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A ^{19}F NMR STUDY OF THE TRANSMISSION OF ELECTRONIC EFFECTS IN TRIARYLPHOSPHINES

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Summary

The nature and efficiency of transmission of electronic effects of substituents through the bridging phosphorus atom in systems of the $\text{Ar}_2\text{PC}_6\text{H}_4\text{F}$ -4 type have been investigated by ^{19}F NMR. Correlation of the obtained data on the fluorine chemical shifts in triarylphosphines with those in the corresponding triaryl-methanes and tetraarylsilanes indicated that the bridging phosphorus atom shows a higher transmitting ability than carbon and silicon. On the basis of the data on two-parameter correlation of the fluorine chemical shifts with the inductive (σ_I) and resonance (σ_R) parameters of the substituents in the aromatic rings for systems with bridged phosphorus, carbon, silicon, tin, nitrogen, and bismuth atoms it has been established that phosphorus occupies an intermediate position between nitrogen and bismuth as regards the nature of transmission of electronic effects, i.e. interactions through the $\text{P}-\text{C}_{\text{ar}}$ bonds occur both by an inductive and, to some extent, a resonance mechanism.

The distinguishing feature of the electron structure of the elements of Group VB in the trivalent state is the presence of a lone electron pair in their valency shells which can, in principle, undergo resonance interactions with adjacent π -electron systems and impart to these atoms properties of increased electron transmittance. Judging by the available data, in the case of diaryl and triaryl derivatives of Group VB elements this property is indeed manifested by nitrogen, an element of the second Period [1,2], and is entirely absent in the case of antimony and bismuth, "heavy" elements of Periods IV and V [2,3], which behave similarly to the carbon atom [1,2].

Therefore it seemed of great interest to investigate the nature of transmission of electronic effects of substituents through the bridging trivalent phosphorus atom in the triarylphosphine system, for which purpose it was proposed to apply ^{19}F NMR, as before [1,3].

TABLE 1

FLUORINE CHEMICAL SHIFTS IN DIARYL-*p*-FLUOROPHENYLPHOSPHINES IN CHCl₃ RELATIVE TO INTERNAL C₆H₅F

Compound	¹⁹ F chemical shift (ppm)
(4-(CH ₃) ₂ NC ₆ H ₄) ₂ PC ₆ H ₄ F-4	1.2
(4-CH ₃ C ₆ H ₄) ₂ PC ₆ H ₄ F-4	-0.5
(3-CH ₃ C ₆ H ₄) ₂ PC ₆ H ₄ F-4	-0.7
(C ₆ H ₅) ₂ PC ₆ H ₄ F-4	-1.0
(4-FC ₆ H ₄) ₂ PC ₆ H ₄ F-4	-1.3
(3-PC ₆ H ₄) ₂ PC ₆ H ₄ F-4	-1.9
(4-ClC ₆ H ₄) ₂ PC ₆ H ₄ F-4	-1.7
(3-ClC ₆ H ₄) ₂ PC ₆ H ₄ F-4	-2.4
(3,4-Cl ₂ C ₆ H ₃) ₂ PC ₆ H ₄ F-4	-3.1
(3,4,5-Cl ₃ C ₆ H ₂) ₂ PC ₆ H ₄ F-4	-4.4

For this purpose we synthesized a number of model compounds of the type Ar₂PC₆H₄F-4 (where Ar = 4-(CH₃)₂NC₆H₄, 4-CH₃C₆H₄, 3-CH₃C₆H₄, C₆H₅, 4-FC₆H₄, 3-FC₆H₄, 4-ClC₆H₄, 3-ClC₆H₄, 3,4-Cl₂C₆H₃, 3,4,5-Cl₃C₆H₂) and determined the fluorine chemical shifts in these relative to internal fluorobenzene in 0.2 M solutions in CHCl₃ (Table 1).

Consideration of the data obtained shows that the fluorine chemical shifts in the diaryl-*p*-fluorophenylphosphines investigated substantially depend on the nature of the substituents in the aromatic rings. The range of variation of the chemical shifts in going from acceptor substituents to donor ones is 5.6 ppm. [

To establish the nature of transmission of electronic effects through the bridging fluorine atom we correlated the fluorine chemical shifts with the polar constants of the substituents in the aromatic rings, which characterize the electronic effect of a mono- and polysubstituted aromatic radical in the presence (σ [4]) or in the absence (σ° [5]) of resonance interactions of the substituent in the aromatic ring with the indicator centre (Table 2).

