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^{19}F NMR CHEMICAL SHIFTS IN FLUOROPHENYL DERIVATIVES OF SILICON–PLATINUM COMPLEXES

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SUMMARY

^{19}F NMR chemical shifts in acetone or benzene relative to fluorobenzene have been measured for the *trans*-complexes $[Pt(C_6H_4F\text{-}m)(SiPh_3)(PMe_2Ph)_2]$, $[Pt(C_6H_4F\text{-}p)(SiPh_3)(PMe_2Ph)_2]$, and $[Pt(C_6H_4F\text{-}p)(Cl)(PMe_2Ph)_2]$, and for the compounds (*m*- and *p*-$FC_6H_4)_3SiX$, where X = Br, H, Me, Ph, $PtCl(AsMe_2Ph)_2$-*trans*, and $PtCl(PMe_2Ph)_2$-*trans*. The results indicate that in comparison with other common ligands, the Ph_3Si group acts as a good σ-donor and good π-acceptor when bonded to platinum.

INTRODUCTION

A method of determining inductive and resonance effects of substituents, X, from the ^{19}F NMR spectra of *m*- and *p*-FC_6H_4X compounds has been developed by Taft and his colleagues[1]. In this, if δ_m^F and δ_p^F represent the ^{19}F chemical shifts for *m*- and *p*-XC_6H_4F, respectively, relative to that for fluorobenzene, then the inductive, σ_I, and resonance substituent constants, σ_R^0, are given by the empirically derived eqns. (1) and (2).

$$\delta_m^F = -7.10\,\sigma_I + 0.60 \qquad (1)$$

$$\delta_p^F = -29.5\,\sigma_R^0 + \delta_m^F \qquad (2)$$

Although the theoretical basis of this treatment has been severely criticized (see, *e.g.*, ref. 2), and some anomalies in its application pointed out (see, *e.g.*, ref. 3), it does, nevertheless, serve as a useful empirical source of information on substituent effects, which gives values for substituent constants in essential agreement with those obtained by other methods[1,4].

Inorganic and organometallic chemists have made considerable use of the Taft approach in studying the influences of groups attached to metals (see, *e.g.*, refs. 3, and 5–10), and especially in investigating the *trans*-influences of ligands, Y, by studying complexes containing *trans*-$Y\text{–}M\text{–}C_6H_4F$ linkages[5–8,10]. In studying such *trans*-influences in platinum complexes, Parshall did not derive σ_I- and σ_R^0-constants by use of eqns. (1) and (2), but instead used δ_m^F as the measure of the inductive influence (or σ-donor ability) of Y and the quantity $(\delta_m^F - \delta_p^F)_Y$ as a measure of the resonance effect, and furthermore took the quantity $[(\delta_p^F - \delta_m^F)_{Me} - (\delta_p^F - \delta_m^F)_Y]$ as a measure of the π-acceptor ability of Y, on the assumption that the methyl group can have no resonance interaction with the platinum atom[5]. This measure of π-acceptor abilities has been criticized by Stewart and Treichel on the ground that its derivation, as the small difference between two relatively large numbers, is liable to substantial error[6], and by Church and Mays on the grounds that (*a*), it neglects the interaction between the inductive and resonance effects of the ligand Y (inductive electron-release by Y will increase the ability of the metal atom, M, to enter into π-bonding) and (*b*), in some cases it gives orders of π-acceptor abilities at variance with those generally accepted on the basis of other evidence[7]. Nevertheless use of the Parshall approach continues (see, *e.g*, refs. 8 and 10), and is probably justified provided its limitations are kept in mind and not too much is deduced from small differences.

We describe below the use of the ^{19}F NMR spectra of (*a*) the complexes [*m*- and *p*-$FC_6H_4Pt(SiPh_3)(PMe_2Ph)_2$], and (*b*) compounds of the type (*m*- and *p*-$FC_6H_4)_3SiX$, in order to provide information about the nature of the Si–Pt bond. The ^{19}F NMR chemical shifts for a large number of FC_6H_4SiXYZ compounds have been measured and analysed by Lipowitz[11].

