) parameters of the substituents in the aromatic rings has led to similar conclusions. The inductive transmission through the bridging Sb and Bi atoms has been assigned to the absence of conjugation of lone pair and vacant d -orbitals of the metals with π -electron systems of the aromatic rings. On the basis of the values of the ρ coefficients for the correlation equations obtained it has been established that the transmitting ability of the $\text{Bi}-\text{C}_{\text{ar}}$ bonds is close to that of the $\text{C}_{\text{al}}-\text{C}_{\text{ar}}$ bonds and considerably lower than the transmitting ability of the $\text{N}-\text{C}_{\text{ar}}$ bonds.

Introduction

To date, transmission of electronic effects through bridging groups has been studied in quite good detail [1–3] for the bridges containing carbon or heteroatoms such as nitrogen, oxygen, sulphur, or selenium. In contrast, the ability of heavy non-transition metals and the respective metal–carbon bonds to transmit substituent electronic effects has been dealt with rather rarely. This is mainly due to the fact that these model systems are less available since the metal–carbon

bonds are highly reactive and, consequently, do not permit chemical techniques to be applied for solving the problem. On the other hand, the problem is of considerable importance for theoretical organometallic chemistry. Earlier, a ^{19}F NMR study was made of electronic effect transmission through the tin or bismuth bridges [4,5].

The present paper aims at applying one and the same method to investigating electronic effect transmission through aromatic carbon—antimony and aromatic carbon—bismuth bonds and collating the results obtained with those obtained for aromatic carbon—nitrogen and aliphatic carbon—aromatic carbon bonds. The previous paper [6] presented the evidence obtained by us by ^{19}F NMR for organometallic groups of the $(\text{C}_6\text{H}_5)_2\text{Sb}$ and $(\text{C}_6\text{H}_5)_2\text{Bi}$ type. These were found to interact with the aromatic ring predominantly, in terms of the inductive pattern, unlike the groups $(\text{C}_6\text{H}_5)_2\text{N}$ and $(\text{C}_6\text{H}_5)_2\text{CH}$. Accordingly, we might expect that electronic effect transmission through the antimony or bismuth bridges would be inductive as well, thus differing from the transmission through the nitrogen or carbon bridges. On the other hand, it was quite probable that antimony and bismuth atoms would have a greater transmittance, owing to the higher polarizability of electron shells of heavy metals [7,8]. Finally, a comparative study of the transmission in systems of the type Ar_2EAr ($\text{E} = \text{CH}, \text{N}, \text{Sb}, \text{Bi}$) allows one to hope that the difference between the patterns of interaction of the groups with an aromatic ring may be visualised at a deeper level.

Results and discussion

To solve the problems outlined, we chose, as before, ^{19}F NMR which allows one to study labile organometallics and had been employed successfully for investigating electron effect transmission through bridged groups of various types [9–12]. We have synthesized a number of *p*-fluorophenyl-antimony and -bismuth compounds, as well as their nitrogen- or carbon-containing analogues: $\text{Ar}_2\text{SbC}_6\text{H}_4\text{F}-4$, $\text{Ar}_2\text{BiC}_6\text{H}_4\text{F}-4$, $\text{Ar}_2\text{CHC}_6\text{H}_4-4$ and $\text{Ar}_2\text{NC}_6\text{H}_4\text{F}-4$.

Fluorine chemical shifts were measured for the compounds mentioned, with fluorobenzene as internal reference, in dilute solutions in chloroform. Chloroform was chosen since it dissolves the compounds under study rather well, being at the same time quite inert [6] to the solutes. The fluorine chemical shifts obtained are listed in Table 1.

Table 1 demonstrates that fluorine chemical shifts in the organometallic compounds and their analogues depend essentially on substituents in the rings. For comparable compounds, the increment in the chemical shift observed on going from donor substituents to acceptor substituents is, for the species studied, lower than it is for 4-fluoro-substituted triphenylamines. Consequently, even at this preliminary step one may say that bridging nitrogen transmits electron effects better than do the heavy metal bridges or the carbon bridges.

To clarify this in more detail, correlation analysis was made for the fluorine chemical shifts as a function of polar constants of the substituents within the framework of one- or two-parameter correlation techniques. In the one-parameter case, the quantities σ^0 or σ were employed. They describe electronic effect of a mono- or poly-substituted phenyl group which does or does not, respectively, display direct polar conjugation of the substituent with the reaction or

TABLE 1

FLUORINE CHEMICAL SHIFTS, IN CHLOROFORM RELATIVE TO INTERNAL FLUOROBENZENE

Compound	$\delta(F)$ (ppm)
$[4-(CH_3)_2NC_6H_4]_2BiC_6H_4F-4$	1.20
$(4-CH_3OC_6H_4)_2BiC_6H_4F-4$	0.41
$(4-CH_3C_6H_4)_2BiC_6H_4F-4$	0.50
$(C_6H_5)_2BiC_6H_4F-4$	0.11
$(4-ClC_6H_4)_2BiC_6H_4F-4$	0.63
$(3-ClC_6H_4)_2BiC_6H_4F-4$	0.97
$(4-FC_6H_4)_2BiC_6H_4F-4$	-0.32
$(3,4-Cl_2C_6H_3)_2BiC_6H_4F-4$	-1.60 ^a
$(3,4,5-Cl_3C_6H_2)_2BiC_6H_4F-4$	-2.66 ^a
$(4-CH_3C_6H_4)_2SbC_6H_4F-4$	-0.23
$(C_6H_5)_2SbC_6H_4F-4$	-0.58
$(4-ClC_6H_4)_2SbC_6H_4F-4$	-1.62
$(3-ClC_6H_4)_2SbC_6H_4F-4$	-2.05
$(4-FC_6H_4)_2SbC_6H_4F-4$	-1.13
$[4-(CH_3)_2NC_6H_4]_2CHC_6H_4F-4$	4.75
$(4-CH_3OC_6H_4)_2CHC_6H_4F-4$	4.13
$(3-CH_3OC_6H_4)CHC_6H_4F-4$	3.68
$(4-CH_3C_6H_4)_2CHC_6H_4F-4$	3.98
$(3-CH_3C_6H_4)_2CHC_6H_4F-4$	3.94
$(C_6H_5)_2CHC_6H_4F-4$	3.75
$(4-ClC_6H_4)_2CHC_6H_4F-4$	2.82
$(3-ClC_6H_4)_2CHC_6H_4F-4$	2.75
$(4-FC_6H_4)_2CHC_6H_4F-4$	3.17
$(3,4-Cl_2C_6H_3)_2CHC_6H_4F-4$	1.81
$(3,4,5-Cl_3C_6H_2)_2CHC_6H_4F-4$	0.73
$(3-CF_3C_6H_4)_2CHC_6H_4F-4$	0.41
$[4-(CH_3)_2NC_6H_4]_2NC_6H_4F-4$	11.30
$(4-CH_3C_6H_4)_2NC_6H_4F-4$	7.77
$(C_6H_5)_2NC_6H_4F-4$	6.60
$(4-ClC_6H_4)_2NC_6H_4F-4$	5.14
$(3-ClC_6H_4)_2NC_6H_4F-4$	4.22
$(4-FC_6H_4)_2NC_6H_4F-4$	6.90
$(3,4-Cl_2C_6H_3)_2NC_6H_4F-4$	3.28

