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# The prediction of the $^{19}$F NMR spectra of fluoro-substituted arenetricarbonylchromium complexes. Part II

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## Abstract

$^{19}$F NMR data from a previous publication (Mahaffy *et al., Inorg. Chim. Acta, 191* (1992) 189) has been reanalysed using a more sophisticated model which predicts the $^{19}$F NMR signal position using the field, resonance and Charlton steric parameters together with molar refractivity. The final equation uses these parameters to predict the spectrum with a correlation coefficient of 0.99.

## Introduction

In Part I [1] we described a statistical method to predict the $^{19}$F NMR spectra of arenetricarbonylchromium complexes where the required field and resonance parameters were split up into *ortho*, *meta* and *para* groups thus enabling the accurate prediction of the $^{19}$F NMR positions in this group of complexes.

Unfortunately it was necessary to have two prediction equations, one (1) for thirty-five complexes with a single fluorine substituent and another somewhat different equation (2) for the seven available difluoroarenetricarbonylchromium complexes. These equations had correlation coefficients of 0.986 and 0.993 respectively.

$$\Delta^{F} = -4.650\mathcal{F}_o + 31.882\mathcal{R}_o - 2.066\mathcal{F}_m - 0.780\mathcal{R}_m + 0.169\mathcal{F}_p + 13.252\mathcal{R}_p - 135.637 \qquad (1)$$

$$\Delta^{F} = -20.771\mathcal{F}_o + 32.951\mathcal{R}_o - 3.887\mathcal{F}_m + 3.992\mathcal{R}_m + 15.811\mathcal{R}_p - 130.497 \qquad (2)$$

In the present paper we describe a new statistical equation which allows both types of complexes to be predicted using a single equation which is derived from a model which uses the Charlton steric parameter $\nu$ [2] and the molar refractivity *MR* [3] in addition to the field $\mathcal{F}$ and resonance $\mathcal{R}$ parameters previously used. The complexes studied are given in Table 1 and the parameters used in the calculations are given in Table 2. In all cases these parameters are split up into *ortho*, *meta* and *para* components, but not all of the twelve possible parameters initially used were found to be significant. The final equation requires only seven parameters to yield a correlation coefficient of greater than 99% for all the available complexes.

## Experimental

The preparation and spectral characteristics of all complexes in the data set used in this study have been previously described [1]. Statistical procedures were done using the REG (regression) routine of SAS (Statistical Analysis System) software running on a MicroVAX 3800. The REG routine calculates the coefficients of the linear equation (in this case with 12 predictor variables) which best fits the data in the least-squares sense. REG also calculates the multiple correlation coefficient and gives information concerning the statistical significance of the variables.

## Statistical analysis

Traditionally in the correlation of $^{19}$F NMR signal positions with predictor parameters in both the free arenes [4] and their tricarbonylchromium complexes [5] it has been the *ortho* substituents which have given the most trouble. In fact, in the majority of these studies the *ortho*-substituted compounds have been left out completely. It is clear that the *ortho* substituent has a

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TABLE 1. Arenetricarbonylchromium complexes; $^{19}$F NMR signal positions (observed and predicted) and residuals