RESULTS AND DISCUSSION

A. ^{19}F NMR spectra of trans-[$Pt(C_6H_4F)(SiPh_3)(PMe_2Ph)_2$] complexes

The ^{19}F chemical shifts, measured in acetone relative to internal fluorobenzene

TABLE 1

^{19}F NMR CHEMICAL SHIFTS FOR *trans*-[$PtX(C_6H_4F)(PR_3)_2$] COMPLEXES[a]

Complex	δ^F_m	δ^F_p
[$Pt(C_6H_4F$-*p*$)(SiPh_3)(PMe_2Ph)_2$]		9 93
[$Pt(C_6H_4F$-*m*$)(SiPh_3)(PMe_2Ph)_2$]	2 70	
[$Pt(C_6H_4F$-*p*$)(Cl)(PMe_2Ph)_2$]		9 80
[$Pt(C_6H_4F$-*p*$)(Cl)(PEt_3)_2$]		10 10[b]
[$Pt(C_6H_4F$-*m*$)(Cl)(PEt_3)_2$]	2 11[b]	

[a] In ppm, relative to fluorobenzene, in acetone [b] Results from ref 5

TABLE 2

^{19}F NMR CHEMICAL SHIFTS AND DERIVED PARAMETERS FOR *trans*-[$PtX(C_6H_sF)(PEt_3)_2$] COMPLEXES[a]

X	δ^F_m	δ^F_m	$[(\delta^F_p-\delta^F_m)_{Me}-(\delta^F_p-\delta^F_m)_X]$
Me	3 93	11 70	0 0
Ph	3 46	10 92	0 3
PhC≡C	3 21	10 40	0 6
CN	2 27	9 32	0 7
Cl	2 13	10 11	−0 2
I	1 56	9 54	−0 2
$SnCl_3$	−0 23	6 96	0 6
$SiPh_3$	3 00[b]	10 23[b]	0 5

[a] Results mainly from ref 5; measurements (in ppm) in acetone [b] Measurements were actually on the Me_2-PhP complex (see Table 1), and an adjustment of +0 30 ppm has been applied (see text)

are shown in Table 1 for the *trans*-complexes, $[Pt(C_6H_4F\text{-}m)(SiPh_3)(PMe_2Ph)_2]$ and $[Pt(C_6H_4F\text{-}p)(SiPh_3)(PMe_2Ph)_2]$. It would have been better to use triethylphosphine complexes, as did Parshall[5], but these were not accessible to us. We have assumed that the difference of 0 30 ppm observed between the shift for $[Pt(C_6H_4F\text{-}p)(Cl)(PMe_2Ph)_2]$ and that for $[Pt(C_6H_4F\text{-}p)(Cl)(PEt_3)_2]$ applies in every case for the change of ligand. This procedure is unlikely to lead to any serious errors, and, in particular, the *difference* $(\delta_p^F - \delta_m^F)$, which leads to the measure of the π-ability, is most unlikely to be significantly affected by the change in phosphine ligand.

In Table 2, we include the δ_m^F and $[(\delta_p^F - \delta_m^F)_{Me} - (\delta_p^F - \delta_m^F)_X]$ values for the Ph_3Si group along with a representative list of the values derived by Parshall[5]. It will be seen that the Ph_3Si group appears to be a good σ-donor*, though it is significantly less effective in this respect than the Me group, or even the Ph group; we return to this latter aspect below. In π-acceptor ability, the Ph_3Si group appears to be only a little less effective that the CN group. Thus the Ph_3Si group can be taken to act as both a good σ-donor and a good π-acceptor when attached to platinum. [This is reasonably in accord with the conclusions reached by Graham[12], who found that Ph_3Si, Ph_3Ge and Ph_3Sn ligands could be classed as strong σ-donors and moderate π-acceptors when attached to manganese, as indicated by the carbonyl stretching frequencies in $MnX(CO)_5$ complexes, though the theoretical basis of his analysis has been seriously questioned[7].] There is a marked contrast between the Ph_3Si and Cl_3Sn groups; both have rather similar π-acceptor abilities, but while the Ph_3Si group is a strong σ-donor, the Cl_3Sn group has a σ-donor ability well below that of the halogens

The fact that the Ph_3Si group appears, by the Parshall measure, to be a weaker σ-donor than the Me group is not consistent with the large *trans*-influence of R_3Si groups compared with Me groups[13,14] if these influences are, as is frequently assumed, associated predominantly with the inductive effects of the ligands It is doubtful, however, whether the accuracy of the Parshall measure or the validity of the relationship between *trans*-influences and inductive effects is such as to justify further speculation on this point. Certainly the *trans*-influences of various organic ligands (*e.g.*, Me, Ph, PhC≡C, COPh) are quite inconsistent with the inductive effects of the groups as they are normally measured (*cf.* ref. 15).

