

A ^{19}F NUCLEAR MAGNETIC RESONANCE STUDY OF A SERIES OF PENTAFLUOROCHROMARENES ($\text{C}_6\text{F}_5\text{X}$) $\text{Cr}(\text{C}_6\text{H}_6)$

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Summary

The ^{19}F NMR spectra of a series of complexes ($\text{C}_6\text{F}_5\text{X}$) $\text{Cr}(\text{C}_6\text{H}_6)$ show marked differences from the spectra of the corresponding $\text{C}_6\text{F}_5\text{X}$ molecules. On complexation the ^{19}F chemical shifts are shielded by 30–50 ppm, the correlation of the *para* fluorine shift with the Taft parameters of the substituent no longer obtains nor does the correlation of the *para* shift with $J(2,4)$. The two *ortho* coupling constants, $J(2,3)$ and $J(3,4)$, in the chromium complex are no longer close to -20 Hz but are now very large (70–100 Hz) and are of opposite sign. An internal compensation mechanism is discussed by which excess electron density in the fluorinated ring of the sandwich is buffered by the C_6H_6 ring.

Introduction

Pentafluorophenyl compounds have long interested NMR spectroscopists [1–10]; they provide a rigid 5-spin system with three ^{19}F chemical shifts and six different fluorine–fluorine coupling constants. The ready incorporation into the sixth position of a variety of substituents of greatly disparate electronic character has allowed the compilation of many data with which one can probe the perturbations brought about by the substituent upon the ring. It is now clear [10] that there exist correlations between the three *meta* coupling constants and the chemical shift of the *para* fluorine. Graham [11] has attempted to rationalise these results in terms of changes in the electron density distribution within the ring and, in particular, he examined the ability of the substituents to interact by π -type overlap with the ring.

We noted some years ago [12] that π -complexation of the fluoroarenes with zero-valent chromium moieties led to large upfield shifts of the fluorine nuclei. Thus, in arene- $\text{Cr}(\text{CO})_3$ systems, 20 ppm upfield shifts are typical [12,13], while in arene-chromium sandwich complexes (chromarenes) 35–50 ppm shifts

are the norm [14]. Such effects had been noted previously with other nuclei in π -systems and, in a recent solid state ^{13}C NMR study, it was shown that, in the case of arene $\text{Cr}(\text{CO})_3$ systems, this effect is primarily attributable to a change in only one of the tensor elements [15]. Thus, it is naive to assume that the large chemical shift and coupling constant changes frequently observed on complexation can be explained solely by changes in gross electron density.

It is also well-established that, upon complexation, intra-ring hydrogen—fluorine coupling constants are markedly reduced [16] but that through-space interactions not proximate to the metal are almost unaffected [17].

Our recent synthetic endeavours [18] have now made available a series of π -complexed pentafluorophenyl derivatives, viz., the pentafluorochromarenes $(\text{C}_6\text{F}_5\text{X})\text{Cr}(\text{C}_6\text{H}_6)$. We here report chemical shift and coupling constant data and note the very remarkable changes which occur on complexation.

Results and discussion

Pentafluorophenyl complexes exhibit three absorption positions which in most cases are assignable (with increasing field) to *ortho*, *para* and *meta* fluorines [10]. In contrast, in the pentafluorochromarenes, absorptions are assignable to *ortho*, *meta* and *para* fluorines, respectively, as the field is increased. Indeed, the *meta* and *para* fluorine resonances occur (see Table 1) in rather narrowly defined ranges and seem to be relatively insensitive to the identity of the substituent X. In some respects, this behaviour parallels that of the *meta*-substituted $(\text{C}_6\text{H}_4\text{FX})\text{Cr}(\text{CO})_3$ complexes in which the fluorine resonance is unaffected by the identity of X; it was suggested [12] that transmission of the substituent effect to the *meta* position (presumably via the σ -framework of the arene ring) is drastically attenuated upon complexation.

However, we have already shown that, in the $(\text{C}_6\text{F}_n\text{H}_{6-n})\text{Cr}(\text{C}_6\text{H}_6)$ systems, the changes in electron-donating or -attracting characteristics of the substituents in the fluorinated ring are reflected in the ^1H and ^{13}C chemical shifts of the C_6H_6 ring [19]. That is, the changes in electron density need not be tolerated solely by the fluorinated arene but are, in fact, to a great extent electronically buffered by transmission of electron density via the chromium atom to the other ring. This is closely analogous to the electronic buffering effect of the $\text{Cr}(\text{CO})_3$ moiety on arenes; thus electron-donating substituents do not increase the electron density in the ring as much as occurs in the free arenes since the excess electron density is siphoned off via the chromium atom to the π^* orbitals of the carbonyls whose $\nu(\text{CO})$ values concomitantly decrease. In contrast, in *ortho*, *meta* and *para* $(\text{C}_6\text{H}_4\text{FX})_2\text{Cr}$ systems, in which no self-compensating mechanism is available, the ^{19}F chemical shifts correlate directly with the inductive and resonance parameters of the substituent X [14].

