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^{19}F AND ^{31}P NMR SUBSTITUENT EFFECTS IN THE *N*-ARYL-, *N*-(TRIARYLMETHYL)-, AND *N*-(TRIARYLSILYL)-TRIARYLPHOSPHINIMINES

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Summary

Substituent effects in the *N*-aryl-, *N*-(triarylmethyl)-, and *N*-(triarylsilyl)-triarylphosphinimines have been investigated by ^{19}F and ^{31}P NMR.

The *para* ^{19}F substituent chemical shift (SCS) of the *N*-(*p*-fluorophenyl)-triarylphosphinimines show that the triarylphosphinimine group is a good supplier of electron density by induction and by resonance. ^{31}P SCS indicate that in the protonation of *N*-(*p*-fluorophenyl)-tris(*p*-methoxyphenyl)phosphinimine, the positive charge is localized on the phosphorus atom.

Interposition of a $Ph_2C=$ group between the fluorophenyl and the triarylphosphinimine groups in the above compounds produces a deshielding of the *para* ^{19}F nucleus, which is attributed to loss of resonance. Interposition of a $Ph_2Si=$ group between the above groups produces a large deshielding effect, which is best explained by the withdrawing of electron density into vacant silicon acceptor orbitals.

The silicon *para* ^{19}F phenyl SCS of the *N*-(triarylsilyl)triarylphosphinimines do not show evidence supporting a resonance structure between silicon and nitrogen.

The range of the silicon *para* ^{19}F phenyl SCS in the series of compounds $FC_6H_4SiPh_2—N=P(C_6H_4Y)_3$, where Y is H, OCH_3, F, or Cl is over 1 ppm and the ^{19}F shift on changing substituent Y is concentration independent. The deshielding of the phosphorus *para* fluorophenyl groups vs. the *meta* fluoro groups may be explained by a mechanism similar to that advanced for the silicon fluorophenyl group; namely, withdrawing of electron density into vacant phosphorus acceptor orbitals.

^{31}P SCS of the *N*-(triarylsilyl)triarylphosphinimines do not rule out a resonance mechanism operating over the entire 11 bonds of these silicon compounds, although other explanations are also plausible.

Introduction

Previously reported [1] transmission effects in triarylsilanes suggested a resonance mode of transmission. However, as with all investigations of substituent effects where the change of substituent occurs at or near the detector site, questions of structural effects at the detector site, classical inductive influences, contributions from "no-bond resonance" and local polar effects make unambiguous interpretations difficult. What is needed is a system where the change in substituent is at a distance large enough to minimize the aforementioned influences. Furthermore, a system was desired where the silicon—donor interaction could be examined by comparison with a similar carbon system. For these reasons, the ^{19}F and ^{31}P NMR of the following three classes of phosphinimines were investigated:

A. *N*-Aryltriarylphosphinimines (Ia-d, Table 1)
B. *N*-(Triarylmethyl)triarylphosphinimines (IIa-h, Table 2)
C. *N*-(Triarylsilyl)triarylphosphinimines (IIIa-t, Table 3)

Binding energies determined by ESCA (Electron Spectroscopy Chemical Analysis) indicated very high electron density at the nitrogen in compound IIa (N_{1s} 397.0 eV) and in compound IIIa (N_{1s} 396.8 eV; reference C_{1s} binding energy = 285.0 eV). The ionization energy for N_{1s} in CN^- is 399.5 eV. Therefore, these types of compounds may provide an excellent opportunity for investigation of a $p\rightarrow d$ π-type interaction involving silicon 3*d*, nitrogen 2*p* orbitals.