We should note, at this point, that the δ_m^F values in Table 1, in so far as they specifically measure inductive effects at all, do not actually measure the inductive effect of the ligand X, but rather the inductive effect of the whole $Pt(PR_3)_2X$ group on the aromatic ring. The inductive and π-bonding effects of X on the platinum atom are not, in fact, wholly independent (*cf.* ref.7), and acceptance of π-electrons by X from platinum will lower the electron density at platinum, and this will lead to a lower σ-donation from platinum to the aromatic ring (and, of course, also to X). The δ_m^F value may thus be a fairly poor guide to the inherent inductive (σ-donor) effect of X, *i.e.*, the effect which would operate in the absence of π-bonding. Nevertheless, to the extent that δ_m^F values are indicators of the overall inductive release of electrons by the $Pt(PR_3)_2X$ group to the aromatic ring, they should also provide a reasonable measure

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* It will be appreciated that in writing of the Ph_3Si group as a good σ-donor towards platinum we do not imply that the bond is polarized in the direction $Si^+–Pt^-$, but only that the Ph_3Si group donates σ-electrons relative to many other common ligands Just as the hydrogen atom of the Pt–H bond is hydridic, so the Pt–Si bond is probably polarized in the direction $Pt^+–Si^-$

of such release to a chlorine or hydrogen atom attached to platinum, and thus, on the simplest assumptions, of *trans*-influences as indicated by physical properties of Pt–Cl and Pt–H bonds.

B. ^{19}F NMR spectra of $(FC_6H_4)_3SiX$ compounds

We originally intended to make this study with $FC_6H_4SiMe_2X$ compounds, and carried out several syntheses in this series, but then were unable to obtain in a pure state the crucial complex *trans*-$[PtCl\{SiMe_2(C_6H_4F\text{-}p)\}(PMe_2Ph)_2]$. We thus turned to $(FC_6H_4)_3SiX$ compounds, which are less satisfactory, since the shift δ^F_m refers to the group $Si(C_6H_4F\text{-}m)_2X$ while the measured $[\delta^F_p]$ value refers to the group $Si(C_6H_4F\text{-}p)_2X$. Thus, while the δ^F_m shifts provide the normal measure of the σ_I effect of the group $Si(C_6H_4F\text{-}m)_2X$, true σ^0_R values cannot be derived. However, the differential effects of the *m*- and *p*-fluorophenyl groups on silicon are probably quite small, and, furthermore, we are interested only in the *differences* between the effects of the X groups, and these differences can be reasonably assumed not to be significantly affected by the change from *m*- to *p*-fluorophenyl groups; in other words, the quantities $(\delta^F_p - \delta^F_m)$ listed in Table 3 for several X groups give a satisfactory guide to the influence of X on the acceptance of π-electrons by the silicon atom. We have derived pseudo σ^0_R-constants, $[\sigma^0_R]$, for $Si(C_6H_4F)_2X$ groups in order to provide an indication of the magnitude of the π-acceptor ability of the silicon atom in such groups, but these $[\sigma^0_R]$ values should not be compared directly with properly-derived σ^0_R values.

The results are shown in Table 3, and it will be seen (*i*) that all the $Si(C_6H_4F)_2X$ groups are electron-withdrawing by both inductive and resonance mechanisms, (*ii*) that there are no significant differences between the influences of $[PtCl(PMe_2Ph)_2]$ and $[PtCl(AsMe_2Ph)_2]$ substituents, and (*iii*) that in comparison with, say, Me or H substituents, the $[PtCl(QMe_2Ph)_2]$ (Q=As or P) substituents significantly reduce both the σ- and π-electron-withdrawal by the silicon atom. While all the differences in Table 3 are small, the change in σ_I on going from X=H to X=$[PtCl(QMe_2Ph)_2]$ is as great as that on going from X = Br to X = H, implying a strong release of electrons to silicon by the platinum atom relative to a hydrogen atom, and it is reasonable to assume that this mainly represents a donation of σ-electrons.

