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The prediction of the ^{19}F NMR spectra of fluoro-substituted arenetricarbonylchromium complexes*

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Abstract

The tricarbonylchromium complexes of the following derivatives of fluorobenzene have been prepared: 2,4- and 3,5-dimethyl-, 2,4,6-trimethyl-, 3,4- and 3,5-dimethoxy- and 4-methoxy-2-methylfluorobenzene, 4-fluorocumene, 4-fluoro-*N,N*-dimethylaniline, 3-fluoro-2-methoxyaniline and 4-fluoro-2-methylacetophenone. Preparative, microanalytical, IR, UV–Vis and ^1H and ^{19}F NMR spectral data are presented for these new compounds. Both literature and new ^{19}F NMR spectral data have been analysed for thirty-five monofluoro complexes and seven difluoro complexes. A statistical prediction method for both these types of complexes is presented with correlation coefficients of observed versus predicted line positions of 0.986 and 0.993, respectively.

1. Introduction

Today there are many hundred arenetricarbonylchromium complexes known [1–10] and several score containing fluorine substitution. However there are remarkably few reports concerning the ^{19}F NMR spectra of this latter group of complexes.

In one report the ^{19}F NMR spectra have been put to good use by Fletcher and McGlinchey [1] to study the bonding in complexes with one *meta* or *para* substituent besides the fluorine, but in this paper there was no consideration of *ortho*-substituted complexes, complexes containing polysubstitution of non-fluorine substituents or complexes of substituted di-fluoro systems. There was also no attempt at statistical prediction of the ^{19}F NMR line position.

In the present work we have studied complexes containing two and three substituents besides the fluorine, and compounds containing two fluorine substituents. A statistical method of prediction for the ^{19}F NMR spectra of both these groups of complexes has been found.

Experimental

Preparation of complexes

The free arenes to synthesize complexes no. 8, 11, 12, 21 and 22 were purchased from Trans World Chemicals, nos. 13 and 33 from the Aldrich Chemical Company/Alfred Bader Library of Rare Chemicals, nos. 22 and 32 from Aldrich Chemical Company and no. 27 from American Tokyo Kasei, Inc. All new complexes were prepared by previously published methods [2–7, 9]. Preparative microanalytical, IR, UV–Vis and ^1H NMR data for these new complexes are given in Tables 1–5. The references to the preparation of previously reported complexes are given in Tables 6 and 7. ^1H NMR spectra were determined using a Bruker WH400 instrument, IR spectra with a Perkin-Elmer 983 and UV spectra with a Perkin-Elmer lambda 3B instrument.

^{19}F NMR spectra

Tables 6 and 7 contain both literature data and new data presented here for the first time. References are given in Tables 6 and 7. The new data were determined by Spectral Data Services, Champaign, IL using a Nickolet NT360 spectrometer operating at 338.7 MHz

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*This paper is dedicated to Professor P. L. Pauson on the occasion of his sixty-fifth birthday.

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TABLE 1. Reaction of arenes with 4.0 g (18.2 mmol) of $Cr(CO)_6$ (12 h) to give the corresponding η^6-arenetricarbonylchromium complexes

No.	Arene (mmol)	Yield		Melting point (°C)	Color
		(g)	(%)		
8	4.0	0.15	14	42–44	Yellow
11	4.0	0.25	24	108–109	Yellow
12	3.6	0.35	35	101–102	Yellow
13	4.05	0.2	18	34–35	Yellow
20	3.2	0.65	69	95–97	Yellow
21	3.2	0.69	74	129–31	Yellow
22	3.6	0.44	45	59.5–61.5	Yellow
27	4.0	0.70	64	83–84.5	Orange
32	0.9	0.14	57	100–102.5	Yellow
33	3.39	0.13	14	62–65	Orange

TABLE 2. Microanalytical data for new compounds

No.	Calculated			Found		
	C	H	N	C	H	N
8	50.8	3.5		50.55	3.4	
11	50.8	3.5		50.6	3.3	
12	52.55	4.0		52.2	4.0	
13	52.6	4.0		52.3	4.1	
20	45.2	3.1		45.1	3.0	
21	45.2	3.1		45.1	3.1	
22	47.8	3.3		47.7	3.3	
27	48.0	3.6	5.1	48.1	3.5	5.0
32	43.3	2.9	5.05	43.6	3.0	4.8
33	50.0	3.15		49.5	2.9	

TABLE 3. IR spectra of new compounds in C_6H_{12}

No.	ν(CO) (cm^{-1})		
8	1975.2	1908	
11	1978.4	1914.4	1907
12	1970.8	1970.8	
13	1984.8	1922.8	1911.6
20	1976.8	1910.8	1900
21	1977	1906	
22	1979.0	1911	
27	1970.2	1901	1891
32	1974	1905.6	1898.4
33	1992.6	1935.8	1926.0

using Freon-11 as external standard and chloroform-d as solvent.