Experimental

General

Melting points are uncorrected. Analyses were performed by MHW Laboratory, Garden City, Michigan and by Micro-Analysis, Inc., Wilmington, Delaware. The ^{19}F NMR spectra were obtained on a Bruker Model HFX-90 spectrophotometer at 84.6 MHz (*a*) in the continuous wave mode using a Nicolet Model 1085 computer as a time-averaging system, or (*b*) in the Fourier mode with protons broad band decoupled at 90 MHz using a Bruker Model BSV-2 decoupler. Selected ^{19}F spectra were obtained using a Varian HR60 operating at 56.4 MHz. The ^{31}P spectra were recorded with the Bruker HFX-90 operating at 36.43 MHz in the Fourier mode with protons broad band decoupled at 90 MHz. Selected duplicate ^{31}P spectra were obtained on a Varian Model HA-100 operating at 40.5 MHz in the CW mode utilizing a Varian C-1024 time-averaging system. Chemical shifts obtained by pulse methods are reported to the nearest address. Unless otherwise noted, the solvent used to provide a deuterium lock signal was NMR grade chloroform-*d* containing by volume 4% trichlorofluoromethane. All compounds reported were soluble in chloroform-*d* to at least 5 wt. %. ^{19}F substituent chemical shifts (SCS) were determined at concentrations of 5 to 1 wt. % and extrapolated to infinite dilution, using fluorobenzene as the reference. ^{31}P SCS were determined on 0.05 *M* to 0.02 *M* solutions using 85% phosphoric acid as the external reference. The reported compounds show only small (less than 0.15 ppm) concentration effects in chloroform-*d* for the ^{19}F spectra over the concentration range investigated. The ^{31}P spectra show a concentration effect of 0.3 ppm or less. Positive ^{19}F and ^{31}P chemical shifts are downfield

from the reference compound. All the chemical shifts are reported in ppm.

The ESCA equipment and techniques used to obtain the data presented in this work have been described elsewhere [2]. All compounds were further characterized by mass spectrometry, ^{1}H NMR, infrared analysis, and ^{13}C NMR where applicable. Intermediates whose preparations are not described in this section were reported in ref. 1 or purchased from commercial suppliers and recrystallized or distilled as required. No attempt was made to achieve maximum yields in the preparative procedures.

Syntheses

N-(p-Fluorophenyl)- and N-(m-fluorophenyl)-triphenylphosphinimines (Ia and Ic). Prepared as described in ref. 3.

N-(p-Fluorophenyl)-tris(p-methoxyphenyl)phosphinimine (Ib). *p*-Fluoroaniline (0.012 mol) and triethylamine (0.034 mol) were added to a tetrahydrofuran (THF) solution (70 ml) of freshly prepared dichlorotris(*p*-methoxyphenyl)-phosphorane (0.01 mol) [4] and the mixture stirred under nitrogen for five days. The white precipitate formed was removed by filtration, the filtrate was reduced to one-half volume and to the residual solution an equal amount of hexane was added. An oily pink mass separated which was extracted with THF to give after evaporation of the solvent the hydrochloride of *N*-(*p*-fluorophenyl)-tris(*p*-methoxyphenyl)phosphinimine (2.0 g) as beige, oily crystals. Ammonia was bubbled through a suspension of this hydrochloride in hexane to give a 100% conversion of the hydrochloride to the phosphinimine Ib as a light yellow oil.

N-(m-Fluorophenyl)-tris(p-methoxyphenyl)phosphinimine (Id). Prepared as described above for compound Ib using *m*-fluoroaniline in place of *p*-fluoroaniline. A 10% yield of Id as large crystals (hexane/THF) was obtained. The physical properties and N analyses of compounds Ia-d are listed in Table 1.

N-(Triarylmethyl)triarylphosphinimines (IIa-h). Prepared by reacting the triarylchloromethanes with the appropriate triarylphosphinimine following the procedure used by Appel et al. [4] for preparing IIa.

$$(C_6H_5)_3C{-}Cl + 2(C_6H_5)_3P{=}NH \rightarrow (C_6H_5)_3C{-}N{=}P(C_6H_5)_3 + (C_6H_5)_3P{=}NH_2{}^{+}Cl^{-}$$