The $[\sigma^0_R]$ values, or the experimental quantities $[(\sigma^F_p) - \sigma^F_m]$, similarly indicate

TABLE 3

^{19}F NMR CHEMICAL SHIFTS AND DERIVED DATA FOR (*m*- AND *p*-$FC_6H_4)_3SiX$ COMPOUNDS[a]

X	δ^F_m [b]	$[\delta^F_p]$ [c]	$[\delta^F_p]-\delta^F_m$	σ_I [d]	$[\sigma^0_R]$ [e]
Br	−1.97	−5.32	−3.35	+0.36	+0.11
H	−1.01	−3.57	−2.55	+0.23	+0.09
Ph	−1.12	−2.98	−1.86	+0.24	+0.06
Me	−0.69	−2.50	−1.81	+0.18	+0.06
$PtCl(AsMe_2Ph)_2$	−0.12	−0.32	−0.22	+0.10	+0.01
$PtCl(PMe_2Ph)_2$	+0.05	−0.12	−0.17	+0.08	+0.005

[a] In ppm, relative to fluorobenzene, in benzene [b] Refers to $(C_6H_4F\text{-}m)_3SiX$ [c] Refers to $(C_6H_4F\text{-}p)_3SiX$ [d] Normal σ_I value for $Si(C_6H_4F\text{-}m)_2X$ [e] Pseudo-σ^0_R value, see text

that the π-acceptor ability of the silicon atom is markedly reduced on going from X = H to X = [PtCl(QMe$_2$Ph)$_2$]. The changes cannot be associated only with the π-electron-release from X to Si, since the σ- and π-electronic effects are not wholly independent as we have seen, but since the change in $[\sigma_R^0]$ on going from X = H to X = [PtCl(QMe$_2$-Ph)$_2$] is some three times as great as that in going from X = Br to X = H, even though the change in σ_I in going from X = Pt to X = H is similar to that in going from X = H to X = Br, it seems reasonable to conclude that the fairly large influence of the [PtX-(QMe$_2$Ph)$_2$] groups on $[\sigma_R^0]$ is attributable mainly to π-electron release from platinum to silicon.

The implications of the σ_I and $[\sigma_R^0]$ values are much the same as those of the Parshall indicators, *viz.* that there is substantial π-donation from platinum to silicon, and at the same time a σ-donation in the same direction which is smaller than with most common ligands (*i.e.*, the R$_3$Si group appears as a fairly strong σ-donor in comparison with most of these ligands). However, since platinum releases σ-electrons markedly more readily to silicon than does a Me group or hydrogen atom (as indicated by the σ_I values above), it is somewhat anomalous that in terms of the Parshall type measurements, the Me ligand appears to release σ-electrons to platinum significantly more readily than does the Ph$_3$Si group. The explanation may lie in the uncertainty inherent in the deductions from the Parshall-type measurements.

EXPERIMENTAL

General

IR spectra were recorded with Nujol mulls unless otherwise indicated. Petrol refers to light petroleum, b p. 60–80°.

Preparations of $(FC_6H_4)_3SiX$ *compounds* ($X = H$, *Br*, *Me*, *Ph*)

The compounds *m*- and *p*-(FC$_6$H$_4$)$_3$SiH were prepared from *m*- and *p*-fluorophenylmagnesium bromide and trichlorosilane in ether as previously described[14].

Bromine (5.4 g, 0.03 mol) in carbon tetrachloride (25 ml) was added to a solution of tris-*p*-fluorophenylsilane (10 g, 0.03 mol) in carbon tetrachloride (25 ml) during 2 h. The mixture was then boiled under reflux for 2 h and distilled under reduced pressure. The fraction of b.p. 154–156°/0.05 mm gave upon cooling a white solid, which was recrystallised from petrol to give bromo(tris-*p*-fluorophenyl)silane (nc.) (90 %), m.p. 69–71° (Found: C, 54.8; H, 3.4; Br, 20.4. C$_{18}$H$_{12}$BrF$_3$Si calcd. C, 55.0; H, 3.1; Br, 20.3 %). Similarly, from tris(*m*-fluorophenyl)silane was prepared impure bromo(tris-*m*-fluorophenyl)silane (nc.), b.p. 160–162°/0.02 mm (Found: C, 58.2; H, 3.1; Br, 21 6 %).

Methyllithium (3.3 ml of 1.4 *M* solution in ether) was added to a solution of tris(*p*-fluorophenyl)silane (1.74 g, 4.4 mmol) in ether. After the addition, the mixture was boiled for 2 h, then treated with saturated aqueous NH$_4$Cl. The ether layer was separated, dried, and solvent was distilled off to leave a white solid, which was recrystallised from petrol to give tris(*p*-fluorophenyl)(methyl)silane (nc.) (91 %), m.p. 77–79° (Found: C, 69.0; H, 4.7. C$_{19}$H$_{15}$F$_3$Si calcd.: C, 69.5; H, 4.6 %.). An analogous preparation using tris(*m*-fluorophenyl)silane yielded tris(*m*-fluorophenyl)(methyl)-silane (nc) (85 %), m.p. 43° (from petrol) (Found: C, 69.8; H, 4.7 %.)