^a The chemical shift was measured for a mixture of the compounds.

the indicator centre [2]. Analysis of the results obtained (Table 2, Figs. 1—3) shows that the systems containing bridging antimony, bismuth, or carbon give a good linear correlation of the fluorine chemical shift with the substituted aryl σ^0 constants. For substituted tris(4-fluorophenyl)amines, the correlation is markedly worse. When the quantities σ are used as polar constants of the substituents, the correlation with the systems bridged by bismuth or carbon deteriorates but the correlation for substituted tris(4-fluorophenyl)amines improves.

The two-parameter correlation approach was applied to the fluorine chemical shifts as a function of inductive and resonance constants of the substituents in the aromatic rings [11] bridged by bismuth, carbon, or nitrogen atoms (Table 3). The results agree with those obtained via the one-parameter technique. E.g., the best correlation for compounds of the diaryl-*p*-fluorophenylbismuth and diaryl-*p*-fluorophenylmethane type was given by the σ_I and σ_R^0 constants whereas the polar σ_I and σ_R constants provided the optimal results for substituted tris(4-fluorophenyl)amines.

TABLE 2

CORRELATION EQUATION PARAMETERS, $y = \rho x + C$

y	x	n	C	S_C	ρ	S_ρ	S	r
$\text{Ar}_2\text{BiC}_6\text{H}_4\text{F}-4$	$\Sigma\sigma^0$	9	0.05	0.02	-2.71	0.05	0.07	0.999
$\text{Ar}_2\text{SbC}_6\text{H}_4\text{F}-4$	$\Sigma\sigma^0$	5	-0.06	0.66	-3.52	0.28	0.12	0.991
$\text{Ar}_2\text{CHC}_6\text{H}_4\text{F}-4$	$\Sigma\sigma^0$	13	3.66	0.04	-2.85	0.08	0.01	0.996
$\text{Ar}_2\text{NC}_6\text{H}_4\text{F}-4$	$\Sigma\sigma^0$	7	7.34	0.30	-7.21	0.86	0.72	0.966
$\text{Ar}_2\text{BiC}_6\text{H}_4\text{F}-4$	$\Sigma\sigma$	9	-0.13	0.06	-2.52	0.12	0.17	0.991
$\text{Ar}_2\text{SbC}_6\text{H}_4\text{F}-4$	$\Sigma\sigma$	5	-0.79	0.07	-3.50	0.35	0.14	0.986
$\text{Ar}_2\text{CHC}_6\text{H}_4\text{F}-4$	$\Sigma\sigma$	13	3.51	0.07	-2.67	0.16	0.24	0.980
$\text{Ar}_2\text{NC}_6\text{H}_4\text{F}-4$	$\Sigma\sigma$	7	6.93	0.14	-6.76	0.39	0.37	0.992
$\text{Ar}_2\text{BiC}_6\text{H}_4\text{F}-4$	$\text{Ar}_2\text{CHC}_6\text{H}_4\text{F}-4$	9	-3.44	0.11	0.96	0.03	0.12	0.996
$\text{Ar}_2\text{SbC}_6\text{H}_4\text{F}-4$	$\text{Ar}_2\text{CHC}_6\text{H}_4\text{F}-4$	5	5.39	0.54	1.29	0.16	0.18	0.977
$\text{Ar}_2\text{NC}_6\text{H}_4\text{F}-4$	$\text{Ar}_2\text{CHC}_6\text{H}_4\text{F}-4$	7	-2.17	1.32	2.62	0.39	0.91	0.949

Collation of the correlation analysis results demonstrates that electronic effect transmission through aromatic carbon-bismuth and aromatic carbon-antimony bonds resembles the transmission pattern of aliphatic carbon-aromatic carbon bonds. Within the framework of the approach employed, electronic effects are transmitted through the metal or carbon bridges by an inductive mechanism implying no classical conjugation between aromatic ring π -electron systems and lone pairs or vacant orbitals of the metal. It is noteworthy that in triphenylmethane derivatives a part may be played in electronic effect transmission by σ , π -conjugation of C-H and C-C bonds with aromatic rings, as witnessed by a high resonance constant, σ_R^0 , of the $(\text{C}_6\text{H}_5)_2\text{CH}$ group [6]. The correlation analysis using σ^0 or σ constants cannot, however, reveal any σ , π -conjugation effect since the σ^0 constants were derived from the data obtained for the systems in which σ , π -conjugation of C-H and C-C bonds with aromatic ring is already