The physical characteristics and the N analyses of compounds IIa-h are

TABLE 1

N-ARYL-TRIARYLPHOSPHINIMINES (Ia-d) $XC_6H_4{-}N{=}P(C_6H_4Y)_3$

Compound	X	Y	M.p. (°C)	^{19}F SCS [a]	^{31}P SCS [b]	N(%)	
						Calcd.	Found
Ia	*p*-F	H	134-135.5	−15.45	+4.17	3.77	3.90
Ib	*p*-F	*p*-OCH_3	oil	−15.79	+3.88	3.03	3.16
Ib · HCl [c]				−5.88	+40.20 [d]		
Ic	*m*-F	H	134-136	−2.02 [e]	+4.65	3.77	3.49
Id	*m*-F	*p*-OCH_3	141-142	−1.95	+4.49	3.03	2.76

[a] ±0.03 ppm. [b] ±0.06 ppm. [c] Hydrochloride of Ib, Found: Cl, 7.87; calcd.: 7.14%. [d] In C_6D_6. [e] J(PF) = 1.4 Hz.

TABLE 2

N-(TRIARYLMETHYL)TRIARYLPHOSPHINIMINES (IIa-h) $XC_6H_4-C(C_6H_4X')(C_6H_4X'')-N=P(C_6H_4Y)_3$

Compound	X	X'	X''	Y	M.p. (°C)	^{19}F SCS [a]	^{31}P SCS [b]	N (%)	
								Calcd.	Found
IIa	H	H	H	H	228.5-229.5		−12.30	2.70	2.88
IIb	H	H	H	*p*-OCH_3	130-132		−12.60	2.30	2.60
IIc	*p*-OCH_3	*p*-OCH_3	*p*-OCH_3	H	173-174		−12.12	2.30	2.44
IId	*p*-OCH_3	H	H	H	180-181		−12.00	2.55	2.55
IIe	*p*-F	H	H	H	179-181	−6.12	−12.35	2.60	2.66
IIf	*p*-F	H	H	*p*-OCH_3	139-144	−6.36	−12.30	2.23	2.23
IIg	*m*-F	H	H	H	194-196	−1.63		2.60	2.65
IIh	*m*-F	H	H	*p*-OCH_3	dec.	−1.81	−11.35	2.23	2.09

[a] ±0.03 ppm. [b] ±0.06 ppm.

listed in Table 2. The intermediate triarylchloromethanes for compounds IIa and IIb [5, 6], IIc [7], IId [8, 9], IIe-h [1] and the intermediate triarylphosphinimines for compounds IIa [6], IIc-e [6], and IIg [6] are known compounds.

tris(p-Methoxyphenyl)phosphinimine. To a solution of tris(*p*-methoxyphenyl)phosphine (0.017 mol) in THF (100 ml) was added rapidly at 10°C under nitrogen a solution of hydrazoic acid (0.04 mol) in diethyl ether (100 ml) and the mixture brought to room temperature over a 3 h period. The solvents were removed under reduced pressure, the white residue was mixed with an additional amount of tris(*p*-methoxyphenyl)phosphine (0.017 mol) and the mixture placed in a 110°C bath. The bath temperature was raised over a 1 h period to 160°C, during which time the mixture melted and degassing occurred. The escaping gas was basic to litmus and had a definite ammonia odor indicating decomposition. The melt was allowed to cool to room temperature. Several attempts to isolate this product analytically pure failed. Nitrobenzene (45 ml) was added and the obtained solution was used to prepare compounds IIb, IIf and IIh.

N-(Triarylsilyl)triarylphosphinimines (IIIa-t). Prepared by reacting the azidotriarylsilanes with the appropriate triarylphosphine (tri-n-butylphosphine was used for compound IIIt), following two methods, based on the Staudinger reaction:

$$(C_6H_5)_3SiN_3 + (C_6H_5)_3P \rightarrow (C_6H_5)_3Si{-}N{=}P(C_6H_5)_3 + N_2$$

Method A. This method is essentially the same as that described by Thayer and West [10] for preparing *N*-(triphenylsilyl)triphenylphosphinimine.