Phenyllithium (4 ml of 1.5 *M* solution in ether) was added to bromo(tris-*p*-fluorophenyl)silane (2.21 g, 5 6 mmol) in ether (25 ml) and the mixture was boiled under reflux for 2 h. The usual work-up, culminating in evaporation of the dried ether extract, gave a pale yellow residue which was recrystallised from methanol to give white needles of tris(*p*-fluorophenyl)(phenyl)silane (nc.) (87 %), m.p. 120–122° (Found: C, 73.4; H, 4.5. $C_{24}H_{17}F_3Si$ calcd.: C, 73.8; H, 4.4 %.) Tris(*m*-fluorophenyl)(phenyl)silane, m.p. 191–192° (from ethanol) (lit.[16] m.p. 192–193°), was similarly prepared in 78 % yield from bromo(tris-*m*-fluorophenyl)silane.

Preparations of platinum complexes

(*i*). The *trans*-complexes $[Pt(C_6H_4F\text{-}m)(SiPh_3)L_2]$, $[Pt(C_6H_4F\text{-}p)(SiPh_3)L_2]$, $[PtCl\{Si(C_6H_4F\text{-}m)_3\}L_2]$, $[PtCl\{Si(C_6H_4F\text{-}p)_3\}L_2]$, where $L = PMe_2Ph$, and $[PtCl\{Si(C_6H_4F\text{-}m)_3\}L'_2]$, $[PtCl\{Si(C_6H_4F\text{-}p)_3\}L'_2]$, where $L' = AsMe_2Ph$, were prepared as previously described[13,14,17].

(*ii*). A solution of *cis*-$[PtCl_2(PMe_2Ph)_2]$(1.0 g, 1.8 mmol) in tetrahydrofuran (40 ml) was added dropwise with stirring to *p*-fluorophenylmagnesium bromide (4.3 mmol) in ether (20 ml), and the mixture was subsequently refluxed for 1 h. The solvent was removed under reduced pressure and benzene (50 ml) was added. Treatment with cold dilute hydrochloric acid (5 ml), followed by separation, washing and drying (Na_2SO_4) of the organic layer gave a yellow oil, which was extracted with petrol. The residue was recrystallised from benzene/petrol to give the white *trans*-$[Pt(C_6H_4F\text{-}p)_2(PMe_2Ph)_2]$ (nc.) (0.5 g, 42 %), m.p. 154–156°, ν(C–F), 1208 cm^{-1} (Found: C, 51.0; H, 5.0. $C_{28}H_{30}F_2P_2Pt$ calcd.: C, 50.8; H, 4.6 %); the PMR spectrum in C_6D_6 showed three triplets centred at τ 8.78, with J(P–H) 3.5 and J(Pt–H) 32.0 Hz.

(*iii*). A solution of *trans*-$[Pt(C_6H_4F\text{-}p)_2(PMe_2Ph)_2]$ (0.54 g, 0.81 mmol) in benzene (10 ml) was treated with anhydrous hydrogen chloride (0.82 mmol) in benzene. After 5 min the solution was evaporated to dryness, and the residue was crystallised from n-hexane to give colourless needles of *trans*-$[Pt(C_6H_4F\text{-}p)(Cl)(PMe_2Ph)_2]$ (0.28 g, 58 %), m.p. 105–106°, ν(C–F), 1204 cm^{-1}; ν(Pt–P), 425 cm^{-1}; ν(Pt–Cl), 287 cm^{-1} (in polythene discs). (Found: C, 43.8; H, 4.3. $C_{22}H_{26}ClFP_2Pt$ calcd.: C, 43.9; H, 4.3%); the PMR spectrum in C_6D_6 showed three triplets centred at τ 8.71, with J(P–H) 3.5 and J(Pt–H) 32.0 Hz.

^{19}F NMR measurements

Measurements on the $[Pt(C_6H_4F)(X)(PMe_2Ph)_2]$ complexes were made in acetone with fluorobenzene as internal standard. Those on $(FC_6H_4)_3SiX$ compounds were made in benzene (conc. ca. 1*M*) with chlorotrifluoromethane as internal standard, and the chemical shift for the latter relative to fluorobenzene was measured under identical conditions.

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