Thus, to return to the case at hand, the relative constancy of the chemical shifts of the *meta* and *para* fluorine nuclei in the pentafluorochromarenes is again a reflection of the ability of the π - $\text{Cr}(\text{C}_6\text{H}_6)$ moiety to function as a reservoir of electron density.

We note, however, that the chemical shifts of the *ortho* fluorine nuclei in the pentafluorochromarenes vary over a moderate range and also correlate tolerably well with the shifts in the corresponding non-complexed pentafluoro-

TABLE 1

CHEMICAL SHIFTS OF *ortho*, *meta* AND *para* FLUORINE NUCLEI IN $(C_6F_5)_2XCr(C_6H_6)_2$; ALL SHIFTS ARE TO HIGH FIELD OF $CFCF_3$.

X	δ (ppm)			$\Delta_o^{d,e}$	Δ_m	Δ_p	$J(2, 3)$ (Hz)	$J(3, 4)$ (Hz)	$J(2, 4)$ (Hz)
	<i>Ortho</i>	<i>Meta</i>	<i>Para</i>						
PPh ₂	-175.1	-192.8	-198.8	-47.4	-31.8	-48.2	71	-106	43
SiMe ₃	-175.2	-194.0	-200.0	-48.7	-31.9	-47.1	72	-102	42
Ph	-179.1	-192.8	-199.3	-35.0	-29.8	-42.6	80	-103	44
SMe	-179.8	-192.2	-197.4	-44.0	-27.8	-40.2	76	-107	46
CO ₂ Et	-181.8	-193.7	-196.5	-43.0	-32.4	-44.8	76	-99	43
CONHC ₆ H ₄ F	-183.3	-194.3	-196.7	—	—	—	77	-102	47
CO-C ₄ H ₃ O ^a	-184.9	-194.4	-197.7	—	—	—	71	-107	44
H	-185.2	-194.7	-198.2	-47.0	-32.3	-44.5	72	-109	44
CH(OH)Fc ^b	-187.3	-197.3	-201.2	—	—	—	78	-109	45
F	-193.0	-193.0	-193.0	-29.9	-29.9	-29.9	—	—	—
Rh ^c	-165.8	-193.6	-199.4	-40.9	-33.0	-50.0	78	-101	42

^a C₄H₃O is 2-furyl; ^b Fc is ferrocenyl; ^c Rh is $[(C_6H_6)Cr(C_6F_5PPh_2)_2Rh(CO)Cl]_d$; $\Delta = \delta$ complex — δ free arene; ^e Chemical shift data for free arenes taken from refs. 10, 11, 25 and 26.

TABLE 2

J(F) VALUES FOR $(C_6F_5)_2PPh_2Rh(CO)Cl$ AND C_6F_5SMe AND THEIR CHROMARENE ANALOGUES. ALL VALUES IN Hz.

$J(2, 3)$	$J(2, 4)$	$J(3, 4)$	$J(2, 5)$	$J(2, 6)$	$J(3, 5)$	$(C_6F_5)_2PPh_2Rh(CO)Cl^a$			$(C_6H_6)Cr(C_6F_5PPh_2)_2Rh(CO)Cl$		
						ΔJ	$C_6F_5SMe^b$	$C_6H_6CrC_6F_5SMe$	ΔJ	$C_6F_5SMe^b$	$C_6H_6CrC_6F_5SMe$
-23.0	+4.6	-20.6	+7.7	0	-5.8	+77.6	+100.6 or -54.6	-26.5	+76.4	+102.9 or -49.9	
+4.6	-20.6	+7.7	0	-5.8		+42.3	+37.7 or -46.9	+1.7	+45.7	+44.0 or -47.4	
-20.6	+7.7	0	-5.8			-100.8	-80.2 or +121.4	-22.8	-106.5	-83.7 or +129.3	
+7.7	0	-5.8				0	-7.7 or -7.7	+9.0	0	-9.0 or -9.0	
0	-5.8					+12.0	+12.0 or -12.0	-2.0	+9.4	+11.4 or -7.4	
-5.8						-6.0	-0.2 or +11.8	-3.5	-7.2	-3.7 or +10.7	

^a Values taken from ref. 24. ^b Values taken from ref. 10.

phenyl molecules. Of course, it was long ago recognized [20] that simple electronic effects do not account for the *ortho* shifts and among the factors which have been invoked is the steric bulk of the substituent X. While complexation would be expected to promote the usual large upfield shifts as for the *meta* and *para* fluorine nuclei, any direct interaction (steric or otherwise) of the substituent with the *ortho* fluorines would not be attenuated by the compensating ability of the other (i.e. the C_6H_6) ring. We see then that the so-called "ortho-effect" on fluorine chemical shifts is preserved in the pentafluorochromarene series.