| No. | Arene in arenetricarbonylchromium complex | | $\Delta^F_{obs}$ | $\Delta^F_{pred}$ | Residual |
|---|---|---|---|---|---|
| 1 | Fluorobenzene | | −135.9 | −135.6 | −0.3 |
| 2 | *m*-Chlorofluorobenzene | | −136.6 | −136.6 | 0.0 |
| 3 | *p*-Chlorofluorobenzene | | −137.2 | −136.5 | −0.7 |
| 4 | 2-Fluorotoluene | | −138.6 | −139.9 | 1.3 |
| 5 | 3-Fluorotoluene | | −135.3 | −135.6 | 0.3 |
| 6 | 4-Fluorotoluene | | −137.8 | −137.6 | −0.2 |
| 7 | 2,3-Dimethylfluorobenzene | | −137.3 | −139.8 | 2.5 |
| 8 | 2,4-Dimethylfluorobenzene | | −142.9 | −141.8 | −1.1 |
| 9 | 2,6-Dimethylfluorobenzene | | −143.8 | −144.1 | 0.3 |
| 10 | 3,4-Dimethylfluorobenzene | | −137.1 | −137.5 | 0.4 |
| 11 | 3,5-Dimethylfluorobenzene | | −136.1 | −135.5 | −0.6 |
| 12 | 2,4,6-Trimethylfluorobenzene | | −148.2 | −146.1 | −2.1 |
| 13 | 4-Fluorocumene | | −136.4 | −137.0 | 0.6 |
| 14 | *m*-Fluorobenzotrifluoride | | −135.8 | −136.5 | 0.7 |
| 15 | *p*-Fluorobenzotrifluoride | | −133.5 | −132.1 | −1.4 |
| 16 | 4-Fluorostyrene | | −136.0 | −136.6 | 0.6 |
| 17 | 2-Fluoroanisole | | −154.8 | −153.5 | −1.3 |
| 18 | 3-Fluoroanisole | | −136.7 | −136.2 | −0.5 |
| 19 | 4-Fluoroanisole | | −142.4 | −141.4 | −1.0 |
| 20 | 3,4-Dimethoxyfluorobenzene | | −140.2 | −141.9 | 1.7 |
| 21 | 3,5-Dimethoxyfluorobenzene | | −138.9 | −136.7 | −2.2 |
| 22 | 4-Methoxy-2-methylfluorobenzene | | −147.7 | −145.6 | −2.1 |
| 23 | 2-Fluoroaniline | | −156.3 | −156.7 | 0.4 |
| 24 | 3-Fluoroaniline | | −136.3 | −135.7 | −0.6 |
| 25 | 4-Fluoroaniline | | −146.2 | −144.4 | −1.8 |
| 26 | 4-Fluoro-*N*-methylaniline | | −146.1 | −145.4 | −0.7 |
| 27 | 4-Fluoro-*N*,*N*-dimethylaniline | | −146.8 | −147.4 | 0.6 |
| 28 | 2-Fluoro-5-methylaniline | | −160.1 | −158.7 | −1.4 |
| 29 | 3-Fluoro-2-methylaniline | | −138.0 | −139.9 | 1.9 |
| 30 | 3-Fluoro-4-methylaniline | | −138.9 | −139.9 | 1.0 |
| 31 | 3-Fluoro-6-methylaniline | | −136.2 | −137.6 | 1.4 |
| 32 | 3-Fluoro-2-methoxyaniline | | −152.3 | −153.6 | 1.3 |
| 33 | 4-Fluoro-2-methylacetophenone | | −134.1 | −132.0 | −2.1 |
| 34 | Ethyl 2-fluorobenzoate | | −133.4 | [a] | [a] |
| 35 | Ethyl 4-fluorobenzoate | | −133.7 | [a] | [a] |
| 36 | *m*-Difluorobenzene | | −136.4 | −136.6 | 0.2 |
| 37 | *p*-Difluorobenzene | | −134.0 | −138.8 | 4.8 |
| 38 | 2,3-Difluoroaniline | (2) | −178.8 | −179.8 | 1.0 |
| | | (3) | −158.7 | −158.8 | 0.1 |
| 39 | 2,4-Difluoroaniline | (2) | −155.8 | −157.7 | 1.9 |
| | | (4) | −143.4 | −145.3 | 1.9 |
| 40 | 2,5-Difluoroaniline | (2) | −161.7 | −159.8 | −1.9 |
| | | (5) | −137.8 | −138.8 | 1.0 |
| 41 | 3,4-Difluoroaniline | (3) | −158.3 | −158.8 | 0.5 |
| | | (4) | −169.0 | −167.5 | −1.5 |
| 42 | 3,5-Difluoroaniline | | −139.6 | −136.6 | −3.0 |

[a] See text.

greater steric and polarization effect than substituents in *meta* and *para* positions. We therefore chose to investigate a model which describes these complexes in terms of the aforementioned field and resonance parameters but also includes the Charlton steric factor and the molar refractivity of the substituent in question. The Charlton steric factors were chosen over the Taft steric factors [2e, 3] because of the greater availability of the former.