Software for statistical computations

Statistical computations were done using routines written in SAS (Statistical Analysis System) running on a Microvax Model 3900.

TABLE 4. UV–Vis spectra of new compounds

No.	Wavelength		Wavelength	
	(nm)	(ϵ_{max})	(nm)	(ϵ_{max})
8	215	(29000)	314	(11300)
11	216	(24100)	310	(10000)
12	215	(20200)	315	(7600)
13	218	(22400)	312	(9400)
20	213	(35300)	312	(8300)
21	210	(22300)	312	(8100)
22	212	(20000)	312	(5300)
27	216	(28100)	318	(6000)
32	217	(39100)	314	(8000)
33	208	(27800)	321	(9200)

Results and discussion

The complete ^{19}F NMR data set for monofluoro complexes used in this study is given in Table 6. We have included for completeness eleven complexes (nos. 1–3, 5, 6, 14, 15, 18, 19, 24, 25) first reported by Fletcher and McGlinchey [1]. Of the remaining twenty-six, eleven (nos. 8, 11–13, 20–22, 27, 32, 33) are new complexes for which the preparative, microanalytical, IR, UV and ^1H NMR spectral data are reported in Tables 1–5. The rest are complexes whose synthesis has been previously reported but the ^{19}F NMR is reported in this paper. (see references given in Table 6).

The data set for the difluoro complexes is given in Table 7. The parent complexes have been previously reported [1]. The remaining difluoroaniline complexes have already been prepared [8] but the ^{19}F NMR spectra are reported here.

Statistical analysis

Our first attempts to predict the ^{19}F NMR spectra of arenetricarbonylchromium complexes using the various available Hammett parameters was largely unsuccessful yielding only low correlation coefficients. The correlation coefficients are given in Table 8 together with sample sizes which are different for the different data sets since some of the σ values are unavailable from the literature. Table 9 lists the various σ values used in these computations.

Monofluoro substituted complexes

In order to obtain a better statistical fit, we studied the work of Fletcher and McGlinchey [1] where it was shown, although not explicitly stated, that for *para*-substituted fluorobenzenetricarbonylchromium complexes, the position of the ^{19}F NMR line can be predicted from the field parameter $\mathscr{F}$ and the resonance parameter $\mathscr{R}$ by a linear function

$$\Delta^F = f\mathscr{F} + r\mathscr{R} + c \qquad (1)$$

TABLE 5. ^{1}H NMR spectra (δ from TMS in $CDCl_3$) for new complexes (coupling constants in Hz)

No.	Ring protons	Other protons
8	5.14 (1H,d of t,H-5, $J_{H\text{-}5,H\text{-}6}=6.85$, $J_{H\text{-}3,H\text{-}5}=1.84$, $J_{H\text{-}5,F}=1.84$) 5.24 (1H,d of d,H-3, $J_{HH}=1.49$, $J_{HF}=3.99$) 5.50 (1H,d of d,H-6, $J_{HH}=6.60$, $J_{HF}=5.14$)	2.09 (3H,s,4-Me) 2.24 (3H,d,2-Me, $J_{HF}=1.66$)
11	4.64 (1H,br.s,H-4) 5.16 (2H,d,H-2,6, $J_{HF}=5.1$)	2.27 (6H,s,Me)
12	5.02 (2H,d,H-3,5, $J_{HF}=4.27$)	2.09 (3H,s,4-Me) 2.27 (6H,s,2,6-Me)
13	5.245–5.35 (2H,m)} AA′BB′X 5.45–5.47 (2H,m) }	1.19 (6H,d,Me, $J=6.90$) 2.50 (1H, 7 lines, $C\underline{H}Me_2$, $J=6.89$)
20	5.04 (1H,d of d of d,H-6, $J_{H\text{-}5,H\text{-}6'}=6.88$, $J_{H\text{-}2,H\text{-}6}=2.49$, $J_{HF}=2.50$) 5.42–5.45 (2H,m)	3.73 (3H,s,4-MeO) 3.89 (3H,s,3-MeO)
21	4.94 (1H,br.s,H-4) 5.15 (2H,d of d,H-2,6, $J_{HH}=4.88$, $J_{HF}=1.82$) 5.14–5.16 (2H,m)	3.78 (6H,s,MeO)
22	4.84 (1H,d,H-4, $J_{HH}=6.37$) 5.35 (1H,d of d,H-3, $J_{HH}=4.86$, $J_{HF}=6.37$) 5.34–5.37 (1H,m) 5.41–5.43 (1H,m)	2.16 (3H,s,Me) 3.78 (3H,s,MeO)
27	4.77–4.80 (2H,m)} AA′BB′ 5.60–5.63 (2H,m)}	2.815 (6H,s,NMe_2)
32	4.56 (1H,d,H-6, $J_{HH}=6.50$) 4.95 (1H,br.t,H-4, $J=5.83$) 5.33 (1H,d of t,H-5, $J_{HH}=6.48$, $J_{HF}=2.42$)	3.99 (2H,br.s,NH_2) 3.99 (3H,d,MeO, $J=1.66$)
33	5.23 (1H,d of d,H-3, $J_{HF}=5.36$, $J_{HH}=2.24$) 5.30 (1H,d of d of d,H-5, $J_{H\text{-}3,H\text{-}5}=2.30$, $J_{H\text{-}5,H\text{-}6}=6.73$, $J_{HF}=4.27$) 5.97 (1H,d of d,H-6, $J_{HH}=2.96$, $J_{HF}=6.89$)	2.46 (3H,s,Me) 2.50 (3H,s,(CO)Me)