Turning now to an examination of the changes in the fluorine-fluorine coupling constants brought about by complexation, we see that they can only be described as dramatic. A simple first-order analysis reveals that the spectra are dominated by three large coupling constants, viz., $J(2, 3)$, $J(2, 4)$ and $J(3, 4)$ which have approximate values of 74, 45 and 100 Hz, respectively. As a typical example, full analysis of the six-spin systems $[C_6F_5PPh_2]_2Rh(CO)Cl$ and its chromarene analogue are listed in Table 2. In favorable cases such as this one or when $X = SCH_3$ (see Fig. 1) the entire spectrum can be assigned, but, when the *meta* and *para* resonances overlap greatly, we cannot with certainty extract all the $J(FF)$ values. It is clear that one cannot regard the π -complexed chromium atom as just a minor perturbation on the pentafluorophenyl ring; assignment of coupling constants and especially the signs of those coupling constants by analogy to the non-complexed C_6F_5X systems would be very hazardous.

In non-complexed C_6F_5X systems, *ortho*- $J(FF)$ values range only from about 18 to 26 Hz [10] and, since the *ortho*- $J(FF)$ values in C_6F_6 have been shown to be negative [21], one can with some confidence assign a negative value to them in all C_6F_5X molecules. However, in the pentafluorochromarenes, the magnitude of the changes, especially to the *ortho*- $J(FF)$ values, is such that

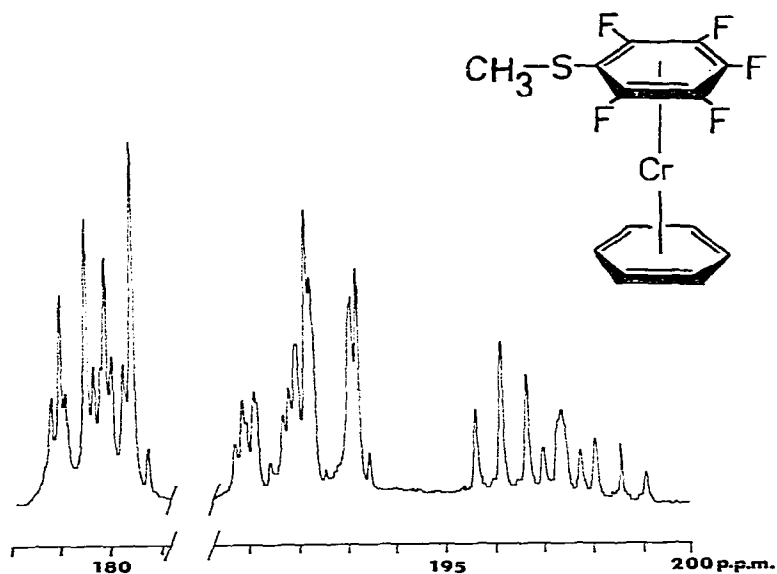


Fig. 1. ^{19}F NMR spectrum of $C_6H_6CrC_6F_5SCH_3$.

one can no longer assume them to be negative. Indeed, computer simulation of the spectra reveals quite clearly that any combination of coupling constants in which $J(2,3)$ and $J(3,4)$ have the same sign is incompatible with the experimental spectrum. We present in Table 2 a set of coupling constants but it is, of course, possible that all of them should be of opposite absolute sign. Hence, one must list two possibilities in each case for the change in $J(FF)$ on complexation. We plan to determine the absolute sign of the *ortho*-coupling constants in $(C_6F_6)Cr(C_6H_6)$ by measurements in liquid crystal solvents.

We note again with the coupling constants, as with the *meta* and *para* chemical shifts, that there is no pronounced dependence on the substituent X, and that apparently the electronic buffering effect of the π -Cr(C_6H_6) moiety neutralises the changes brought about by the substituent.

We are, at the moment, loath to speculate on the significance of the large *ortho*- $|J(FF)|$ values except to comment that they are more typical of fluorobenzenium ions [22], such as $C_6H_5F_2^+$, than of fluoroaromatics. We hope to gain some understanding of these systems when we have completed some calculations of coupling constants in collaboration with our colleague Professor D.P. Santry.