Method B. Equimolar amounts of the appropriate azidotriarylsilane and triarylphosphine were charged into an oven-dried vacuum sublimation apparatus equipped with a magnetic stirrer. The system was placed under vacuum, then flushed with nitrogen several times. The apparatus was then placed in an oil bath at approximately 85°C and the mixture stirred under nitrogen for 72 h. By the end of the reaction period, the melt solidified and the stirring stopped. Unreacted starting materials were removed by sublimation under vacuum (0.1 Torr or less) over a 24-48 h period. The residue was extracted with several portions of hot ether and THF. The portions were combined, concentrated, cooled and the product precipitated by addition of hexane. Typical yields were about 75%.

The m.p.'s and the analytical results of compounds IIIa-t are listed in Table 3. The intermediate azidotriarylsilanes for preparing compounds IIIa-m and IIIt and all the triarylphosphines are known compounds. The azidotriarylsilanes used for preparing compounds IIIn-s are new and were prepared as follows:

Azido(p-methoxyphenyl)diphenylsilane. A mixture of sodium azide (5.5 g), catalytic amounts of anhydrous aluminum chloride and THF (500 ml) was heated to reflux for 1 h. Sublimed chloro(*p*-methoxyphenyl)diphenylsilane [11] (28.6 g) was added and the heating at reflux continued for 110 h under nitrogen. The THF was removed under vacuum, dry hexane (200 ml) was added and the mixture warmed and filtered. Evaporation of the solvents from the filtrate under reduced pressure gave the azido compound, b.p. 170°C/0.01 Torr, in 80% yield.

Anal. Found: C, 68.76; H, 5.02; N, 12.96. $C_{19}H_{17}N_3OSi$ calcd.: C, 68.88; H, 5.14; N, 12.69%.

TABLE 3

N-(TRIARYLSILYL)TRIARYLPHOSPHINIMINES (IIIa-t) $XC_6H_4-Si(Ph)(C_6H_4Y')-N=P(Ph)(C_6H_4Y'')-C_6H_4Y$

Compound	X	Y	Y'	Y''	Method	Crystallization solvent	M.p. (°C)	^{19}F SCS [a]	^{31}P SCS [b]	N (%)	
										Calcd.	Found
IIIa	H	H	H	H	B		218-220		+2.99	2.61	2.62
IIIb	H	*m*-F	*m*-F	*m*-F	B		176-177	+1.83	0 [c] and −0.52 [d]	2.38	2.20
IIIc	H	*p*-F	H	H	B	THF/Hexane	190-191	+4.10	+2.38 [e]	2.53	2.56
IIId	*p*-F	H	H	H	A	Ether/Hexane	171-174	−0.84 and −0.30 [f]	+3.65	2.53	2.51
IIIe	*p*-F	*p*-OCH_3	*p*-OCH_3	*p*-OCH_3	A	Ether/Hexane	130-131	−1.07 and −0.56 [f]	+3.68	2.18	2.09
IIIf	*p*-F	*m*-OCH_3	*m*-OCH_3	*m*-OCH_3	B	Ethanol	104-105	−0.66	+4.51	2.18	2.39
IIIg	*p*-F	*p*-Cl	*p*-Cl	*p*-Cl	B	Hexane	145-146	−0.04, +0.23 [f] and +0.08 [d]	+1.21	2.13	2.02
IIIh	*p*-F	*p*-F	*p*-F	*p*-F	B	Hexane	127-128	−0.27 [g], −0.20 [g, d] +5.00 [h] and +4.70 [h, d]	+1.44	2.31	2.15
IIIi	*p*-F	*m*-F	*m*-F	*m*-F	B	Extraction with ether	155-157	−0.04 [g] and +2.07 [h]	+0.30	2.31	2.26
IIIj	*p*-F	*p*-F	H	H	A	Ether/Hexane	182.5-184	−0.51 [g] and +4.30 [h]		2.45	2.45
IIIk	*m*-F	H	H	H	A	Ethanol	192.5-195	−1.97	+4.02	2.53	2.74
IIIl	*m*-F	*p*-OCH_3	*p*-OCH_3	*p*-OCH_3	A	Ether/Pet. Ether	126-127	−1.95		2.17	2.39
IIIm	*m*-F	*p*-Br	H	H	A	1) THF/Pet. Ether 2) Acetonitrile	165-167	−1.68		2.15	2.19
IIIn	*p*-OCH_3	H	H	H	B	Ether/Hexane	141.5-143.5		+2.88	2.48	2.58
IIIo	*p*-OCH_3	*p*-F	*p*-F	*p*-F	B	Pet. Ether	150-151.5	+4.81 and +5.05 [d]	+0.50 [i]	2.26	2.24
IIIp	*p*-OCH_3	*m*-F	*m*-F	*m*-F	A	Pet. Ether	114.5-116	+1.75	−0.20	2.26	2.33
IIIq	*p*-OCH_3	*p*-F	H	H	B	Pet. Ether	141.5-143	+4.11	+2.63	2.40	2.44
IIIr	*m*-OCH_3	*p*-F	*p*-F	*p*-F	B		136-138.5	+4.84	+0.80	2.26	2.33
IIIs	*m*-OCH_3	*m*-F	*m*-F	*m*-F	A	Pet. Ether	98-100	+1.90		2.26	2.19
IIIt	*p*-F	[j]	[j]	[j]	B	Hexane		−1.05 and −1.04 [d]	+14.81	2.83	2.60