where *f*, *r* and *c* are estimated from a sample of six such compounds (nos. 1, 3, 6, 15, 19 and 25). Fletcher and McGlinchey omitted *p*-difluorobenzenetricarbonylchromium from the computations, as it seemed to be anomalous. We will discuss this apparent anomaly later in the section on difluoro-substituted complexes. The correlation coefficient is given as 99.4%. Adding five *para*-substituted complexes presented in the present paper (nos. 13, 16, 26, 27, 35) to the above six, we estimated *f*, *r* and *c* based on this sample of eleven using standard linear regression techniques provided by the SAS software to obtain the equation

$$\Delta^F = 0.364\mathcal{F} + 13.406\mathcal{R} - 135.691 \tag{2}$$

The correlation coefficient is 99.0%.

Using the same procedure for the five *meta*-substituted complexes (nos. 2, 5, 14, 18, 24) in ref. 1 we obtained eqn. (3) for these compounds with a correlation coefficient of 99.7%.

$$\Delta^F = -1.703\mathcal{F} + 1.739\mathcal{R} - 135.104 \tag{3}$$

Because *p*-difluorobenzenetricarbonylchromium had been omitted from the computations for the *para*-substituted complexes in ref. 1, we left *m*-difluorobenzenetricarbonylchromium out of the computations for the *meta*-substituted complexes.

Using our own small sample of four *ortho*-substituted complexes (nos. 4, 17, 23, 34) and the same technique, we derived eqn. (4) for *ortho*-substituted complexes. The correlation coefficient is 99.8%.

$$\Delta^F = -8.424\mathcal{F} + 33.437\mathcal{R} - 133.881 \tag{4}$$

Thus using whichever is appropriate of eqns. (2), (3) or (4) we can predict quite accurately the position of the ^{19}F NMR line for singly-substituted fluorobenzenetricarbonylchromium complexes. The fact that the coefficients are different depending on whether the substituent is in the *ortho*, *meta* or *para* position means that $\mathcal{F}$ and $\mathcal{R}$ do not have the same effect in different positions. The field effect is small in the case of *para* and *meta* substitution and somewhat larger in the case of *ortho* substitution. The resonance effect is small for *meta* substitution, large in the case of *para* substitution

TABLE 6. Monofluorobenzenetricarbonylchromium complexes, ^{19}F NMR signal position (observed and predicted) and values for field and resonance parameters