From the data of Table 2 it follows that in passing from the constants $\Sigma\sigma^\circ$ to $\Sigma\sigma$ the quality of the correlation dependences obtained improves slightly, but the difference detected is not so pronounced as in the case of diaryl-*p*-fluorophenylmethanes, for which the fluorine chemical shifts yield appreciably better correlation with the constants $\Sigma\sigma^\circ$ than with the constants $\Sigma\sigma$, or in the case of diaryl-*p*-fluorophenylamines, for which the situation is reversed [2]. Therefore in this case it cannot be asserted with confidence that the constants σ reflect best the electronic effects of the substituents on the fluorine chemical shifts in the indicator fluorophenyl grouping and, hence, the transmission of electronic effects through the phosphorus bonds — aromatic carbon occurs both by an inductive and a resonance mechanism.

To verify this hypothesis we compared with the aid of the statistical criterion of the equality of two values [6], the transmitting abilities of the bridging phosphorus, carbon, and silicon atoms in diaryl-*p*-fluorophenylphosphines and the previously investigated diaryl-*p*-fluorophenylmethanes [2] and in triaryl-*p*-fluorophenylsilanes [7] (Table 2). In comparing the values of ρ characterizing the ease of transmission of electronic effects in organophosphorus and organosilicon

TABLE 2

PARAMETERS OF CORRELATION EQUATION $y = \rho x + c$ ^a

System	x	y	n	ρ	s_ρ	$\Delta\rho$	$\Delta\rho\%$	c	S_c	S	R
$\text{Ar}_2\text{PC}_6\text{H}_4\text{F}-4$	δ_{F}	$\Sigma\sigma^c$	10	-3.66	0.18	0.41	11	-0.78	0.08	0.22	0.990
$\text{Ar}_2\text{PC}_6\text{H}_4\text{F}-4$	δ_{F}	$\Sigma\sigma$	10	-3.35	0.12	0.28	8	-0.94	0.06	0.16	0.997
$\text{Ar}_3\text{SiC}_6\text{H}_4\text{F}-4$	δ_{F}	$\Sigma\sigma$	11	-3.67	0.22	0.49	13	-2.61	0.09	0.30	0.981
$\text{Ar}_2\text{PC}_6\text{H}_4\text{F}-4$ (I)	δ_{F} (II)	δ_{F} (I)	10	0.90 (1.35) ^b	0.06	0.14 (0.20) ^b	15	1.32	0.22	0.30	0.983
$\text{Ar}_3\text{SiC}_6\text{H}_4\text{F}-4$ (II)											
$\text{Ar}_2\text{CHC}_6\text{H}_4\text{F}-4$	δ_{F}	$\Sigma\sigma$	13	-2.68	0.16	0.35	13	3.52	0.06	0.24	0.977
$\text{Ar}_2\text{PC}_6\text{H}_4\text{F}-4$ (I)											
$\text{Ar}_2\text{CHC}_6\text{H}_4\text{F}-4$ (II)	δ_{F} (II)	δ_{F} (I)	10	1.28	0.10	0.23	18	-5.45	0.12	0.35	0.985

^a n = the number of points; s = the standard deviation of the points from the straight line; S_c = the standard deviation of the coefficient c; S_ρ = the standard deviation of the coefficient ρ ; $\Delta\rho$ = the absolute error of determination of the coefficient ρ for the 95% confidence level; $\Delta\rho\%$ = the relative error of determining of the coefficient ρ for the 95% confidence level; R = the correlation coefficient. ^b The value of ρ calculated from the additive scheme.

TABLE 3

PARAMETERS OF THE CORRELATION EQUATION $\delta_{\text{F}19} = \rho_1\sigma_1 + \rho_2\sigma_2 + c$ ^a