[a] ±0.03 ppm. [b] ±0.06 ppm. [c] $J(PF) = 6.1$ Hz. [d] In C_6D_6. [e] $J(PF) = 1.8$ Hz. [f] In THF. [g] Si end. [h] P end. [i] $J(PF) = 2.0$ Hz. [j] n-Butyl group instead of aryl.

Azido(m-methoxyphenyl)diphenylsilane. A solution of (*m*-methoxyphenyl)-magnesium bromide (0.26 mol) in THF (500 ml) was added to diphenyldichlorosilane and the mixture heated at 42°C for 60 h. The THF was removed to approximately 160 ml and hexane (250 ml) added. The suspension was filtered, the hexane removed under reduced pressure from the filtrate and the residue distilled under vacuum. The fraction of b.p. 170°C at 0.06 Torr was added to a solution of sodium azide (4.7 g) in THF (500 ml). The mixture was heated at reflux for 69 h. The volume of THF was reduced to approximately 100 ml under vacuum, hexane (250 ml) was added, the mixture warmed, filtered and the filtrate evaporated to dryness under vacuum. Distillation of the residue under reduced pressure gave azido(*m*-methoxyphenyl)diphenylsilane, b.p. 180°/0.05 Torr.

Anal. Found: C, 68.85; H, 5.05; N, 12.40. $C_{19}H_{17}N_3OSi$ calcd.: C, 68.88; H, 5.14; N, 12.69%.

Results and discussion

^{19}F substituent chemical shifts

The ^{19}F substituent chemical shift (SCS) of the *N*-(fluorophenyl)triarylphosphinimines (Table 1) show the *para* ^{19}F isomers to be upfield 13-14 ppm in comparison with the *meta* ^{19}F isomers, indicating an electron-rich *para* position in the *N*-aryl ring. By using the *para* SCS values of compounds Ia and Ic and applying the method of Taft [12], one obtains for the —N=PPh_3 group a σ_R^0 value of —0.45 (about that for —NH_2) and a σ_I of —0.20.

From the observed ^{19}F SCS of the *N*-aryltriarylphosphinimines (Table 1), the —N=PPh_3 group is a good supplier of electron density by induction and resonance.

A σ_I of similar value (—0.18) for the —N=PPh_3 group is also obtained from the ^{19}F SCS of compound IIe by applying the equation [1]:

$$para\ ^{19}F\ SCS = 5.76\ \sigma_I\ (X) = 4.14$$

which describes the linear relationship between *para* ^{19}F SCS and σ_I (X) for *p*-$FC_6H_4CPh_2X$, where X is H, Cl, Br, OH, etc. The *para* ^{19}F SCS of —5.17 obtained for compound IIe in benzene was used in the above equation.