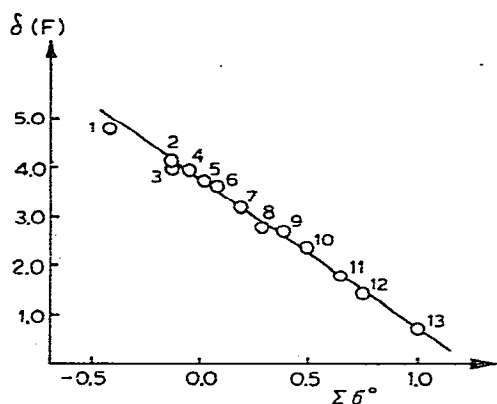


Fig. 1. Fluorine chemical shift in $\text{Ar}_2\text{CHC}_6\text{H}_4\text{F}-4$ as a function of $\Sigma\sigma^0$ of the aryl radical: 1, 4- $(\text{CH}_3)_2\text{NC}_6\text{H}_4$; 2, 4- $\text{CH}_3\text{OC}_6\text{H}_4$; 3, 4- $\text{CH}_3\text{C}_6\text{H}_4$; 4, 3- $\text{CH}_3\text{C}_6\text{H}_4$; 5, C_6H_5 ; 6, 3- $\text{CH}_3\text{OC}_6\text{H}_4$; 7, 4- FC_6H_4 ; 8, 4- ClC_6H_4 ; 9, 3- ClC_6H_4 ; 10, C_6H_5 ; 11, 3,4- $\text{Cl}_2\text{C}_6\text{H}_3$; 12, 3,5- $\text{Cl}_2\text{C}_6\text{H}_3$; 13, 3,4,5- $\text{Cl}_3\text{C}_6\text{H}_2$.

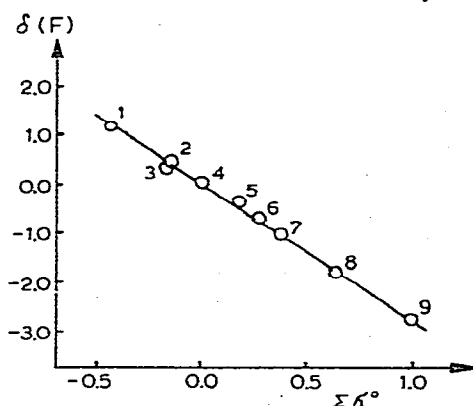


Fig. 2. Fluorine chemical shift in $\text{Ar}_2\text{BiC}_6\text{H}_4\text{F}-4$ as a function of $\Sigma\sigma^0$ of the aryl radical: 1, 4- $(\text{CH}_3)_2\text{NC}_6\text{H}_4$; 2, 4- $\text{CH}_3\text{OC}_6\text{H}_4$; 3, 4- $\text{CH}_3\text{C}_6\text{H}_4$; 4, C_6H_5 ; 5, 4- FC_6H_4 ; 6, 4- ClC_6H_4 ; 7, 3- ClC_6H_4 ; 8, 3,4- $\text{Cl}_2\text{C}_6\text{H}_3$; 9, 3,4,5- $\text{Cl}_3\text{C}_6\text{H}_2$.

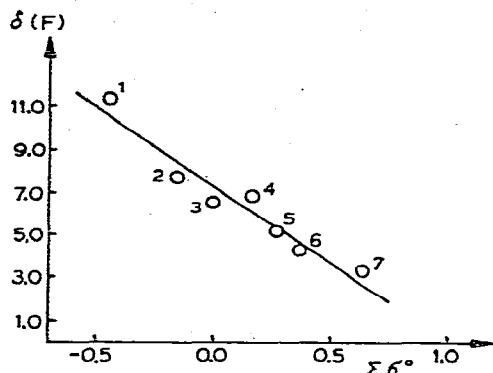


Fig. 3. Fluorine chemical shift in $\text{Ar}_2\text{NC}_6\text{H}_4\text{F}-4$ as a function of $\Sigma\sigma^\circ$ of the aryl radical: 1, $4-(\text{CH}_3)_2\text{NC}_6\text{H}_4$; 2, $4-\text{CH}_3\text{C}_6\text{H}_4$; 3, $4-\text{FC}_6\text{H}_4$; 4, C_6H_5 ; 5, $4-\text{ClC}_6\text{H}_4$; 6, $3-\text{ClC}_6\text{H}_4$; 7, $3,4-\text{Cl}_2\text{C}_6\text{H}_3$.

present [2]. In aromatic organometallic groups of the type $(\text{C}_6\text{H}_5)_2\text{Sb}$ and $(\text{C}_6\text{H}_5)_2\text{Bi}$ the metal is bonded to the aromatic rings directly, so the σ , π -conjugation effect is less probable because the metal-carbon bond orbitals to a small extent overlap with the aromatic ring π -electrons, the small overlap being due to the fact that the carbon-metal bond is longer than the carbon-carbon bond while the metal orbital sizes differ from the carbon orbital sizes. This agrees with the low resonance constants found for the organometallic substituents mentioned [6]. Consequently, electron transmittance of bridged antimony or bismuth is similar to that of bridged tin [4]. In contrast, electron transmittance of aromatic carbon-nitrogen bonds is greatly contributed to by classical resonance effects caused by competitive conjugation of lone pair with aromatic rings and substituents therein. The data obtained here on electron effect transmission through the carbon or nitrogen bridges fit in with the literature data [11,12,4].

The inductive transmission observed in this work for bridged antimony and bismuth atoms may be, generally speaking, caused either by the fact that there is indeed no conjugation of the lone pair and the vacant d -orbitals with the aromatic ring π -electrons, or by mutual compensation of the effects mentioned. The inductive pattern of interactions through aromatic carbon-lead and aromatic carbon-tin bonds [13,14], where the metals involved possess vacant $5d$ or $6d$ orbitals like antimony and bismuth, points to the first alternative. The absence of conjugation of bismuth and antimony lone pairs with aromatic ring π -electrons may, in turn, be due to weak overlapping of the respective orbitals [15] and/or predominant s -character of the lone pair [16]. The latter factor may be thought to prevail if we remember the data on triphenylbismuth geometry [17] and on phosphorus-containing substituents [18].