No.	Arene in arenetricarbonylchromium complex	Δ^F		$\mathscr{F}$ ortho	$\mathscr{R}$ ortho	$\mathscr{F}$ meta	$\mathscr{R}$ meta	$\mathscr{F}$ para	$\mathscr{R}$ para	Ref. [b]	Ref. [c]
		obs	pred								
1	Fluorobenzene	−135.9	−135.6	0.000	0.000	0.000	0.000	0.000	0.000	1	2
2	*m*-Chlorofluorobenzene	−136.6	−136.9	0.000	0.000	0.690	−0.161	0.000	0.000	1	1
3	*p*-Chlorofluorobenzene	−137.2	−137.7	0.000	0.000	0.000	0.000	0.690	−0.161	1	1
4	2-Fluorotoluene	−138.6	−139.9	−0.052	−0.141	0.000	0.000	0.000	0.000	[a]	3
5	3-Fluorotoluene	−135.3	−135.4	0.000	0.000	−0.052	−0.141	0.000	0.000	1	3
6	4-Fluorotoluene	−137.8	−137.5	0.000	0.000	0.000	0.000	−0.052	−0.141	1	3
7	2,3-Dimethylfluorobenzene	−137.3	−139.7	−0.052	−0.141	−0.052	−0.141	0.000	0.000	[a]	3
8	2,4-Dimethylfluorobenzene	−142.9	−141.8	−0.052	−0.141	0.000	0.000	−0.052	−0.141	[a]	[a]
9	2,6-Dimethylfluorobenzene	−143.8	−144.1	−0.104	−0.282	0.000	0.000	0.000	0.000	[a]	6
10	3,4-Dimethylfluorobenzene	−137.1	−137.3	0.000	0.000	−0.052	−0.141	−0.052	−0.141	[a]	6
11	3,5-Dimethylfluorobenzene	−136.1	−135.2	0.000	0.000	−0.104	−0.282	0.000	0.000	[a]	[a]
12	2,4,6-Trimethylfluorobenzene	−148.2	−146.0	−0.104	−0.282	0.000	0.000	−0.052	−0.141	[a]	[a]
13	4-Fluorocumene	−136.4	−137.0	0.000	0.000	0.000	0.000	−0.050	−0.100	[a]	[a]
14	*m*-Fluorobenzotrifluoride	−135.8	−137.1	0.000	0.000	0.631	0.186	0.000	0.000	1	1
15	*p*-Fluorobenzotrifluoride	−133.5	−133.1	0.000	0.000	0.000	0.000	0.631	0.186	1	1
16	4-Fluorostyrene	−136.0	−136.7	0.000	0.000	0.000	0.000	0.070	−0.080	[a]	7
17	2-Fluoroanisole	−154.8	−153.5	0.413	−0.500	0.000	0.000	0.000	0.000	[a]	3
18	3-Fluoroanisole	−136.7	−136.1	0.000	0.000	0.413	−0.500	0.000	0.000	1	3
19	4-Fluoroanisole	−142.4	−142.2	0.000	0.000	0.000	0.000	0.413	−0.500	1	3
20	3,4-Dimethoxyfluorobenzene	−140.2	−142.7	0.000	0.000	0.413	−0.500	0.413	−0.500	[a]	[a]
21	3,5-Dimethoxyfluorobenzene	−138.9	−136.6	0.000	0.000	0.826	−1.000	0.000	0.000	[a]	[a]
22	4-Methoxy-2-methylfluorobenzene	−147.7	−146.4	−0.052	−0.141	0.000	0.000	0.413	−0.500	[a]	[a]
23	2-Fluoroaniline	−156.3	−157.5	0.037	−0.681	0.000	0.000	0.000	0.000	[a]	3
24	3-Fluoroaniline	−136.3	−135.2	0.000	0.000	0.037	−0.681	0.000	0.000	1	1,3
25	4-Fluoroaniline	−146.2	−144.7	0.000	0.000	0.000	0.000	0.037	−0.681	1	1,3
26	4-Fluoro-*N*-methylaniline	−146.1	−145.5	0.000	0.000	0.000	0.000	−0.110	−0.740	[a]	4
27	4-Fluoro-*N*,*N*-dimethylaniline	−146.8	−147.8	0.000	0.000	0.000	0.000	0.100	−0.920	[a]	[a]
28	2-Fluoro-5-methylaniline	−160.1	−159.4	0.037	−0.681	0.000	0.000	−0.052	−0.141	[a]	6
29	3-Fluoro-2-methylaniline	−138.0	−139.4	−0.052	−0.141	0.037	−0.681	0.000	0.000	[a]	3
30	3-Fluoro-4-methylaniline	−138.9	−139.4	−0.052	−0.141	0.037	−0.681	0.000	0.000	[a]	4
31	3-Fluoro-6-methylaniline	−136.2	−137.1	0.000	0.000	0.037	−0.681	−0.052	−0.141	[a]	3
32	3-Fluoro-2-methoxyaniline	−152.3	−153.0	0.413	−0.500	0.037	−0.681	0.000	0.000	[a]	[a]
33	4-Fluoro-2-methylacetophenone	−134.1	−132.7	0.000	0.000	−0.052	−0.141	0.534	0.202	[a]	[a]
34	Ethyl-2-fluorobenzoate	−133.4	−133.7	0.552	0.140	0.000	0.000	0.000	0.000	[a]	5
35	Ethyl-4-fluorobenzoate	−133.7	−133.7	0.000	0.000	0.000	0.000	0.552	0.140	[a]	6

[a] This paper. [b] Reference to ^{19}F NMR spectrum. [c] Reference to preparation of complex.