A significant effect on ^{19}F SCS is achieved by interposing a Ph_2C= or a Ph_2Si= group between the fluorophenyl and the triphenylphosphinimine groups in the *N*-(fluorophenyl)triphenylphosphinimines Ia and Ic (see Table 4). The ^{19}F SCS listed in Table 4 show that in the *para* fluoro compounds the Ph_2C= group produces a change in the ^{19}F SCS of +9.33 ppm and the Ph_2Si= group produces a deshielding of the ^{19}F nucleus of +14.61 ppm, whereas in the *meta* fluoro compounds the ^{19}F SCS remain relatively large and unaffected by the interposing of the above groups.

The deshielding in the *para* fluoro compounds containing a Ph_2C= group can be attributed in large part to a loss of resonance donation from the nitrogen to the fluorophenyl group. The small deshielding in the *meta* fluoro isomers observed by interposing a Ph_2C= group may be the result of a decrease in the inductive component as well. As previously proposed for the *p*-fluorophenyldiphenylsilanes [1], the large deshielding effect caused by the Ph_2Si= group is

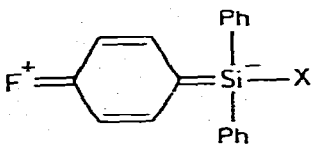
TABLE 4

EFFECT ON ^{19}F SCS BY INTERPOSING A $Ph_2C=$ OR A $Ph_2Si=$ GROUP BETWEEN THE FLUOROPHENYL AND THE TRIPHENYLPHOSPHINIMINE GROUPS OF COMPOUNDS Ia AND Ic

Compound	Formula [a]	^{19}F SCS
Ia	p-FC_6H_4X	−15.45
IIe	p-$FC_6H_4CPh_2X$	−6.12
IIId	p-$FC_6H_4SiPh_2X$	−0.84
Ic	m-FC_6H_4X	−2.02
IIg	m-$FC_6H_4CPh_2X$	−1.63
IIIk	m-$FC_6H_4SiPh_2X$	−1.97

[a] $X = -N=PPh_3$.

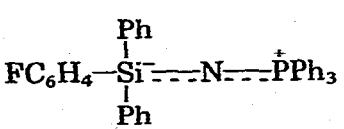
probably best explained by the withdrawing of electron density into vacant silicon acceptor orbitals (Structure A).



(A)

Support for the Si—aryl p—d π-interaction is given by the deshielding in the p-fluoro substituted silicon compounds. Such deshielding cannot be only the result of poor transmission of inductive effects through silicon atoms when compared to carbon atoms because similar values are obtained when the *meta* ^{19}F SCS for both the *N*-(fluorophenyldiphenylmethyl)- and *N*-(fluorophenyldiphenylsilyl)-triarylphosphinimines (II and III) are compared with the ^{19}F SCS of *m*-fluorophenyldiphenyl-methanes and -silanes previously reported [1].

The incremental difference between the *para* ^{19}F SCS of silicon compound IIId and the *para* ^{19}F SCS of carbon compound IIe of +5.28 ppm appears to be in good agreement with the incremental differences (+5-6 ppm) obtained for the *p*-fluorophenyldiphenyl-methanes and -silanes [1]. Therefore, there is no definitive evidence for a resonance-type interaction involving silicon and the nitrogen of the group $-N=PPh_3$, based on ^{19}F SCS such as depicted in structure B:



(B)

If such a resonance contribution is present, it is not detectable at the phenyl ring by ^{19}F NMR chemical shift methods. Later in this paper, evidence to support structure B is presented based on ^{31}P SCS data.

Further insight into the electronic effects in these molecules may be obtained by examining the ^{19}F and ^{31}P NMR of the compounds listed in Table 5.