	n	$-\rho_1$	$-\rho_2$	$\lambda \equiv \rho_1/\rho_2$	S_{ρ_1}	S_{ρ_2}	c	S	R
$(4\text{-XC}_6\text{H}_4)_2\text{CHC}_6\text{H}_4\text{F}-4$	6	2.64	1.50	0.57	0.12	0.16	3.75	0.14	0.985
$(4\text{-XC}_6\text{H}_4)_3\text{SiC}_6\text{H}_4\text{F}-4$	6	3.71	2.08	0.56	0.19	0.14	-2.20	0.14	0.994
$(4\text{-XC}_6\text{H}_4)_3\text{SnC}_6\text{H}_4\text{F}-4$	6	3.31	1.92	0.58	0.03	0.10	-1.51	0.08	0.997
$(4\text{-XC}_6\text{H}_4)_2\text{BIC}_6\text{H}_4\text{F}-4$	6	2.21	1.28	0.58	0.13	0.09	0.23	0.08	0.993
$(4\text{-XC}_6\text{H}_4)_2\text{NC}_6\text{H}_4\text{F}-4$	5	5.74	6.09	1.06	0.44	0.35	6.69	0.29	0.994
$(4\text{-XC}_6\text{H}_4)_2\text{PC}_6\text{H}_4\text{F}-4$	5	3.13	2.80	0.89	0.07	0.06	-0.95	0.06	0.999

^a n = the number of points; S = the standard deviation of the points from the plane; S_{ρ_1} = the standard deviation of the coefficient ρ_1 ; S_{ρ_2} = the standard deviation of the coefficient ρ_2 ; R = the correlation coefficient.

systems we took into consideration that the bridging silicon atom, as distinguished from phosphorus, transmits the effect of three, and not two, varied substituents. Therefore, if the additivity principle is valid and also if the transmitting abilities of the phosphorus and silicon atoms had been equal, the value of the coefficient ρ for the former should have been 2/3 of the silicon coefficient, namely -2.45 ± 0.16 . The substantially higher value of the slope ($\rho = -3.35 \pm 0.28$) of the correlation line actually obtained, seems to indicate that the phosphorus atom possesses a higher efficiency with respect to transmission of electronic effects of the substituents than the silicon atom. This is also supported by the larger-than-unity value of the coefficient $\rho = 1.35 \pm 0.14$ (due allowance being made for the correction of 1.5 introduced according to the additivity principle) for the correlation dependence, which establishes the relationship between the fluorine chemical shifts in triarylphosphines and tetraarylsilanes.

In addition, on the basis of the tabulated quantitative data (Table 2) it can be asserted with 95% confidence that the bridging phosphorus atom ($\rho(-P-) = -3.35 \pm 0.28$) exceeds the methine group ($\rho(-CH-) = -2.68 \pm 0.35$) as well in its transmitting ability.

Since transmission of the electronic effects through the aliphatic carbon—aromatic carbon bonds occurs mainly by an inductive mechanism [2,8], the better transmission properties of phosphorus as compared with the methine group may be attributed to the contribution of the resonance interactions to the overall mechanism of transmission of electronic effects through the bridging phosphorus atom. The possibility of partial transmission of electronic effects in the triarylmethane series by direct interaction between the electron systems of the aromatic rings [9] and the absence of such interaction in compounds of the triphenylphosphine type [10] must result in a still greater difference of the true transmitting abilities of the aliphatic carbon—aromatic carbon and phosphorus—aromatic carbon bonds.

Proceeding from the fact that phosphorus and silicon atoms are the closest neighbours in the Period III and possess identical vacant $3d$ -orbitals, which (as shown for tetraarylsilanes [7]) do not take any substantial part in transmission of electronic effects, it may be assumed that in the case of the bridging phosphorus atom the lone pair takes some part in resonance interactions.

At the same time, in discussing the possible causes for the increased transmitting ability of phosphorus as compared with silicon and carbon one must take into account the fact that the polarizability of the electron shell of phosphorus is slightly higher, as witnessed by the atomic refraction data [11]. Thus it is impossible to give preference exclusively either to the contribution of the resonance interactions, or to the increased polarizability of the electron shell, which explain the behaviour of the bridging phosphorus atom, on the basis of the data of one-parameter correlation treatment.

Therefore we applied the method of two-parameter correlation of fluorine chemical shifts with the inductive and resonance parameters of the substituents in the aromatic rings [12] for the systems with bridging atoms of phosphorus, carbon, silicon, tin [13], nitrogen, and bismuth (Table 3). In applying this method we found an interesting regularity in the values of λ , which characterize the relative contribution of the resonance component to the overall transmission

of electronic effects through the element—aromatic carbon bonds.

Thus, for all the bridging atoms (C, Si, Sn, Bi) through which (as was established previously) the electronic effects are transmitted mainly by an inductive mechanism, the value of λ remains practically unchanged and is equal to 0.56–0.58. The value of λ found exceeds unity ($\lambda = 1.06$) for the bridging nitrogen atom, in the case of which the resonance interactions due to conjugation of the lone pair with the aromatic rings are of great importance for the transmission of the electronic effects. Finally, for phosphorus the value of λ is approximately equal to the arithmetical mean of the two indicated values ($\lambda = 0.89$).