TABLE 7. Difluorobenzenetricarbonylchromium complexes, ^{19}F NMR signal positions (observed and predicted) and values for field and resonance parameters

No.	Arene in arenetricarbonylchromium complex	Δ^F		$\mathcal{F}$ ortho	$\mathcal{R}$ ortho	$\mathcal{F}$ meta	$\mathcal{R}$ meta	$\mathcal{F}$ para	$\mathcal{R}$ para	Ref. [b]	Ref. [c]
		obs	pred								
36	*m*-Difluorobenzene	−136.4	−134.6	0.000	0.000	0.708	−0.336	0.000	0.000	1	1
37	*p*-Difluorobenzene	−134.0	−135.8	0.000	0.000	0.000	0.000	0.708	−0.336	1	1
38	2,3-Difluoroaniline	−178.8 (2)	−179.5	0.745	−1.017	0.000	0.000	0.000	0.000	[a]	8
		−158.7 (3)	−159.1	0.708	−0.336	0.037	−0.681	0.000	0.000	[a]	
39	2,4-Difluoroaniline	−155.8 (2)	−157.8	0.037	−0.681	0.708	−0.336	0.000	0.000	[a]	8
		−143.4 (4)	−145.4	0.000	0.000	0.708	−0.336	0.037	−0.681	[a]	
40	2,5-Difluoroaniline	−161.7 (2)	−159.0	0.037	−0.681	0.000	0.000	0.708	−0.336	[a]	8
		−137.8 (5)	−138.7	0.000	0.000	0.037	−0.681	0.708	−0.336	[a]	
41	3,4-Difluoroaniline	−158.3 (3)	−159.1	0.708	−0.336	0.037	−0.681	0.000	0.000	[a]	8
		−169.0 (4)	−167.0	0.708	−0.336	0.000	0.000	0.037	−0.681	[a]	
42	3,5-Difluoroaniline	−139.6	−137.5	0.000	0.000	0.745	−1.017	0.000	0.000	[a]	8

[a] This paper. [b] Reference to ^{19}F NMR spectrum. [c] Reference to preparation of complex.

TABLE 8. Correlation coefficients of ^{19}F NMR signal position with various sigma parameters

σ Parameter	Correlation coefficient	Sample size
σ_m	0.45	37
σ_p	0.60	37
σ_p^-	0.38	31
σ_p^0	0.49	32
σ_p^+	0.59	35
All	0.54	31

and very large for *ortho* substitution, presumably representing perturbation of the electronic structure from steric hindrance.

Any model to predict the position of the ^{19}F NMR line in fluorobenzenetricarbonylchromium complexes having two or more substituents must take into account the fact that $\mathcal{F}$ and $\mathcal{R}$ have a different effect depending on the position of the substituents, and so we sought to use a model of the form

$$\Delta^F = f_o\mathcal{F}_o + r_o\mathcal{R}_o + f_m\mathcal{F}_m + r_m\mathcal{R}_m + f_p\mathcal{F}_p + r_p\mathcal{R}_p + c \qquad (5)$$

The values of f_o and r_o are those estimated for *ortho*-substituted compounds in eqn. (4), f_m and r_m are those for *meta*-substituted compounds from eqn. (3) and f_p and r_p are those estimated for *para*-substituted compounds from eqn. (2). $\mathcal{F}_o$ and $\mathcal{R}_o$ are the $\mathcal{F}$ and $\mathcal{R}$ values for the substituent in the *ortho* position or the sums of such values if there are two *ortho* substituents. $\mathcal{F}_m$ and $\mathcal{R}_m$ are the $\mathcal{F}$ and $\mathcal{R}$ values for the *meta* substituent or the sums of these values if there are two. $\mathcal{F}_p$ and $\mathcal{R}_p$ are the $\mathcal{F}$ and $\mathcal{R}$ values for the *para* substituent. It is not clear which of the three values of c to use, and in any case, logically c should be the ^{19}F NMR value for the unsubstituted complex, that is, for fluorobenzenetricarbonylchromium. Thus the value −135.9 given in ref. 1 was used.

For our sample of substituted fluorobenzenetricarbonylchromium complexes consisting of fourteen di- and one tri-substituted complexes (nos. 7, 8, 9, 10, 11, 12, 20, 21, 22, 28, 29, 30, 31, 32, 33), this model works rather well yielding a correlation coefficient of 96.0%. For all 35 complexes (see Table 6) including those with only a single substituent, the above procedure gives a correlation coefficient of 97.8%.

