

Application of scalar ^{13}C – ^{19}F spin–spin couplings between carbonyl carbons and aromatic fluorine to investigation of conformation of tricarbonylchromium complexes of fluorobenzenes

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(Received June 10, 1991)

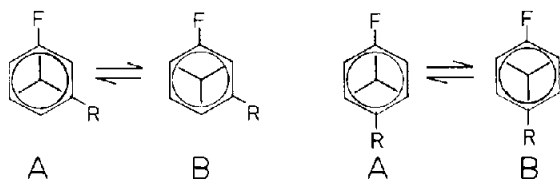
Abstract

The ^{13}C NMR spectra of several *meta* and *para* substituted (η^6 -fluorobenzene)tricarbonylchromium complexes have been recorded. An attempt to apply the ^{13}C – ^{19}F couplings between carbonyl carbons and aromatic fluorine to investigation of the $\text{Cr}(\text{CO})_3$ tripod conformation was undertaken.

Introduction

Complexation of the aromatic ring with a tricarbonylchromium moiety causes pronounced changes in its chemical reactivity. For example, the nucleophilic substitution of aromatic hydrogen, a reaction which in the case of uncomplexed arenes is restricted to a specific class of reagents [1], may be easily performed using a wide range of arenetricarbonylchromiums and a variety of nucleophiles [2]. The observation has been made that the regioselectivity of that and other reactions depends on the conformation of the $\text{Cr}(\text{CO})_3$ tripod; the arene carbons which are in eclipsed conformation with the Cr–CO bond are preferentially attacked by the nucleophiles [2–7]. For this reason, the conformation of the $\text{Cr}(\text{CO})_3$ group is of much interest to chemists.

It has been found that the orientation of the $\text{Cr}(\text{CO})_3$ tripod relative to the aromatic ring varies according to the nature of the ring substituents. Electron-releasing substituents favour the *syn*-eclipsed conformation while electron-withdrawing or bulky substituents favour the *anti*-eclipsed conformation [3]. There are several papers on investigation by NMR of the equilibrium between above conformers (see refs. 9–15 in ref. 8) of which the most reliable seems to be that by Solladié-Cavallo and Suffert [8]. Those authors pointed out that the fraction of each stable conformer in the complexes of mono- and disubstituted arenes can be estimated on the basis of the chemical shifts of the aromatic protons.



Scheme 1.

This paper presents a new approach to the investigation of the equilibrium between conformers in *meta* and *para* substituted (η^6 -fluorobenzene)tricarbonylchromium complexes (Scheme 1). The method is based on the measurements of the scalar spin-spin coupling constants between carbonyl carbons and aromatic fluorine.

Experimental

$\text{Cr}(\text{CO})_3$ [9] and $\text{Cr}(\text{CO})_2\text{CS}$ [10] complexes were prepared by standard methods and their ^{13}C NMR parameters are consistent with previously described structures. Solution of the complexes (ca. 0.5 M) in CDCl_3 were prepared under argon, degassed and sealed in 5 mm NMR tubes. The ^{13}C NMR spectra were recorded with a Bruker AM-500 (at 125.76 MHz) and a Varian XL-300 (operating at 75.4 MHz). Waltz16 proton decoupling was applied throughout. Typical acquisition and processing parameters for the aromatic and (in parentheses) carbonyl regions: pulse width 60° (70°), spectral width < 100 ppm (< 1000 Hz), acquisition time 3 s (6 s), digital resolution < 0.25 points/Hz (ca. 0.1 points/Hz). The central line of the CDCl_3 triplet ($\delta = 77.0$ ppm) was used as the chemical shift reference.

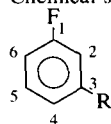
Results and discussion

The ^{13}C chemical shifts and ^{13}C - ^{19}F coupling constants of the complexes are listed in Tables 1 and 2. The ^{13}C NMR signals in the aromatic carbon range were assigned to the relevant carbons on the basis of their chemical shifts, ^{13}C and ^{19}F coupling constants and intensities.

It is difficult to distinguish unequivocally the signals from carbons 3 and 5 in *ortho*-substituted complexes, likewise those from carbons 2 and 6 in *meta*-substituted complexes (for carbon atom numbering see Table 1). In the former case it has been assumed that the fluorine carbon 5 coupling constants (~ 7.5 Hz) should differ less than the fluorine carbon 3 coupling constants (~ 4.5 Hz) from the $^3J(\text{C}-\text{F})$ values found for *para* and *meta* substituted complexes (6.5–8.5 Hz). In both cases the influences of the substituents on the chemical shifts of uncomplexed arene carbons were taken into consideration during the assignment of signals.