TABLE 5

COMPARISON OF THE *para* ^{19}F AND ^{31}P SCS OF PHOSPHINIMINES I, II AND III

Compound	Formula [a]	^{19}F SCS	^{31}P
Ia	$FC_6H_4—N=PPh_3$	—15.45	+4.17
Ib	$FC_6H_4—N=P(C_6H_4OCH_3)_3$	—15.79	+3.88
Ib · HCl	$[FC_6H_4—\underset{\displaystyle H}{\underset{\displaystyle |}{N}}—P(C_6H_4OCH_3)_3]^+Cl^-$	—5.88	+40.29
IIe	$FC_6H_4\underset{\displaystyle Ph}{\underset{\displaystyle |}{C}}—N=PPh_3$	—6.12	—10.21
IIf	$FC_6H_4\underset{\displaystyle Ph}{\underset{\displaystyle |}{C}}—N=P(C_6H_4OCH_3)_3$	—6.36	—12.30
IIId	$FC_6H_4\underset{\displaystyle Ph}{\underset{\displaystyle |}{Si}}—N=PPh_3$	—0.84	+2.99
IIIe	$FC_6H_4\underset{\displaystyle Ph}{\underset{\displaystyle |}{Si}}—N=P(C_6H_4OCH_3)_3$	—1.07	+3.68

[a] All aryl substituents are in the *para* position.

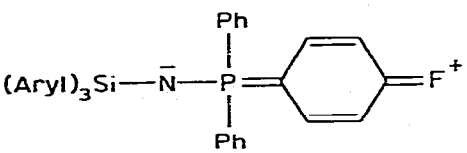
Replacement of the H atoms in the phosphorus phenyl groups of the arylphosphinimine Ia with *p*-OCH_3 groups produces a small shielding effect for both ^{19}F and ^{31}P SCS (Ia vs. Ib). Formation of the hydrochloride of Ib results in deshielding around the *para* ^{19}F to an extent similar to that observed by interposing a $Ph_2C=$ group between the fluorophenyl and the triphenylphosphinimine group of compound Ia (see compounds Ib HCl and IIe). This effect most probably is due in part to a loss of the resonance component donation to the fluorophenyl group as well as to a change in induction in both cases. The ^{31}P NMR indicates a shielding effect caused by the interposition of a $Ph_2C=$ group in compound Ib (see compound IIf) and a large deshielding of the ^{31}P nucleus caused by the formation of the hydrochloride of Ib. These results indicate that a significant part of the positive charge introduced by protonation is localized on the phosphorus and is not delocalized into the fluorophenyl ring.

To prove the mechanism of transmission of substituent effects in the series *N*-(*p*-fluorophenyldiphenylsilyl)triarylphosphinimines, $FC_6H_4SiPh_2—N=P-(C_6H_4Y)_3$, the influence of the nature of Y on the ^{19}F SCS was investigated. Table 3 shows the following ^{19}F shielding order for group Y: *p*-OCH_3 > H > *m*-OCH_3 > *p*-F > *m*-F > *p*-Cl. The range of SCS is over 1 ppm which is relatively large when one considers the substituent-to-detector distance (11 bonds for *m*-Y, 12 bonds for *p*-Y) and the type of substituents. The ^{19}F shift on changing group Y is apparently concentration independent throughout the concentration range investigated (between 0.73 and 7 wt. %). Replacement of two of the fluorine atoms in the trifluorophenyl groups of compound IIIh by H (see com-

pound IIIj) results in a nearly proportional reduction of the ^{19}F SCS, indicating a cumulative transmission mechanism.

Linear regression analysis shows a better correlation of the *para* ^{19}F SCS with σ^0 of Y, i.e., ^{19}F SCS = 0.83 Σ (σ^0 of X) —0.78; correlation coefficient 0.961, than with σ, i.e., ^{19}F SCS = 0.60 Σ (σ of Y) —0.62; correlation coefficient 0.881. The substituent constant term is expressed as a sum in order to include the monofluorinated case. The better correlation with σ^0 may indicate that the transmission occurs by a non-resonance mechanism. Further discussion on this point follows.