The correlation coefficients ρ suggest that the aromatic carbon-bismuth bond transmittance is close to that of aliphatic carbon-aromatic carbon bonds and is markedly lower than the aromatic carbon-nitrogen bond transmittance. The aromatic carbon-antimony bond transmittance is probably somewhat higher although the difference observed is not significant at the 95% confidence level. The conclusions arrived at also agree with the slopes of the respective straight lines describing fluorine chemical shifts in the systems with bridged

TABLE 3

CORRELATION EQUATION PARAMETERS, $\delta_F = \rho_I \sigma_I + \rho_R x + C$

n	x	$-\rho_I$	$-\rho_R$	$\lambda \equiv \rho_R / \rho_I$	$S_{\rho I}^a$	$S_{\rho R}$	C	S	R
6	σ_R^0	2.43	2.24	0.92	0.09	0.11	0.14	0.05	0.997
6	σ_R	2.21	1.28	0.58	0.13	0.09	0.23	0.08	0.993
6	σ_R^0	2.96	2.49	0.84	0.20	0.23	3.69	0.12	0.988
6	σ_R	2.64	1.50	0.57	0.22	0.16	3.75	0.14	0.985
5	σ_R^0	6.93	10.15	1.46	0.62	0.79	6.47	0.39	0.989
5	σ_R	5.74	6.09	1.06	0.44	0.35	6.69	0.29	0.994

^a $S_{\rho I}$ = standard error of the coefficient ρ_I ; $S_{\rho R}$ = standard error of the coefficient ρ_R ; S = standard deviation of the points from the plane; R = general correlation coefficient.

nitrogen, antimony, or bismuth atoms as a function of fluorine chemical shifts in diaryl-*p*-fluorotriphenylmethanes (Table 2).

The closeness of the aromatic carbon—bismuth and aliphatic carbon—aromatic carbon transmittances found for the systems under study suggests that there is no increased electronic effect transmission in bismuth-bridged systems compared with the carbon-bridged ones. An increase of the kind might be expected, owing to easier polarizability of electron shells in heavy metals. Its absence may be attributed either to the fact that the transmittances are indeed equal for the σ -bonds under discussion or explained by assuming that electronic effect transmission through a bridged carbon is contributed to not only by inductive polarisation of aliphatic carbon—aromatic carbon σ -bonds but also by some other factors. One of these may be assigned to σ, π -conjugation of C—H and C—C bonds with aromatic ring [19–21]. Its possible contribution to the transmission through bridged carbon has been discussed above. Another factor may be that the transmission in triphenylmethane systems may be due, in part, to direct through-space interaction of aromatic π -electron ring systems [22], absent from triphenylantimony compounds [23]. The latter factor may also play a role in substituted triphenylamines. The higher transmittance of the bridged nitrogen compared with the bridged carbon is, however, undoubtedly due to competitive conjugation of lone pair with aromatic rings.

An attractive problem is a study of electronic effect transmission through the phosphorus or arsenic bridges, in order to find whether the higher transmittance is specific to bridged nitrogen only or if it operates as well in other bridged atoms of the Group VB elements.

Experimental

General comments

Fluorine NMR spectra were recorded on an R-20 Hitachi—Perkin—Elmer spectrometer (56.4 MHz) at 34°C. All measurements were made with dilute (below 0.2 *M*) solution. Chloroform was purified in the standard way and dried by distilling it over phosphorus pentoxide. The fluorine chemical shifts were measured accurately to ± 0.1 ppm.

Symmetrical arylbismuth compounds were obtained from the substituted phenylmagnesium bromides and bismuth tribromide. Tris(*p*-dimethylaminophenyl)bismuth [24] was synthesized by a known method [24] from the aryllithium and bismuth tribromide.

Unsymmetrical diaryl(*p*-fluorophenyl)bismuth compounds were synthesized from *p*-fluorophenylmagnesium bromide and the respective diarylbismuth chlorides or bromides [24,25] obtained by decomposing the triaryl bismuth compounds with bismuth trichloride or tribromide [24]. We failed to synthesize diaryl-*p*-fluorophenylbismuth compounds containing strong electron-acceptor aryl rings (3,4-Cl₂C₆H₃, 3,5-Cl₂C₆H₃, 3,4,5-Cl₃C₆H₂). E.g., *p*-fluorophenylmagnesium bromide, when treated with the product resulting from the interaction of the respective triaryl bismuth with bismuth tribromide, gave nothing but symmetrical triaryl bismuth compounds while the amount of the desired diaryl-*p*-fluorophenylbismuth was shown by ¹⁹F NMR to be insignificant.

Arylbismuth dihalides are known [26] to be unstable. The ¹⁹F NMR method

(continued on p. 194)

TABLE 4

ANALYSES AND PHYSICAL PROPERTIES OF ARYL-BISMUTH AND -ANTIMONY COMPOUNDS AND THEIR NITROGEN- AND CARBON-CONTAINING ANALOGUES