The model therefore which was used is given as eqn. (3).

$$\begin{aligned}\Delta^F = {} & f_o\mathcal{F}_o + r_o\mathcal{R}_o + a_o\nu_o + b_oMR_o \\ & + f_m\mathcal{F}_m + r_m\mathcal{R}_m + a_m\nu_m + b_mMR_m \\ & + f_p\mathcal{F}_p + r_p\mathcal{R}_p + a_p\nu_p + b_pMR_p + c \end{aligned} \quad (3)$$

where $\mathcal{F}_i$ is the field parameter of the substituent in the *i*th position or the sum of the field parameters of

TABLE 2. Field, resonance and Charlton steric parameters and molar refractivities for substituents in *ortho*, *meta* and *para* positions

| No. | $\mathcal{F}_o$ | $\mathcal{R}_o$ | $\nu_o$ | $MR_o$ | $\mathcal{F}_m$ | $\mathcal{R}_m$ | $\nu_m$ | $MR_m$ | $\mathcal{F}_p$ | $\mathcal{R}_p$ | $\nu_p$ | $MR_p$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| 2 | 0.000 | 0.000 | 0.000 | 0.000 | 0.690 | −0.161 | 0.550 | 6.030 | 0.000 | 0.000 | 0.000 | 0.000 |
| 3 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.690 | −0.161 | 0.550 | 6.030 |
| 4 | −0.052 | −0.141 | 0.520 | 5.650 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| 5 | 0.000 | 0.000 | 0.000 | 0.000 | −0.052 | −0.141 | 0.520 | 5.650 | 0.000 | 0.000 | 0.000 | 0.000 |
| 6 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | −0.052 | −0.141 | 0.520 | 5.650 |
| 7 | −0.052 | −0.141 | 0.520 | 5.650 | −0.052 | −0.141 | 0.520 | 5.650 | 0.000 | 0.000 | 0.000 | 0.000 |
| 8 | −0.052 | −0.141 | 0.520 | 5.650 | 0.000 | 0.000 | 0.000 | 0.000 | −0.052 | −0.141 | 0.520 | 5.650 |
| 9 | −0.104 | −0.282 | 1.040 | 11.300 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| 10 | 0.000 | 0.000 | 0.000 | 0.000 | −0.052 | −0.141 | 0.520 | 5.650 | −0.052 | −0.141 | 0.520 | 5.650 |
| 11 | 0.000 | 0.000 | 0.000 | 0.000 | −0.104 | −0.282 | 1.040 | 11.300 | 0.000 | 0.000 | 0.000 | 0.000 |
| 12 | −0.104 | −0.282 | 1.040 | 11.300 | 0.000 | 0.000 | 0.000 | 0.000 | −0.052 | −0.141 | 0.520 | 5.650 |
| 13 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | −0.050 | −0.100 | 0.760 | 14.960 |
| 14 | 0.000 | 0.000 | 0.000 | 0.000 | 0.631 | 0.186 | 0.910 | 5.020 | 0.000 | 0.000 | 0.000 | 0.000 |
| 15 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.631 | 0.186 | 0.910 | 5.020 |
| 16 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.070 | −0.080 | 1.310 | 10.990 |
| 17 | 0.413 | −0.500 | 0.360 | 7.870 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| 18 | 0.000 | 0.000 | 0.000 | 0.000 | 0.413 | −0.500 | 0.360 | 7.870 | 0.000 | 0.000 | 0.000 | 0.000 |
| 19 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.413 | −0.500 | 0.360 | 7.870 |
| 20 | 0.000 | 0.000 | 0.000 | 0.000 | 0.413 | −0.500 | 0.360 | 7.870 | 0.413 | −0.500 | 0.360 | 7.870 |