Though it is interesting that such a prediction equation for multiply-substituted complexes can be derived from the data for singly-substituted complexes, it seemed likely that the accuracy of prediction could be improved somewhat if the coefficients were estimated from all 35 complexes. For this purpose we ran a six-variable multiple regresssion on eqn. (5) using the data from all 35 data points. Mathematically this amounts to finding the values of the coefficients f_o, r_o, f_m, r_m, f_p, r_p and c for eqn. (5) which best fits the 35 data points in the least-squares sense. This yields equation

$$\Delta^F = -4.650\mathcal{F}_o + 31.882\mathcal{R}_o - 2.066\mathcal{F}_m - 0.780\mathcal{R}_m + 0.169\mathcal{F}_p + 13.352\mathcal{R}_p - 135.637 \qquad (6)$$

The multiple correlation coefficient, which may be interpreted as giving the correlation between predicted and observed values for these 35 complexes, is 98.6%. Using eqn. (6) with only the fifteen di- and tri-substituted complexes yields a correlation coefficient of 97.8%. We believe this equation to be more reliable for polysubstituted complexes, though eqns. (2), (3) and (4) may be marginally better for complexes containing only one substituent. The observed values and values predicted by eqn. (6) for the 35 complexes are shown in Table 6 and Fig. 1.

TABLE 9. Values of σ_m, σ_p, σ_p^-, σ_p^0, σ_p^+, for complexes 1–37 used to compute the correlation coefficients given in Table 8

No.	σ_m	σ_p	σ_p^-	σ_p^0	σ_p^+
1	0.000	0.000	0.00	0.00	0.000
2	0.373	0.227	0.27	0.28	0.035
3	0.373	0.227	0.27	0.28	0.035
4	−0.069	−0.170	−0.15	−0.12	−0.256
5	−0.069	−0.170	−0.15	−0.12	−0.256
6	−0.069	−0.170	−0.15	−0.12	−0.256
7	−0.138	−0.340	−0.30	−0.24	−0.512
8	−0.138	−0.340	−0.30	−0.24	−0.512
9	−0.138	−0.340	−0.30	−0.24	−0.512
10	−0.138	−0.340	−0.30	−0.24	−0.512
11	−0.138	−0.340	−0.30	−0.24	−0.512
12	−0.207	−0.510	−0.45	−0.36	−0.768
13	−0.070	−0.150	[a]	−0.16	−0.280
14	0.430	0.540	0.65	0.54	0.582
15	0.430	0.540	0.65	0.54	0.582
16	0.050	−0.020	[a]	[a]	[a]
17	0.115	−0.268	−0.16	−0.10	−0.648
18	0.115	−0.268	−0.16	−0.10	−0.648
19	0.115	−0.268	−0.16	−0.10	−0.648
20	0.230	−0.536	−0.32	−0.20	−1.296
21	0.230	−0.536	−0.32	−0.20	−1.296
22	0.046	−0.438	−0.31	−0.22	−0.904
23	−0.160	−0.660	−0.15	−0.36	−1.111
24	−0.160	−0.660	−0.15	−0.36	−1.111
25	−0.160	−0.660	−0.15	−0.36	−1.111
26	−0.300	−0.840	[a]	[a]	[a]
27	−0.150	−0.830	−0.12	−0.48	−1.700
28	−0.229	−0.830	−0.30	−0.48	−1.367
29	−0.229	−0.830	−0.30	−0.48	−1.367
30	−0.229	−0.830	−0.30	−0.48	−1.367
31	−0.229	−0.830	−0.30	−0.48	−1.367
32	−0.045	−0.928	−0.31	−0.46	−1.759
33	0.307	0.332	[a]	[a]	0.311
34	0.370	0.450	[a]	[a]	0.472
35	0.370	0.450	[a]	[a]	0.472
36	0.337	0.062	0.05	0.21	−0.247
37	0.337	0.062	0.05	0.21	−0.247

[a] Not available.

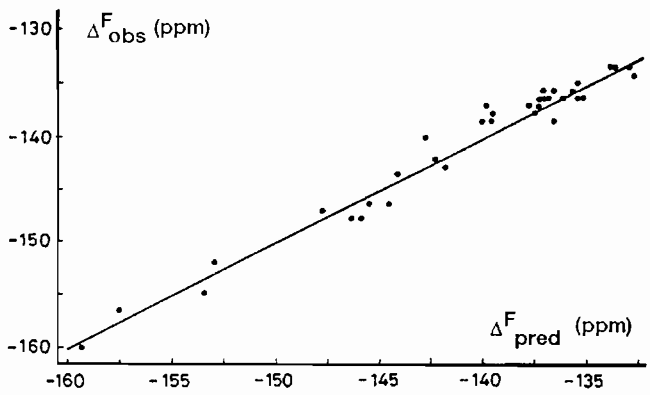

Fig. 1. Plot of observed ^{19}F NMR line position vs. position predicted by eqn. (6) for 35 substituted fluorobenzene complexes.

Difluoro-substituted complexes

We conducted a separate study of substituted difluorobenzenetricarbonylchromium complexes, because the data in ref. 1 seemed to indicate that the two such complexes in that study did not conform to the same pattern as the monofluorobenzenetricarbonylchromium complexes. Our study, which was hampered by the small number of such complexes available and the lack of variety of the substituents*, partly confirms that conclusion, but suggests that a separate prediction theory might be worked out for them if enough complexes were available for study.