Compound	Solvent	Yield (%)	B.p. or m.p. (°C)	n_D^{22}	R_f in light petroleum	Analyses Found (calcd.) (%)	C	H
$(4\text{-CH}_3\text{C}_6\text{H}_4)_2\text{SbC}_6\text{H}_4\text{F-4}$	methanol	90	95-97		0.7	60.35 (60.19)	60.35 (60.19)	4.37 (4.55)
$(4\text{-ClC}_6\text{H}_4)_2\text{SbC}_6\text{H}_4\text{F-4}$	methanol	80	77-79		0.7	49.24 (49.14)	49.24 (49.14)	2.84 (2.75)
$(3\text{-ClC}_6\text{H}_4)_2\text{SbC}_6\text{H}_4\text{F-4}$		75	oil		0.7	48.54 (49.14)	48.54 (49.14)	2.64 (2.75)
$(3,4,5\text{-Cl}_3\text{C}_6\text{H}_2)_3\text{Sb}$	m-xylene	70	204-205		0.6 ^a	32.24 (32.58)	32.24 (32.58)	1.31 (0.91)
$[4\text{-(CH}_3)_2\text{NC}_6\text{H}_4]_2\text{BiC}_6\text{H}_4\text{F-4}$	benzene/ ethanol	50	116-118		0.5	48.37 (48.53)	48.37 (48.53)	4.56 (4.44)
$(4\text{-CH}_3\text{OC}_6\text{H}_4)_2\text{BiC}_6\text{H}_4\text{F-4}$	methanol	30	137-139		0.3	46.00 (46.14)	46.00 (46.14)	3.57 (3.47)
$(4\text{-CH}_3\text{C}_6\text{H}_4)_2\text{BiC}_6\text{H}_4\text{F-4}$	methanol	73	70-73		0.6	49.73 (49.38)	49.73 (49.38)	3.78 (3.70)
$(4\text{-ClC}_6\text{H}_4)_2\text{BiC}_6\text{H}_4\text{F-4}$	ethanol	87	95-96		0.5	40.55 (41.06)	40.55 (41.06)	2.35 (2.28)
$(3,4\text{-Cl}_2\text{C}_6\text{H}_3)_3\text{Bi}$	cyclohexane	90	131-131.5		0.4 ^a	33.47 (33.38)	33.47 (33.38)	1.56 (1.39)
$(3,4,5\text{-Cl}_3\text{C}_6\text{H}_2)_3\text{Bi}$	pyridine	52	241-243		0.3 ^a	28.73 (28.81)	28.73 (28.81)	1.00 (0.8)
$(3,5\text{-Cl}_2\text{C}_6\text{H}_3)_3\text{Bi}$	octane	50	140-142		0.4 ^a	38.38 (38.38)	38.38 (38.38)	1.34 (1.30)
$[4\text{-(CH}_3)_2\text{NC}_6\text{H}_4]_2\text{CHC}_6\text{H}_4\text{F-4}$	light petroleum	29	100-103			82.70 (82.60)	82.70 (82.60)	7.69 (7.47)

(4-CH ₃ OC ₆ H ₄) ₂ CHC ₆ H ₄ F-4	83	215-220 (1 mmHg)	1.5919	0.1	77.92 (78.24)	5.87 (5.94)
(3-CH ₃ OC ₆ H ₄) ₂ CHC ₆ H ₄ F-4	20	180-187 (7 mmHg)	1.5932	0.1	78.12 (78.24)	5.93 (5.94)
(4-CH ₃ C ₆ H ₄) ₂ CHC ₆ H ₄ F-4	50	196-197 (4 mmHg)	1.5855	0.4	86.81 (86.86)	6.53 (6.60)
(3-CH ₃ C ₆ H ₄) ₂ CHC ₆ H ₄ F-4	19	175-179 (2 mmHg)	1.5890	0.5	86.86 (86.86)	6.73 (6.60)
(4-ClC ₆ H ₄) ₂ CHC ₆ H ₄ F-4	25	170-173 (1 mmHg)	1.6141	0.3	69.22 (69.09)	4.11 (3.97)
(3-ClC ₆ H ₄) ₂ CHC ₆ H ₄ F-4	25	196-197 (1-2 mmHg) sublimation	1.6139	0.4	69.57 (69.09)	4.12 (3.97)
(3,4-Cl ₂ C ₆ H ₃) ₂ CHC ₆ H ₄ F-4	40			0.5	57.19 (57.01)	2.73 (2.77)
(3,5-Cl ₂ C ₆ H ₃) ₂ CHC ₆ H ₄ F-4	29	125-126		0.6	57.56 (57.01)	3.13 (2.77)
(3,4,5-Cl ₃ C ₆ H ₂) ₂ CHC ₆ H ₄ F-4	60	159-160		0.5	48.77 (48.63)	1.88 (1.93)
(3-CF ₃ C ₆ H ₄) ₂ CHC ₆ H ₄ F-4	40	162-164 (4 mmHg)	1.5135	0.6	63.38 (63.32)	3.72 (3.29)
(4-FC ₆ H ₄) ₂ CH	45	56-57		0.6	76.21 (76.50)	4.58 (4.39)
[4-(CH ₃) ₂ NC ₆ H ₄] ₂ NC ₆ H ₄ F-4	46	(dec.)			75.46 (75.62)	7.69 (6.92)
(4-CH ₃ C ₆ H ₄) ₂ NC ₆ H ₄ F-4	50	77-78		0.6	82.53 (82.45)	6.09 (6.23)
(4-ClC ₆ H ₄) ₂ NC ₆ H ₄ F-4	22	89-90		0.5	64.36 (65.07)	3.75 (3.64)
(3-ClC ₆ H ₄) ₂ NC ₆ H ₄ F-4	19	74-76		0.8	64.41 (65.07)	3.75 (3.64)
(3,4-Cl ₂ C ₆ H ₃) ₂ C ₆ H ₄ F-4	10	109-110		0.6	53.57 (53.90)	2.53 (2.51)

^a Eluent: light petroleum ether/acetone (10/1).

helped us to show that tris(*p*-fluorophenyl)bismuth with bismuth tribromide in THF may give a solution of bis(*p*-fluorophenyl)bismuth monobromide or *p*-fluorophenylbismuth dibromide, depending on the reactants ratio. The interaction of two moles of triaryl bismuth with one mole of the tribromide gave the monobromide containing an admixture of the dibromide while the ratio of 1/2 led to *p*-fluorophenylbismuth dibromide exclusively. The latter dibromide acted upon by *p*-tolylmagnesium bromide gave us di-*p*-tolyl(*p*-fluorophenyl)-bismuth synthesised earlier from a di-*p*-tolylbismuth halide.

The attempt to obtain bis(3,4-dichlorophenyl)(*p*-fluorophenyl)bismuth from 3,4-dichlorophenylmagnesium bromide and *p*-fluorophenylbismuth dibromide under the conditions of the synthesis of the *p*-tolyl compound led, however, to a partial arylation product. Carrying the reaction out under more drastic conditions gave symmetrical tris(3,4-dichlorophenyl)bismuth; the NMR spectrum of the reaction mixture revealed tris(*p*-fluorophenyl)bismuth and, probably, (3,4-dichlorophenyl)(*p*-fluorophenyl)bismuth. Similar results were obtained when attempting to synthesize other diaryl(*p*-fluorophenyl)bismuth compounds with strong electron-acceptor aryls.