| 21 | 0.000 | 0.000 | 0.000 | 0.000 | 0.826 | −1.000 | 0.720 | 15.740 | 0.000 | 0.000 | 0.000 | 0.000 |
| 22 | −0.052 | −0.141 | 0.520 | 5.650 | 0.000 | 0.000 | 0.000 | 0.000 | 0.413 | −0.500 | 0.360 | 7.870 |
| 23 | 0.037 | −0.681 | 0.350 | 5.420 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| 24 | 0.000 | 0.000 | 0.000 | 0.000 | 0.037 | −0.681 | 0.350 | 5.420 | 0.000 | 0.000 | 0.000 | 0.000 |
| 25 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.037 | −0.681 | 0.350 | 5.420 |
| 26 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | −0.110 | −0.740 | 0.390 | 10.330 |
| 27 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.100 | −0.920 | 0.430 | 15.550 |
| 28 | 0.037 | −0.681 | 0.350 | 5.420 | 0.000 | 0.000 | 0.000 | 0.000 | −0.052 | −0.141 | 0.520 | 5.650 |
| 29 | −0.052 | −0.141 | 0.520 | 5.650 | 0.037 | −0.681 | 0.350 | 5.420 | 0.000 | 0.000 | 0.000 | 0.000 |
| 30 | −0.052 | −0.141 | 0.520 | 5.650 | 0.037 | −0.681 | 0.350 | 5.420 | 0.000 | 0.000 | 0.000 | 0.000 |
| 31 | 0.000 | 0.000 | 0.000 | 0.000 | 0.037 | −0.681 | 0.350 | 5.420 | −0.052 | −0.141 | 0.520 | 5.650 |
| 32 | 0.413 | −0.500 | 0.360 | 7.870 | 0.037 | −0.681 | 0.350 | 5.420 | 0.000 | 0.000 | 0.000 | 0.000 |
| 33 | 0.000 | 0.000 | 0.000 | 0.000 | −0.052 | −0.141 | 0.520 | 5.650 | 0.534 | 0.202 | 0.500 | 11.180 |
| 34 | 0.552 | 0.140 | [a] | 17.470 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| 35 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.552 | 0.140 | [a] | 17.470 |
| 36 | 0.000 | 0.000 | 0.000 | 0.000 | 0.708 | −0.336 | 0.270 | 0.920 | 0.000 | 0.000 | 0.000 | 0.000 |
| 37 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.708 | −0.336 | 0.270 | 0.920 |
| 38(2) | 0.745 | −1.017 | 0.620 | 6.340 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| 38(3) | 0.708 | −0.336 | 0.270 | 0.920 | 0.037 | −0.681 | 0.350 | 5.420 | 0.000 | 0.000 | 0.000 | 0.000 |
| 39(2) | 0.037 | −0.681 | 0.350 | 5.420 | 0.708 | −0.336 | 0.270 | 0.920 | 0.000 | 0.000 | 0.000 | 0.000 |
| 39(4) | 0.000 | 0.000 | 0.000 | 0.000 | 0.708 | −0.336 | 0.270 | 0.920 | 0.037 | −0.681 | 0.350 | 5.420 |
| 40(2) | 0.037 | −0.681 | 0.350 | 5.420 | 0.000 | 0.000 | 0.000 | 0.000 | 0.708 | −0.336 | 0.270 | 0.920 |
| 40(5) | 0.000 | 0.000 | 0.000 | 0.000 | 0.037 | −0.681 | 0.350 | 5.420 | 0.708 | −0.336 | 0.270 | 0.920 |
| 41(3) | 0.708 | −0.336 | 0.270 | 0.920 | 0.037 | −0.681 | 0.350 | 5.420 | 0.000 | 0.000 | 0.000 | 0.000 |
| 41(4) | 0.708 | −0.336 | 0.270 | 0.920 | 0.000 | 0.000 | 0.000 | 0.000 | 0.037 | −0.681 | 0.350 | 5.420 |
| 42 | 0.000 | 0.000 | 0.000 | 0.000 | 0.745 | −1.017 | 0.620 | 6.340 | 0.000 | 0.000 | 0.000 | 0.000 |

[a] See text.