From the above data it can be assumed that as to the character of transmission of electronic effects the bridging phosphorus atom in triarylphosphines occupies an intermediate position between nitrogen, on the one hand, and bismuth, on the other, and interactions through the phosphorus—aromatic carbon bonds proceed both by an inductive and, to some extent, by a resonance mechanism. It is probably due to this that phosphorus shows an increased transmissive ability as compared with the nontransition elements of Periods III and higher of Groups IVB and VB.

In conclusion it should be noted that in order to improve the statistical validity of our conclusions it would undoubtedly be of interest to investigate the transmission of the electronic effects in systems of the triarylboron type and in aryl derivatives of germanium, arsenic, and lead.

Experimental

^{19}F NMR spectra were taken on an R-20 Hitachi—Perkin—Elmer spectrometer (56.4 MHz) at 34°C. All measurements were made for dilute solutions at a concentration not exceeding 0.2 *M*. The fluorine chemical shifts were determined with the use of the substitution method [14]. The experimental error in determining the fluorine chemical shift did not exceed ± 0.1 ppm. The solvent was chloroform, which was purified by the standard procedure and distilled over phosphorus pentoxide.

Tris(*p*-fluorophenyl)phosphine was obtained by reacting *p*-fluorophenylmagnesiumbromide with phosphorus trichloride [15]. Unsymmetric diaryl-*p*-fluorophenylphosphine and, in particular, the diphenyl- and bis(*m*-fluorophenyl)-*p*-fluorophenylphosphine described in the literature [16], were obtained by the reaction of the corresponding arylmagnesiumbromides or aryllithium with *p*-fluorophenyldichlorophosphine, synthesized from phosphorus trichloride and fluorobenzene in the presence of AlCl_3 [17].

The purity of the compounds investigated and the intermediate products was controlled with the aid of fluorine NMR, mass spectroscopy, and thin-layer chromatography on aluminium oxide.

Below we give typical examples of syntheses of diaryl-*p*-fluorophenylphosphines. The analytical data and the physical characteristics of the compounds obtained are given in Table 4.

Bis(p-dimethylaminophenyl)-p-fluorophenylphosphine

A solution of 1.97 g (0.01 mol) *p*-fluorophenyldichlorophosphine in 20 ml abs. ether was added in an atmosphere of dry argon, on cooling, to a solution

TABLE 4
ANALYTICAL DATA AND PHYSICAL PROPERTIES OF DIARYL-*p*-FLUOROPHENYLPHOSPHINES

Compound	Yield (%)	B.p. (°C/mmHg) or m.p. (°C)	R_f^a	m/e	Analysis Found (calc.) (%)		
					C	H	H
[4-(CH ₃) ₂ NC ₆ H ₄] ₂ PC ₆ H ₄ F-4	31	136-138 (methanol)		366	71.76 (72.11)	6.54 (6.60)	5.87 ^b (5.18)
(4-CH ₃ C ₆ H ₄) ₂ PC ₆ H ₄ F-4	31	67-9 (methanol)	0.6	308	77.54 (77.90)	5.80 (5.83)	9.94 (10.04)
(3-CH ₃ C ₆ H ₄) ₂ PC ₆ H ₄ F-4	77	220-30/1	0.7	308	77.26 (77.90)	5.78 (5.88)	9.85 (10.04)
(4-ClC ₆ H ₄) ₂ PC ₆ H ₄ F-4	46	230-5/1	0.6	349	61.97 (61.91)	3.68 (3.48)	8.79 (8.84)
(3-ClC ₆ H ₄) ₂ PC ₆ H ₄ F-4	31	208-13/2	0.7	349	62.36 (61.91)	3.92 (3.48)	5.64 (5.44)
(3,4-Cl ₂ C ₆ H ₃) ₂ PC ₆ H ₄ F-4	76	93-4 (methanol)	0.6	418	51.79 (51.71)	2.53 (2.41)	7.46 (7.41)
(3,4,5-Cl ₃ C ₆ H ₂) ₂ PC ₆ H ₄ F-4	50	130-2 (propanol)	0.7	486	43.86 (44.39)	1.74 (1.65)	6.46 (6.36)