Diaryl(*p*-fluorophenyl)antimonies were synthesized from *p*-fluorophenylmagnesium bromide and diarylantimony dihalides described in the literature [27–29]. In contrast, the reaction of *p*-fluorophenylantimony dichloride with arylmagnesium bromides (the aryl was 4-CH₃C₆H₄, 4-CH₃OC₆H₄, 3,4,5-Cl₃C₆H₂) led to symmetrical compounds of the triarylantimony type. This complication did not allow us to obtain diaryl(*p*-fluorophenyl)antimony compounds with strong electron-donor or electron-acceptor substituents since we could not synthesize the respective diarylantimony chlorides either.

4,4'-Bis(dimethylamino)-4''-fluorotriphenylmethane and 4,4'-dimethoxy-4''-fluorotriphenylmethane were obtained by a method described [30,31] for the synthesis of the fluorine-free analogues. Other diaryl(*p*-fluorophenyl)methanes were obtained by reducing [32] the respective diaryl(*p*-fluorophenyl)carbinols in situ. The carbinols were synthesized by the action of arylmagnesium bromide on methyl *p*-fluorobenzoate. The reduction course was followed by ¹⁹F NMR techniques and by a sulphuric acid test for triaryl carbinols.

The synthesis of 4,4'-bis(dimethylamino)-4''-fluorotriphenylamine was made by analogy with 4,4'-bis(dimethylamino)triphenylamine described in the literature [33]. 4,4'-Dimethyl-4''-fluorotriphenylamine was obtained by condensing di-*p*-tolylamine with *p*-fluoroiodobenzene. Other substituted 4-fluorotriphenylamines were obtained by condensing *p*-fluoroaniline with the respective substituted iodobenzenes [34]. 3,4-Dichloroiodobenzene was obtained by diazotization of 3,4-dichloroaniline followed by decomposition of the diazonium salt with a potassium iodide solution; 3,4,5-trichloroiodobenzene was prepared from 3,4,5-trichlorophenylmagnesium bromide and iodine.

Purity of the compounds obtained was tested by ¹⁹F NMR and thin-layer chromatography on alumina. Constants and analyses of new compounds are listed in Table 4. Typical syntheses are described below.

4,4'-Bis(dimethylamino)-4''-fluorotriphenylamine

Cuprous iodide (0.0005 mol) and bis(*p*-dimethylamino)phenylamine (0.01 mol) dissolved in 20 ml hot dibutyl ether were added in a special purity argon

atmosphere to a solution of phenyllithium in 20 ml absolute diethyl ether obtained from Li (0.025 g-at) and bromobenzene (0.012 mol). The mixture turned orange and a yellow precipitate was formed after some time. Then, fluorobenzene (0.01 mol) in 10 ml absolute diethyl ether was added and benzene (a reaction product) and diethyl ether were distilled off under stirring. The reaction mixture turned greenish-black when heated. The mixture was refluxed for 1 h, cooled down to a nitrogen sweep, extracted three times with 20 ml portions of 5 N HCl and twice with water, diluted up to 200 ml, and the precipitate formed was filtered off. The filtrate was diluted up to 1 l and carefully treated with a diluted ammonia solution. Shortly before the free base started being visible a small amount of sodium hydrogen sulphite was added in order to protect the amine from auto-oxidation. The greenish-black solution turned yellow in the course of sodium hydrogen sulphate addition. Further addition of ammonia led to a brown precipitate which was isolated and dried in vacuo over phosphorus pentoxide. The yield was 1.6 g (46%). The compound gave light green crystals after recrystallization from heptane.

4,4'-Dimethyl-4"-fluorotriphenylamine

A mixture of di-*p*-tolylamine (3.94 g, 0.02 mol), *p*-fluoroiodobenzene (4.44 g, 0.02 mol), potassium carbonate (3 g), and copper metal powder (0.2 g) was refluxed in 50 ml nitrobenzene for 26 h. The reaction mixture was filtered, nitrobenzene was subjected to steam distillation, the residue was extracted with ether and dried over sodium sulphate. Ether was evaporated, the residual black oil was chromatographed on alumina in light petroleum, to give 3 g (50%) of the light yellow crystals melting at 77–78°C after recrystallization from methanol.

4,4'-Dichloro-4"-fluorotriphenylamine

A mixture of *p*-chloroiodobenzene (40.7 g, 0.18 mol), *p*-fluoroaniline (9.43 g, 0.085 mol), copper metal powder (0.8 g), and potassium carbonate (12.8 g) was refluxed in 90 ml nitrobenzene for 23 h. The reaction mixture was filtered, nitrobenzene was subjected to steam distillation, the residue was extracted with ether and dried over sodium sulphate. Ether was evaporated, and the residual violet oil was chromatographed on alumina in light petroleum to give 6.1 g (22%) of the yellow crystalline compound melting at 89–90°C after recrystallization from methanol.

1-Iodo-3,4-dichlorobenzene

3,4-Dichloroaniline (38.9 g, 0.24 mol) was added to a mixture of concentrated HCl (60 ml, 0.75 mol) and 60 ml water. The reaction mixture was cooled down to 0°C and a cold solution of sodium nitrite (17.3 g, 0.24 mol) in 40 ml water was slowly added, with the reaction temperature being kept at 0–5°C. The resulting diazonium solution was poured into a solution of potassium iodide (43.2 g, 0.26 mol) in water and left overnight. The product was subjected to steam distillation, and the precipitate was filtered to give 74 g (97%) of the white crystalline compound melting at 30–32°C after recrystallization from ethanol. Found: C, 26.33; H, 1.13. Calcd.: C, 26.49; H, 1.11%.