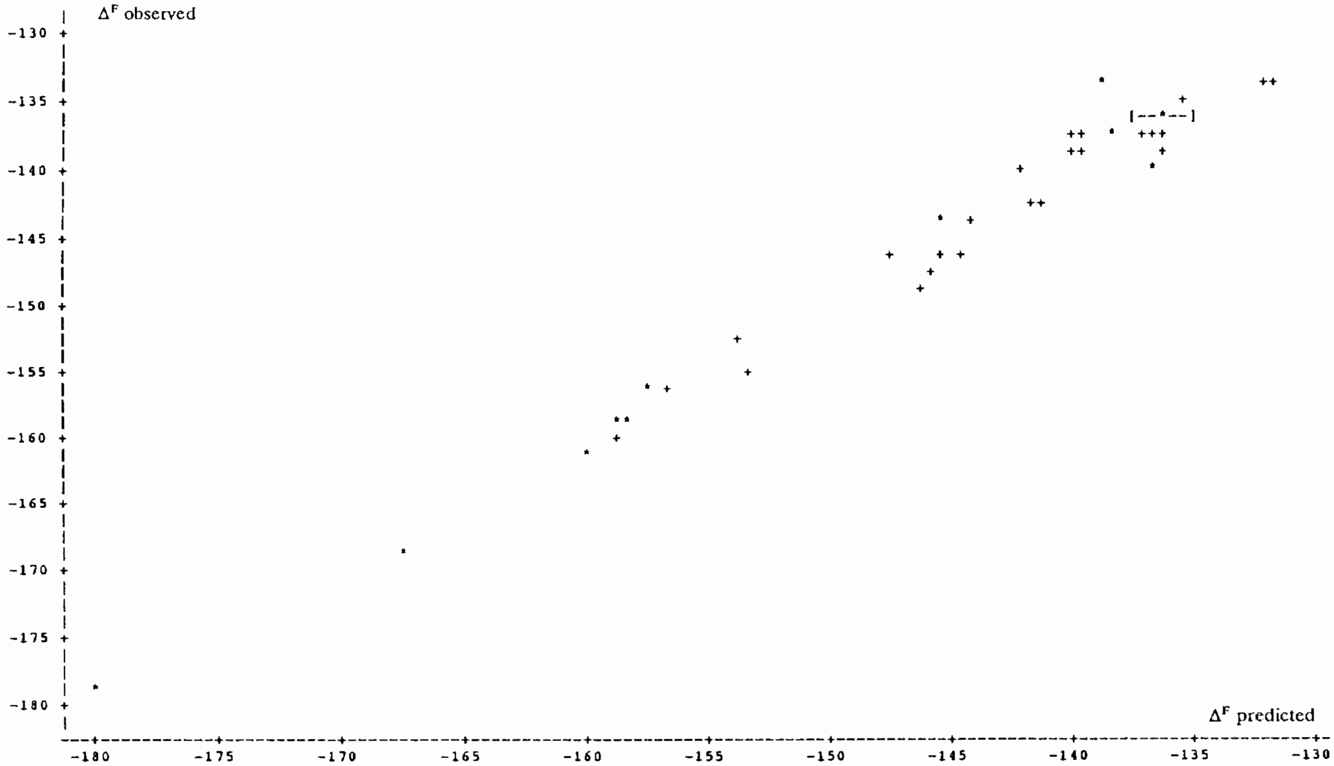

Fig. 1. Observed $^{19}$F NMR signal positions vs. positions predicted by eqn. (5). Note that the region between the brackets contains ten *meta*-substituted complexes including the *m*-difluorobenzene complex which is shown with an asterisk. + = monofluoro complexes, * = difluoro complexes.

the substituents in the *i*th position if there are two, $i = o$, $m$, $p$. $\mathscr{R}_i$ is similarly defined in terms of the resonance parameters, $\nu_i$ is similarly defined in terms of Charlton's steric parameters and $MR_i$ is similarly defined in terms of the molar refractivity.