Experimental

Fluorine-19 NMR spectra were obtained on a Bruker WH90 spectrometer operating at 84.66 MHz; concentrations of 0.04–0.05 M in benzene- d_6 as solvent were used throughout, and $CFCl_3$ was used as an external reference. Spectral simulation was achieved with Nicolet's E28-7011 iterative program and an 1180 computer.

The syntheses of the pentafluorochromarenes are reported elsewhere [17,18, 19,23] except for X = SCH₃ and X = CO · NH · C₆H₄F.

X = SCH₃. A slight excess of methyl thiocyanate was added to a solution of $(C_6F_5Li)Cr(C_6H_6)$ (0.335 mmole) in ether at $-78^\circ C$ under a nitrogen atmosphere. The solution was stirred at $-78^\circ C$ for 2 h by which time the initially red-brown solution had turned yellow. The solution was allowed to warm to room temperature, filtered and the solvent and excess CH₃SCN removed in vacuo. The product was purified by sublimation at $60^\circ C/10^{-2}$ mm Hg to give yellow-orange, air stable 1-methylthio-2,3,4,5,6-pentafluorochromarene 80 mg (70%), m.p. $105^\circ C$ (with decomposition). The ¹H NMR spectrum in C₆D₆ showed a singlet at δ 2.12 ppm (3 H) and a multiplet at δ 4.6 ppm (6 H). Mass spectral data; m/e (%): 344, C₁₃H₉F₅SCr⁺ (70); 326, C₁₃H₁₀F₄SCr⁺ (18); 298, C₁₂H₇F₅Cr⁺ (12); 266, C₇H₃F₅Cr⁺ (17); 251, C₆F₅SCr⁺ (30), 214, C₇H₃F₅S⁺ (45); 199, C₆F₅S⁺ (34); 181, C₆HF₄S⁺ (30); 168, C₆HF₅⁺ (12); 149, C₆HF₄⁺ (50); 130, C₆H₆Cr⁺ (90); 78, C₆H₆⁺ (70); 52, Cr⁺ (100); 47, SCH₃⁺ (40).

X = CO · NH · C₆H₄F. A slight excess of *para*-fluorophenyl isocyanate was added to 0.335 mmol $(C_6F_5Li)Cr(C_6H_6)$ in ether at $-78^\circ C$ under a nitrogen atmosphere. The solution was stirred at $-78^\circ C$ for 2.5 h by which time the initially red-brown solution had turned yellow. The solution was allowed to warm to room temperature and the excess solvent and *p*-fluorophenyl isocyanate were removed in vacuo. The product was recrystallized from benzene to

give orange-red, air stable *N*-(2,3,4,5,6-pentafluorochromarenoyl)-4-fluoroaniline, 155 mg (38%), m.p. 177°C; IR showed $\nu(\text{CO})$ at 1660 cm^{-1} and $\nu(\text{NH})$ at 3295 cm^{-1} . The ^1H NMR spectrum exhibited a multiplet at δ 4.79 ppm (6 H), a doublet (8 Hz) of doublets (8 Hz) at δ 6.9 ppm (2 H), a doublet (12 Hz) of doublets (8 Hz) at δ 7.4 ppm (2 H) and a singlet at δ 3.14 ppm (NH). Mass spectral data; m/e (%): 435, $\text{C}_{19}\text{H}_{11}\text{F}_6\text{NOCr}^+$ (30); 417, $\text{C}_{19}\text{H}_{12}\text{F}_5\text{NOCr}^+$ (10); 357, $\text{C}_{13}\text{H}_5\text{F}_6\text{NOCr}^+$ (60); 305, $\text{C}_{13}\text{H}_5\text{F}_6\text{NO}^+$ (20); 298, $\text{C}_{12}\text{H}_7\text{F}_5\text{Cr}^+$ (8); 287, $\text{C}_{13}\text{H}_6\text{F}_5\text{NO}^+$ (20); 280, $\text{C}_{12}\text{H}_8\text{F}_4\text{Cr}^+$ (20); 270, $\text{C}_{13}\text{H}_5\text{F}_5\text{N}^+$ (32); 219, $\text{C}_6\text{F}_5\text{Cr}^+$ (42); 195, $\text{C}_7\text{F}_5\text{O}^+$ (27); 167, C_6F_5^+ (23); 149, C_6HF_4^+ (43); 138, $\text{C}_7\text{H}_5\text{FNO}^+$ (51); 130, $\text{C}_6\text{H}_6\text{Cr}^+$ (47); 110, $\text{C}_6\text{H}_5\text{FN}^+$ (30); 95, $\text{C}_6\text{H}_4\text{F}^+$ (35); 78, C_6H_6^+ (100); 52, Cr^+ (80).

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