1-Iodo-3,4,5-trichlorobenzene

A solution of 3,4,5-trichlorophenylmagnesium bromide, obtained from 1-bromo-3,4,5-trichlorobenzene (13 g, 0.05 mol) and magnesium metal (1.32 g, 0.055 mol) in 60 ml diethyl ether, was added to a solution of iodine (12.7 g, 0.01 mol) in 50 ml of the same solvent. The reaction mixture was refluxed for 1 h, treated with saturated aqueous ammonium chloride, the ether layer was separated and washed with a solution of $\text{Na}_2\text{S}_2\text{O}_3$ in water, the ether was evaporated, and the residue was subjected to steam distillation. 12.3 g (80%) of the compound were obtained, white nacreous crystals (m.p. 46–48°C) after recrystallization from methanol. Found: C, 23.54; H, 0.66. Calcd.: C, 23.44; H, 0.66%.

4,4'-Dimethylamino-4''-fluorotriphenylmethane

A mixture of *p*-fluorobenzaldehyde (5.58 g, 0.045 mol), dimethylaniline (12.72 g, 0.105 mol), and zinc chloride (12.5 g, 0.09 mol) was refluxed in 300 ml ethanol for 9 h in a nitrogen sweep. Ethanol was evaporated, the green residue was washed with water, and the unreacted materials were subjected to steam distillation. The residue was extracted with light petroleum, dried over CaCl_2 , and the ether was evaporated to give 4.4 g (29%) of the compound, white crystals (m.p. 100–103°C), after recrystallization from light petroleum. The compound rapidly turns green in air.

4,4'-Dimethoxy-4''-fluorotriphenylamine

A mixture of 50 g concentrated H_2SO_4 and 20 g CH_3COOH , cooled down to 0°C, was carefully added to a deeply cooled mixture of anisole (5.36 g, 0.045 mol), *p*-fluorobenzaldehyde (2.85 g, 0.023 mol), and 7.5 g CH_3COOH . The reaction mixture was stirred at 0°C for 4 h, poured into ice, the pink oil formed was separated, and the unreacted materials were subjected to steam distillation. The residue was extracted with light petroleum, dried over calcium chloride, and the ether was evaporated to give 6 g (82.2%) of a colourless oil distilled in a nitrogen atmosphere at 220°C and 1 mmHg.

4,4'-Dimethyl-4''-fluorotriphenylmethane

A solution of methyl *p*-fluorobenzoate in 20 ml absolute ether was added to a solution of *p*-tolylmagnesium bromide obtained from *p*-bromotoluene (13.7 g, 0.08 mol) and magnesium metal (2 g, 0.08 mol) in 30 ml of the same solvent. The mixture turned orange-yellow and heated a little spontaneously. It was heated up to 38°C for 4 h, and a voluminous yellow precipitate was formed in 1/2 h from the beginning of the heating. The mixture was treated with saturated aqueous ammonium chloride, extracted with ether, the ether was evaporated, and the unreacted species were subjected to steam distillation. The residual very viscous yellow oil was dissolved in 20 ml CH_3COOH saturated by hydrogen iodide gas under cooling of the solution. The solution became dark-brown immediately, it was heated up to boiling point, cooled down by cold water at once, and poured into a diluted solution Na_2SO_3 in water. The oil formed was extracted with ether, washed with water, alkali, water again, and dried over calcium chloride. Ether was evaporated, to give 6.8 g of a brown oil distilled in a nitrogen-sweep at 196–197°C at 3–4 mmHg. 4,4'-Dimethyl-4''-fluorotriphenylamine was isolated as a light-yellow viscous oil, n_D^{22} 1.5865.

Interaction of p-fluorophenylantimony dichloride with p-chlorophenylmagnesium bromide

A suspension of *p*-fluorophenylantimony dichloride (1.9 g, 0.006 mol, [35]) in 20 ml absolute ether was added, under stirring and cooling of the reaction mixture, to a solution of *p*-chlorophenylmagnesium bromide obtained from *p*-chlorobromobenzene (2.5 g, 0.013 mol) and magnesium metal (0.33 g, 0.014 mol) in 30 ml absolute ether. The precipitate dissolved spontaneously and a brown oil was formed. The reaction mixture was refluxed for 4 h, treated with saturated aqueous ammonium chloride, the ether layer was separated and dried over calcium chloride. Ether was evaporated to give 1.6 g of a yellow oil which crystallized after triturating it with methanol and melted at 90–92°C after two recrystallizations from the solvent. No fluorine resonances were found in the NMR spectrum. The analysis corresponds to tris(*p*-chlorophenyl)antimony. Found: C, 47.44; H, 2.87. Calcd.: C, 47.36; H, 2.65%.

Interaction of p-fluorophenylbismuth dibromide with 3,4-dichlorophenylmagnesium bromide

A solution of bismuth tribromide (3.1 g, 0.007 mol) in 15 ml absolute THF was added to a solution of tris(*p*-fluorophenyl)bismuth (1.6 g, 0.0035 mol) in 10 ml of the same solvent. The reaction mixture was kept in the dark at room temperature for 1/2 h. The resulting *p*-fluorophenylbismuth dibromide was added, under cooling and intensive stirring of the reaction mixture, to a solution of 3,4-dichlorophenylmagnesium bromide obtained from 3,4-dichlorobenzene (4.52 g, 0.02 mol) and magnesium metal (0.5 g, 0.02 mol) in 50 ml absolute THF. A yellow precipitate was formed which dissolved rapidly to colour the solution bright yellow. The reaction mixture was heated at 70°C for 2 h, the solvent was evaporated, the residue was heated at 100°C for 3 h more, cooled down, treated with saturated aqueous ammonium chloride, and extracted several times with ether. The solvent was removed to give 2.6 g of a yellow oil whose NMR spectrum revealed weak signals assignable to the respective tris(*p*-fluorophenyl)bismuth (–0.2 ppm) and, probably, bis(3,4-dichlorophenyl)-*p*-fluorophenylbismuth (–1.62 ppm). In time the oil crystallized spontaneously, the resulting solid melted in part at 130–170°C, in part above 200°C. It was treated with hot chloroform, the chloroform extract gave a white solid, m.p. 117–120°C, containing no fluorine signals in the NMR spectrum. After recrystallizing it from heptane and alcohol the white solid revealed no melting point depression with tris(3,4-dichlorophenyl)bismuth. The fraction insoluble in hot chloroform was coloured black when treated with Na₂S, indicative of the formation of Bi₂S₃. This is characteristic of incompletely-substituted organobismuth compounds of the type Ar_nBiX_{3-n}, and not characteristic of Ar₃Bi compounds.