The coefficients $f_i$, $r_i$, $a_i$, $b_i$, $i = o$, $m$, $p$, and $c$ were determined by running the REG procedure. The correlation coefficient was very high ($r = 0.99$) thus enabling the $^{19}$F NMR spectra of arenetricarbonylchromium complexes to be predicted very precisely from eqn. (4).

$$\begin{aligned}\Delta^F = {} & -14.310\mathscr{F}_o + 32.470\mathscr{R}_o - 12.615\nu_o + 1.058MR_o \\ & -2.125\mathscr{F}_m - 0.878\mathscr{R}_m + 1.690\nu_m - 0.180MR_m \\ & +1.787\mathscr{F}_p + 12.266\mathscr{R}_p - 0.243\nu_p \\ & -0.082MR_p - 135.3 \qquad (4)\end{aligned}$$

The REG procedure showed that $\mathscr{R}_m$, $\nu_m$, $MR_m$, $\nu_p$ and $MR_p$ were statistically not significant, which means that they have no effect on the signal position or else the effect is too small to detect. Thus these variables were omitted from the model and the REG procedure rerun on this simplified model, the correlation coefficient remaining at 0.99. This simplified model with the coefficients determined from the REG procedure is eqn. (5).

$$\begin{aligned}\Delta^F = {} & -13.820\mathscr{F}_o + 32.411\mathscr{R}_o - 12.569\nu_o \\ & +1.087MR_o - 1.326\mathscr{F}_m \\ & +1.766\mathscr{F}_p + 12.963\mathscr{R}_p - 135.6 \qquad (5)\end{aligned}$$

Each of the four *ortho* variables is highly significant with $p < 0.001$. This means that the probability is less than 1 in 1000 that these variables have no effect. Yet the intercorrelation between $\nu_o$ and $MR_o$ is quite large ($r = 0.95$) which indicates that these two variables are to a considerable extent measuring the same thing, at least insofar as their effect in this particular model. Indeed leaving either, but not both, of them out of the model reduces the correlation coefficient, but not much (to about 0.985). Though the correlation coefficient is reduced only slightly by omitting one of $\nu_o$ or $MR_o$ a very noticeable increase occurs in the residuals of certain complexes. The extreme example is complex no. 32 which has a residual (error of prediction) of 1.4 ppm which rises to 5.3 ppm if $\nu_o$ is omitted and to 5.2 ppm if $MR_o$ is omitted. Of course $\nu_o$ and $MR_o$ have no effect on complexes which have no *ortho* substituent and we believe that both of these are needed for accurate prediction of complexes which have *ortho* substituents.

The observed $^{19}F$ NMR positions and the position predicted by eqn. (5) for the arenetricarbonylchromium complexes studied together with residuals are given in Table 1 and shown graphically in Fig. 1.

Complexes 34 and 35 from the original data set [1] could not be used in the statistical analysis because the Charlton steric parameter was not available for the COOEt group. However it is now possible using eqn. (5) to compute a value of this parameter for the COOEt group.

Assuming the literature values for the other parameters required in eqn. (5) are correct and that eqn. (5) predicts the position exactly of the $^{19}F$ NMR signal for complex no. 34 so that $\Delta^{F}_{obs}$ may be substituted into that equation for $\Delta^{F}$, then the equation can be solved for $\nu_o$. The above procedure gives a value of $\nu$ for COOEt of 1.09. This seems reasonable as the literature value for COOMe is given [2e] as a low of 0.50 and a high of 1.51.

The above work is good evidence that the original tenet of splitting the predictor parameters into *ortho*, *meta* and *para* positions has been successful. An excellent example is seen in the isomeric complexes nos. 38 and 42, which, if the predictor parameters were merely added together must give the same predicted value, but it will be noted that the signal for the 2-position of complex no. 38 and the signal for complex no. 42 appear almost at either end of the observed versus predicted plot shown in Fig. 1.

Thus the $^{19}F$ NMR signal positions for both monofluoro- and difluorosubstituted arenetricarbonylchromium complexes can now be predicted with the same degree of accuracy from a single equation instead of the pair previously required.

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