^a Eluent, petroleum ether : ethylacetate = 50 : 1. ^b Analysis for F.

of *p*-dimethylaminophenyllithium in 50 ml abs. ether obtained from 0.45 g (0.064 g-at) Li and 6.4 g (0.032 mol) *p*-bromodimethylaniline. After stirring for 40 min at room temperature the reaction mixture was decomposed with a saturated aqueous solution of NH_4Cl . The ether layer was separated and extracted with an excess of dilute HCl (1 : 1). The hydrochloric acid extract was neutralized with concentrated NH_4OH and repeatedly extracted with chloroform, and the organic layer was separated and dried with Na_2SO_4 . On removal of the solvent a green oil was obtained which crystallized on treatment with MeOH. Upon crystallization 1.1 g of a white powderlike substance with m.p. 136–38°C (MeOH) was isolated.

Bis(p-tolyl)-p-fluorophenylphosphine

A solution of 1.97 g (0.01 mol) *p*-fluorophenyldichlorophosphine in 20 ml abs. ether was added in an argon atmosphere to a solution of *p*-tolylmagnesiumbromide in 50 ml abs. ether obtained from 5.13 g (0.03 mol) *p*-bromotoluene and 0.72 g (0.03 mol) magnesium and cooled to -50°C . The temperature of the reaction mixture was gradually brought up to room temperature, and stirring was continued for 1 h. After boiling for 2 h the reaction mass was decomposed with a saturated aqueous solution of NH_4Cl , the ether layer was separated and dried with Na_2SO_4 , the ether was removed, and the residue was distilled in vacuo in an atmosphere of dry argon. 0.95 g light yellow oil with a b.p. of 217–27°C/2 mmHg was obtained, which crystallized after chromatographing in a thick layer of Al_2O_3 (eluent, petroleum ether : ethylacetate = 50:1, $R_f = 0.6$). *Bis(p-tolyl)-p-fluorophenylphosphine* was isolated as white crystals with a m.p. of 67–9°C (MeOH).

Bis(3,4,5-trichlorophenyl)-p-fluorophenylphosphine, *bis(m-chlorophenyl)-p-fluorophenylphosphine*, and *bis(3,4-dichlorophenyl)-p-fluorophenylphosphine* were obtained in a similar way.

Bis(m-tolyl)-p-fluorophenylphosphine

A solution of 4.9 g (0.031 mol) *m*-bromotoluene in 20 ml abs. ether was added in an atmosphere of dry argon to a suspension of 0.43 g (0.062 g-at) Li in 30 ml abs. ether. After stirring for 40 min the unreacted lithium was filtered and a solution of 1.97 g (0.01 mol) *p*-fluorophenyldichlorophosphine in 20 ml abs. ether was added to the filtrate cooled to 0°C . After boiling for 2 h the reaction mixture was decomposed with a saturated aqueous solution of NH_4Cl , and the ether layer was dried with Na_2SO_4 . Upon removal of the solvent and distillation in vacuo in an atmosphere of dry argon at 220–30°C/ \times mmHg 2.4 g of *bis(m-tolyl)-p-fluorophenylphosphine* was obtained, which after chromatographing on Al_2O_3 (eluent, petroleum ether: ethylacetate = 50 : 1; $R_f = 0.7$), appeared as a light yellow transparent oil.

Bis(p-chlorophenyl)-p-fluorophenylphosphine

A solution of 5.75 g (0.03 mol) *p*-chlorobromobenzene in 20 ml abs. ether was added gradually in an argon atmosphere to a solution of butyllithium in 50 ml abs. ether obtained from 3.9 g (0.042 mol) butyl chloride and 0.7 g (0.1 g-at) Li and cooled to -50 – 70°C . After stirring for 1 h at the same temperature a solution of 1.97 g (0.01 mol) *p*-fluorophenyldichlorophosphine in 20 ml abs.

ether was added. Upon stirring at room temperature for 1 h and boiling for 4 h the reaction mixture was decomposed with a saturated aqueous solution of NH_4Cl , the ether layer was dried with Na_2SO_4 , the ether was removed, and the residue was distilled in vacuo in an argon atmosphere. 16 g of a viscous light green oil with a b.p. of $290-5^\circ\text{C}/1\text{ mmHg}$ was obtained, which was purified by chromatography on Al_2O_3 (eluent, petroleum ether : ethylacetate = 50 : 1, $R_f = 0.6$).

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