We used the two difluoro complexes (nos. 36, 37) from ref. 1 and five substituted difluoro complexes which we had available from previous work (nos. 38–42). Symmetric complexes (nos. 36, 37, 42) give a single ^{19}F NMR line, while unsymmetric complexes give a pair of spectral lines and show poorly resolved fluorine–fluorine splitting. Because the difluorobenzene complexes can be considered to be fluoro-substituted fluorobenzene complexes, we assumed that they would obey the predicted eqn. (6) approximately, at least well enough that we could interpret the spectra statistically. For the purpose of using eqn. (6), we obtained from each unsymmetric complex two data points, first by thinking of one of the fluorine atoms as being the *ipso* fluorine and the other as a fluoro-substituent and vice versa. This resulted in a sample of eleven ^{19}F NMR signals from seven complexes. This procedure did indeed allow us to interpret the spectra statistically. Using eqn. (6) as a predictor for these eleven signals resulted in a reasonably high correlation coefficient ($r = 93\%$).

Equation (6) works quite well for some difluorobenzene complexes, as can be seen in Fig. 2, but not very well for the four signals from the two bis-*ortho*-complexes situated below the prediction line (nos. 38 and 41). The others have the second fluorine in the *meta* or *para* position. In attempting to derive a separate predictor equation for difluorobenzene complexes we would have preferred to duplicate the methods used in the monofluoro case above, but the paucity of difluorobenzene complexes prevented this. In order to circumvent this problem, we omitted the least significant variable, $\mathcal{F}_p$, and were able to determine the coefficients for the remaining five variables. The correlation coefficient was high ($r = 99.3\%$). We thus obtained eqn. (7) for predicting the ^{19}F NMR line position for difluorobenzene complexes.

$$\Delta^F = -20.771\mathcal{F}_o + 32.951\mathcal{R}_o - 3.887\mathcal{F}_m + 3.992\mathcal{R}_m + 15.811\mathcal{R}_p - 130.497 \qquad (7)$$

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*Unsuccessful attempts were made to synthesize 2,4,6-trifluoroaniline-, 2,4-difluorotoluene- and 2,4-difluoroanisoletricarbonylchromium complexes.

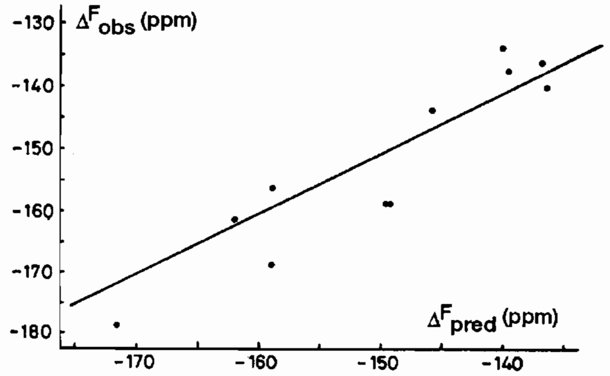

Fig. 2. Plot of observed ^{19}F NMR line position vs. position predicted by eqn. (6) for 11 signals from 7 difluorobenzene complexes.

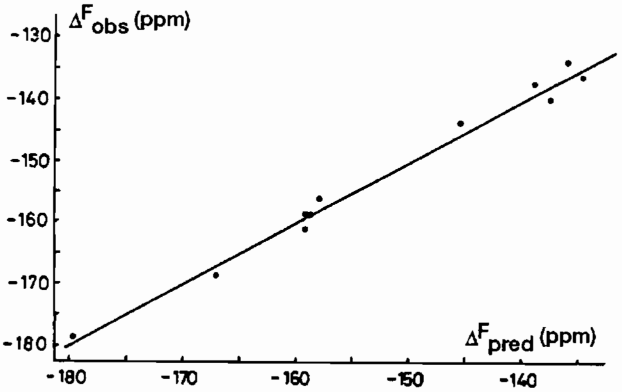

Fig. 3. Plot of the observed ^{19}F NMR line position vs. position predicted by eqn. (7) for 11 signals from 7 difluorobenzene complexes.

Though the data fit this line quite closely (see Table 7 and Fig. 3), the data set from which it is calculated is quite small and consists only of difluoroaniline and two unsubstituted complexes. It is unknown how well it would fit complexes with other substituents. Though the $\mathscr{F}$ and $\mathscr{R}$ values for fluorine are not needed in the calculations for the fluorobenzene complexes, the coefficients calculated for eqn. (7) depend heavily on these values. In ref. 1 it was suggested that the $\mathscr{F}$ value for fluorine might be much higher than the literature values. In any case we found substantial literature disagreement as to the $\mathscr{F}$ value for the fluorine substituent. We used the Swain and Lupton [11] value of 0.708 in computing eqn. (7), though in Hansch and Leo [12] it is given as 0.43. We were able to show that an F value of about 3 would allow the difluorobenzene complexes to fall on the prediction line for fluorobenzene complexes. However it seems unlikely that it could be that high.