Bis(p-dimethylaminophenyl)(p-fluorophenyl)bismuth

A suspension of bis(*p*-dimethylamino)phenylbismuth bromide in absolute THF, obtained from a solution of tris(*p*-dimethylaminophenyl)bismuth (5.12 g, 0.009 mol) in 50 ml absolute THF and a solution of bismuth tribromide (1.97 g, 0.0044 mol) in 10 ml of the same solvent, was added in a nitrogen atmosphere to a solution of *p*-fluorophenylmagnesium bromide in absolute THF, obtained from *p*-fluorobromobenzene (8.3 g, 0.041 mol) and magnesium metal (1.2 g,

0.042 mol). The reaction mixture was heated up to 50°C for 5 h, cooled in a nitrogen atmosphere, treated with saturated aqueous ammonium chloride, extracted with ether, and dried over sodium sulphate. Ether was evaporated, to give 5.1 g of a brown oil which, on refluxing with light petroleum, yielded a white crystalline precipitate (4 g, 50%), m.p. 116–118°C after recrystallization from a 5/1 ethanol/benzene mixture.

Di-(p-tolyl)(p-fluorophenyl)bismuth

A solution of *p*-fluorophenylmagnesium bromide obtained from *p*-fluorobromobenzene (2.27 g, 0.013 mol) and magnesium metal (0.36 g, 0.015 mol) in 20 ml absolute ether was added in a nitrogen atmosphere to a cold (0°C) suspension of di-*p*-tolylbismuth chloride (4.26 g, 0.01 mol) in 20 ml absolute ether. The reaction mixture was stirred at 0°C for 3 h, treated with saturated aqueous ammonium chloride, the ether layer was separated, filtered from a thin precipitate, dried over CaCl₂, and the ether was evaporated. The residue was a yellow oil crystallizable on triturating with methanol. 3.6 g (73%) of the compound was obtained melting at 70–78°C after recrystallization from methanol.

Tris(3,4,5-trichlorophenyl)bismuth

A solution of bismuth tribromide (13.02 g, 0.029 mol) in 50 ml absolute ether was added to an ether solution of 3,4,5-trichlorophenylmagnesium iodide obtained from 3,4,5-trichloriodobenzene (22.2 g, 0.09 mol) and magnesium metal (2.4 g, 0.09 mol) in 100 ml absolute ether. The reaction mixture heated a little spontaneously. It was treated with saturated aqueous ammonium chloride, and the precipitate formed was extracted with hot pyridine. Cooling the pyridine solution down gave 11.4 g (52%) of the compound, white crystals melting at 241–243°C after recrystallization from pyridine.

Tris(3,5-dichlorophenyl)bismuth

A solution of bismuth tribromide (9.88 g, 0.022 mol) in 30 ml absolute ether was added to an ether solution of 3,5-dichlorophenylmagnesium bromide obtained from 3,5-dichlorobromobenzene (16.6 g, 0.073 mol) and magnesium metal (2.06 g, 0.086 mol) in 80 ml absolute ether. Slight spontaneous heating was observed, and the colour changed from yellow to red. Ether was distilled off, the residue was heated at 100°C for 5 h treated with saturated aqueous ammonium chloride, filtered, the precipitate was extracted with hot chloroform, and the chloroform was removed to leave a dark oil which crystallized on triturating it with light petroleum. The yield was 5.5 g (50%), and the compound was recrystallized from octane to give white nacreous leaves melting at 190–192°C.

Bis(m-chlorophenyl)(p-fluorophenyl)antimony

A solution of bis(*m*-chlorophenyl)antimony (85 g, 0.02 mol) in 50 ml absolute ether was gradually added, under vigorous stirring of the mixture and cooling with ice, to an ether solution of *p*-fluorophenylmagnesium bromide obtained from *p*-fluorobromobenzene (3.7 g, 0.021 mol) in 25 ml absolute ether and magnesium metal (0.53 g, 0.022 mol) in 20 ml absolute ether. The reaction mixture turned bright yellow and a white precipitate was formed. Heating it at 40°C for 1 h transformed the precipitate to a black oil. The mixture was heated

at 40°C for 2 h more, cooled down to 0°C, treated with saturated aqueous ammonium chloride, the ether layer was separated, and the ether was removed to give bis(*m*-chlorophenyl)-*p*-fluorophenylantimony, 6.4 g (75%) of a brown oil, purified by chromatographing it on a thick layer of anhydrous alumina in a 10/1 light petroleum/acetone mixture.

Di-*p*-tolyl-*p*-fluorophenylantimony and bis(*p*-chlorophenyl)-*p*-fluorophenylantimony were synthesized in a similar way.

Tris(3,4,5-trichlorophenyl)antimony

Antimony trichloride (2.28 g, 0.01 mol) in 50 ml dry benzene was carefully added, under vigorous stirring of the mixture and cooling, to the Grignard reagent obtained from 3,4,5-trichlorobromobenzene (7.8 g, 0.03 mol) in 50 ml absolute ether and magnesium metal (0.7 g, 0.03 mol) in 30 ml of the same solvent. The reaction mixture was refluxed for 6 h, and a white precipitate gradually formed. The reaction mixture was treated with saturated aqueous ammonium chloride, the precipitate was separated, dissolved in chloroform, and reprecipitated with methanol to give tris(3,4,5-trichlorophenyl)antimony, 4.5 g (70%) of white crystals melting at 204–205°C after recrystallization from xylene.

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