On the basis of p*K*a values for the Ph—N=P($C_6H_4Z)_3$ system (where Z = H, *p*-Cl or *p*-Br), Johnson and Wong [13] have found that basicity follows the σ scale better than σ^0, suggesting that electronic effects are transferred to the nitrogen via a resonance effect. However, an investigation by Kukhar et al. [14] shows the p*K*a of XC_6H_4—N=PPh_3 (where X = H, Cl, CH_3, etc.) follow σ^0 of X better than σ of X, concluding that the effect of X on p*K*a was primarily an inductive one. Taken together, these two studies indicate that while resonance-type transmission is possible from the phosphorus aryls to the nitrogen, electron density may be localized at nitrogen and not further transmitted via a resonance mechanism. This localization of charge at nitrogen may explain in part the high electron density at nitrogen as determined by ESCA. The ^{19}F SCS values listed in Table 3 show that the phosphorus *para* fluorophenyl compounds (IIIh, IIIo and IIIr) are significantly deshielded relative to the corresponding phosphorus *meta* fluorophenyl isomers (IIIi, IIIp and IIIs). This behavior may be explained by a mechanism similar to that advanced for the deshielding of the silicon compounds with the fluorophenyl group at the silicon atom. Like silicon, phosphorus is capable of valence shell expansion and the deshielding of the *para* ^{19}F nucleus is possibly the result of important ground state contributions of resonance structures resembling structure C:



(C)

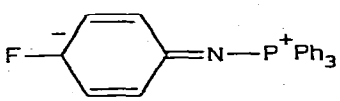
The electron density on nitrogen is apparently not further delocalized by resonance in the aryl group at the silicon. This is supported by the small and nearly identical incremental difference in *para* ^{19}F shift produced in replacing the three H atoms with OCH_3 groups in the phosphorus phenyl groups of *N*-(*p*-fluorophenyldiphenylmethyl)- and of the *N*-(*p*-fluorophenyldiphenylsilyl)-triphenylphosphinimines (IIe vs. IIf and IIId vs. IIIe) *p*-$^{19}FC_6H_4$—MPh_2—N=P-(C_6H_4Y-*p*)$_3$, where M = C or Si and Y = H or —OCH_3.

Comparison of the *para* ^{19}F and ^{31}P chemical shifts (Table 3) of *para*-$FC_6H_4SiPh_2$—N=PPh_3 (IIId) and *para*-FC_6H_4—$SiPh_2$—N=$PButyl_3$ (IIIt) shows the ^{31}P of the tributyl compound to be deshielded relative to the triphenyl, and the *para* ^{19}F chemical shift, while indicating slight shielding in the n-butyl, remains almost unchanged. The deshielding of the ^{31}P nucleus in IIId results

from the loss of charge localization represented in structure C. On electronegativity considerations, n-butyl would be expected to be an electron donor relative to phenyl [15]. The ^{19}F SCS once again suggests no resonance-type delocalization of charge from nitrogen into the fluorophenyl group at the silicon atom and is indicative of transmission primarily by the π-inductive mechanism.

^{31}P Substituent chemical shifts

Comparison of the ^{31}P SCS values listed in Table 5 show a shielded ^{31}P nucleus in the *N*-(triarylmethyl)triarylphosphinimines relative to the *N*-aryl- and the *N*-(triarylsilyl)triarylphosphinimines. One explanation is that the *p—d* nitrogen—phosphorus interaction may be competing with a nitrogen—aryl interaction in the *N*-aryltriarylphosphinimines and with a silicon—nitrogen interaction in the *N*-(triarylsilyl)triarylphosphinimines, i.e., the resonance forms D and B are important.



(D)

A similar resonance form is not possible for the *N*-(triarylmethyl)triarylphosphinimines. The lack of effect on the ^{31}P SCS by successive substitution of OCH_3 at the *para* position of the phenyl groups attached to carbon in the *N*-(triphenylmethyl)triphenylphosphinimine compounds IIa to form IIc appears to substantiate this. Unfortunately, synthetic difficulties have hampered the preparation of the analogous tri-*p*-methoxy substituted silicon compound, and the data obtained from the monosubstituted Si series are not conclusive.

The electronic effects at the *para* ^{19}F and ^{31}P nuclei in the series p-FC_6H_4-$SiPh_2$—N=$P(C_6H_4Y$-$p)_3$, are interdependent as is shown by the *para* ^{19}F chemical shifts and the ^{31}P chemical shifts. A least squares fit produces the relationship: ^{31}P SCS = —2.56 *para* ^{19}F SCS + 1.02 with a correlation coefficient of 0.965. This correlation is based on the values of ^{19}F and ^{31}P SCS of compounds IIIa-t (Table 3).

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