All of the coefficients in eqn. (7) are close to those of eqn. (6) except f_o which is about 4 times larger. This points to an enhanced field effect in the *ortho* position for difluorobenzene compounds.

In ref. 1 the authors were interested in what percent of the effect of substituents on the position of the ^{19}F NMR line position was due to the field and what percent to resonance. This was given as 6%$\mathscr{F}$ and 94%$\mathscr{R}$ for substituents in the *para* position. Our work agrees with this closely. Also, we agree with ref. 1 that *meta* substituents have little effect on the ^{19}F NMR line position. The SAS computations show that r_m is not statistically significant, which means that it could be zero. However, the same computations show that there is only a small probability that f_m is zero, and so we conclude that substituents in the *meta* position do have a small field effect. The SAS computations give 73%$\mathscr{F}$ + 27%$\mathscr{R}$ as the best estimate of the percents for *meta* substituents, though this estimate undoubtedly has a certain margin of error due to the lack of perfect correlation.

Ortho substituents are not considered in ref. 1. We, however, have included several complexes with *ortho* substituents and are thus able to evaluate the effect of such substituents. The large value 31.881 for r_o indicates a very strong resonance effect on the ^{19}F NMR signal position due to *ortho* substituents, and the field effect of such substituents is also substantial. We find 13%$\mathscr{F}$ + 87%$\mathscr{R}$ to be the percentages which give the highest correlation for substituents in the *ortho* position.

Results obtained for difluorobenzene complexes do not seem to be greatly different from those obtained for monofluorobenzene complexes, except for an enhanced field effect in the *ortho* position. *Meta* substituents still have little effect on the line position and the effect from *para* substituents is still close to 100% resonance.

Table 10 contains a summary of the percents of $\mathscr{F}$ and $\mathscr{R}$ as well as the coefficients obtained by multiple regression for monofluoro complexes and difluoro complexes. Because the percents do not allow for comparison of the relative effect between substituents in the *ortho*, *meta* and *para* position, we regard the regression coefficients as carrying more information. The percents may

TABLE 10. Percents of $\mathscr{F}$ and $\mathscr{R}$ and regression coefficients for complexes

	Fluorobenzene complexes				Difluorobenzene complexes			
	%$\mathscr{F}$	%$\mathscr{R}$	f	r	%$\mathscr{F}$	%$\mathscr{R}$	f	r
ortho	13	87	−4.650	31.882	39	61	−20.771	32.951
meta	73	27	−2.066	−0.780	49	51	−3.887	3.992
para	1	99	0.169	13.252	[a]	100	[a]	15.811

[a] Cannot be computed due to small sample size.

be calculated from the coefficients using the following formulas.

$$\%\mathcal{F}_i = \frac{100|f_i|}{|f_i| + |r_i|} \quad \%\mathcal{R}_i = \frac{100|r_i|}{|f_i| + |r_i|} \quad i = o, m, p$$

Conclusions

(1) The ^{19}F NMR line position for poly-substituted fluorobenzenetricarbonylchromium complexes can be predicted accurately from a linear function of field and resonance parameters.

(2) Some additional effect associated with *ortho* substituents prevents some substituted difluorobenzene-tricarbonylchromium complexes from being predicted by the same equation, but it appears that a separate equation with a larger *ortho* field coefficient works well, at least for difluorobenzene and difluoroaniline complexes.

(3) Neither $\mathcal{F}$ nor $\mathcal{R}$ are additive except for substituents both in the *ortho* position or both in the *meta* position. This is demonstrated dramatically in the case of the 2,5-difluoroaniline complex in which the ^{19}F NMR signals are at -161.7 for the fluorine in position 2 and -137.8 for the fluorine in position 5. If $\mathcal{F}$ and $\mathcal{R}$ were additive, the signals would be the same.

(4) $\mathcal{F}$ and $\mathcal{R}$ are apparently additive over two substituents in the *ortho* or two substituents in the *meta* position. This is an assumption of the model we have used and is thus demonstrated by the fact that this model works well.

(5) In both the *ortho* and *para* positions resonance has a greater effect than field. Neither has much effect in the *meta* position. Thus the conclusions from ref. 1 that the $Cr(CO)_3$ group removes electron density primarily from the σ-framework has been extended and also applies to *ortho* position substituents.

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