Table 2 shows that the value of the observed coupling constant between carbonyl carbon and aromatic fluorine, J_{obs} , increases for the *meta* substituted series and decreases for the *para* substituted series as the electron donor ability of the substituent increases. In both series the value of the coupling constant for the fluorine substituted complex (**3** or **4**) is between the values for complexes with electron releasing groups, $\text{R} = \text{NMe}_2$ and Me (see Table 2). This suggests that

Table 1

Chemical shifts (ppm) and $J(^{13}\text{C}-^{19}\text{F})$ values (Hz, in parentheses) for the complexes investigated

Complex	Substituent	Carbons							Other	CO
		1	2	3	4	5	6			
1	<i>m</i> -NMe ₂	149.36 (262.5)	65.83 ^a (23.2)	134.32 (8.4)	70.76 (0)	93.34 (8.1)	72.03 ^a (20.2)	39.74	233.77	
2	<i>p</i> -NMe ₂	138.13 (258.9)	83.46 (21.1)	72.82 (6.5)	130.0 (0)				233.92	
3	<i>m</i> -F	145.54 (268.9;	69.81 (22.7)		75.02 (21.2)	89.23 (7.7)			230.60	
4	<i>p</i> -F	140.30 (265.0)	79.00 (17.9;						230.25	
5	<i>o</i> -CH ₃	144.18 (263.9)	95.48 (15.9)	94.64 ^a (4.7)	87.97 (0)	91.47 ^a (7.1)	79.60 (21.4)	15.35 (1.1)	232.12	
6	<i>m</i> -CH ₃	147.18 (266.0)	77.07 ^a (19.9)	108.97 (7.4)	87.45 (0)	93.07 (7.6)	80.39 ^a (19.2)	20.51 (0.6)	232.04	
7	<i>p</i> -CH ₃	144.18 (265.0)	79.60 (20.0)	93.06 (7.0)	103.12 (12.0)				232.02	
8	<i>o</i> -CH ₂ OH	144.19 (265.8)	97.07 (14.4)	92.99 ^a (4.6)	86.36 (0)	92.27 ^a (7.4)	78.80 (20.8)		231.42	
9	<i>m</i> -CH ₂ OH	144.19 (266.9)	77.21 ^a (20.2)	111.35 (6.5)	84.46 (0)	93.06 (7.5)	78.01 ^a (20.1)	62.66 (0.6)	231.77	
10	<i>p</i> -CH ₂ OH	144.19 (266.2)	78.73 (20.3)	91.92 (7.6)	105.37 (0)			62.66	231.41	
11	H	146.44 (266.3)	79.12 (19.8)	93.20 (7.4)	86.23 (0)				231.62	
12	<i>m</i> -COOMe	144.29 (266.8)	72.73 ^a (20.6)	90.97 (6.7)	88.05 (0)	90.78 (7.3)	80.51 ^a (20.4)	53.21	230.24	
13	<i>p</i> -COOMe	144.22 (267.5)	77.35 (21.1)	93.55 (8.3)	85.01 (0)			164.70 29.66	229.12	

^a Reverse assignment possible.

Table 2

Observed $J(^{13}\text{C}-^{19}\text{F})$ values (Hz) for carbonyl carbons and populations of conformers of type A for investigated complexes

Substituent	<i>meta</i>			<i>para</i>			<i>ortho</i>		
	J_{obs}	x_{A}^{a}	x_{A}^{b}	J_{obs}	x_{A}^{a}	x_{A}^{b}	J_{obs}	x_{A}^{a}	x_{A}^{b}
NMe ₂	2.8	1.00	0.92	0.7	0.26	0.37			
F	2.6	0.93	0.87	1.2	0.43	0.50			
Me	2.4	0.86	0.82	1.6	0.57	0.61	1.5	0.54	0.58
CH ₂ OH	2.2	0.79	0.76	1.9	0.68	0.68	2.0	0.71	0.71
H	2.1	0.75	0.74	2.1	0.75	0.74			
CO ₂ Me	1.6	0.57	0.61	2.2	0.79	0.76			

^a Calculated from eq. 1 assuming $x_{\text{A}} = 1$ for **1**. ^b Calculated from eq. 2 (see text).

mesomeric effect of the substituent plays here a more important role than a purely inductive one. The J_{obs} values for *ortho* substituted fluorobenzene complexes, **5** and **8**, are close to those for appropriate *para* substituted ones. Our previous work has dealt with the scalar ^{13}C - ^{19}F couplings between carbonyl carbons and aromatic fluorine in chelate (η^6 -fluorobenzyl)diphenylphosphitodicarbonylchromiums [11]. There, the coupling under discussion was found only for the carbons of the carbonyl groups located near fluorine. Splitting of the signals from the other carbonyl carbons was not observed. This led us to the conclusion that this coupling results mainly from through-space interaction of the carbon and fluorine nuclei. On the other hand small (~ 0.7 Hz) coupling constants between carbonyl carbons and aromatic protons have been observed [12]. Being independent of conformation, these probably originate from through-bond carbon-proton interaction. Although analogous ^{13}C - ^{19}F interaction in our complexes cannot be ruled out, it could only influence the coupling slightly and the relation between the measured coupling constant, J_{obs} , and the population of the A conformer, x_{A} , may be estimated by the equation:

$$J_{\text{obs}} = (1/3)x_{\text{A}}J_{\text{ts}} \quad (1)$$

where J_{ts} is the through-space coupling constant for the carbon of the carbonyl group in *syn*-eclipsed conformation relative to the C_{Ar} -F bond. Thus one might expect the J_{obs} value to be small for those equilibria in which the rotamer with C_{Ar} -F and Cr-CO bonds in *anti*-eclipsed conformation prevails. This is the case for the *p*-fluoro-*N,N*-dimethylaniline complex (**2**) in which the NMe_2 group stabilizes the conformation with the *syn*-eclipsed conformation of the Cr-CO and C_{Ar} -substituent bonds more strongly than fluorine. This example shows that the *para* substituted series may indicate the relative ability of the substituents to stabilize a particular conformation. The value of the coupling constant observed for complex **1** is the largest measured in this work. Because the conformation of the A type, being stabilized by both ring substituents, dominates overwhelmingly in this case ($x_{\text{A}} \approx 1$) one may calculate the J_{ts} value from eq. 1. This allows estimation of the participations of both types of the conformers for the other complexes investigated (Table 2). The accuracy of that estimation may be illustrated by the x_{A} value obtained for the complex of *p*-difluorobenzene (**4**), where, owing to the ligand symmetry, both conformers are equally populated. The observed discrepancy (~ 0.1) could have arisen for several reasons. Firstly, the most stable conformations are not exactly eclipsed and the twisting from that position may depend on the nature of the ring substituents. This might be an important factor especially in those cases in which both substituents stabilize opposite conformations with comparable strength. Secondly, different substituents may move the chromium atom from its central position over the arene ring and change the distance between chromium and the arene plane. Finally, the substituent induces changes in electron densities on the interacting nuclei. The above factors influence the effectiveness of the through-space overlapping of the carbonyl carbon and fluorine orbitals which in turn affects the coupling constant.

The alternative explanation for the above-mentioned discrepancy of the x_{A} value obtained for **4** takes into consideration the existence of a small through-bond interaction of the coupled nuclei. In this case the relation between J_{obs} and x_{A} is given by eq. 2:

$$J_{\text{obs}} = (1/3)x_{\text{A}}J_{\text{ts}} + J_{\text{tb}} \quad (2)$$

where J_{tb} , the through-bond coupling constant is independent of conformation. Assuming J_{tb} to be of the same order of magnitude as the coupling between carbonyl carbon and aromatic proton ($-$ (or $+$)0.7 Hz) one may evaluate the through-space coupling between fluorine and carbon nuclei in *syn*-eclipsed carbonyl group, J_{ts} , from data for the complex **4**. Out of four values of J_{ts} obtained (J_{obs} , similar to J_{tb} , may be positive or negative) only two, 11.7 and -11.7 Hz, are of a reasonable magnitude. As both coupling constants, J_{tb} and J_{ts} , were found to be of different sign and the theoretical calculations predict positive signs for $^{13}\text{C}-^{19}\text{F}$ through-space couplings [13] the constants were assumed to be 11.4 and -0.7 Hz, respectively. Using those coupling constants a new set of the x_A values was calculated (Table 2).

There are no substantial differences between x_A values found for both approaches. If the through-bond mechanism actually participates in observed coupling its influence would be significant in the range of small x_A values. The other problem for that range is that quite often the preparation of a complex sample which would guarantee sufficiently narrow NMR signals is a difficult task and the coupling constants for a complex for which $x_A < 0.3$ may escape detection.

It is interesting to compare the x_A values obtained in this work with those calculated by the formula of Solladié-Cavallo and Suffert [8]:

$$\langle \Delta\delta \rangle_{3-2} = (2x_A - 1) \cdot 0.84 + (m - o)_{\text{compl}} \quad (3)$$

where $\langle \Delta\delta \rangle_{3-2}$ is the observed difference between chemical shifts of protons *meta* and *ortho* in the complex and $(m - o)_{\text{compl}}$ is the $\text{Cr}(\text{CO})_3$ conformation independent parameter, originating from the contribution made by the electron donor-acceptor properties of the substituent to $\langle \Delta\delta \rangle_{3-2}$. The latter is estimated on the basis of the effect of the substituent on the proton chemical shifts in the free ligand [8]. The chemical shifts of some of the investigated compounds are listed in Table 3. The difference between the ^1H chemical shifts of complexed *p*-difluorobenzene (5.48 ppm) and benzene (5.26 ppm) is of the same magnitude as, but of opposite sign to, the difference between proton chemical shifts of the free ligands (7.02 and 7.27 ppm, respectively). Following the reasoning of Solladié-Cavallo and Suffert, a similar relation was applied for the estimation of the $(m - o)_{\text{compl}}$ value for complexes **11** and **7** on the basis of the chemical shift differences of the protons 3 and 2 for fluorobenzene (0.28 ppm) and *p*-fluorotoluene (0.17 ppm). In the case of complex **2**, the combined contribution of both substituents to the $\langle \Delta\delta \rangle_{3-2}$ value was assumed to be the sum of the $(m - o)_{\text{compl}}$ values estimated for fluorine in fluorobenzene (-0.28 , see Table 3) and for the NH_2 group in aniline (-0.18 , ref.

Table 3

Chemical shifts (ppm) for the aromatic protons in some of the investigated complexes

Ligand	δ_{lig}		δ_{compl}	
	H-2	H-3	H-2	H-3
<i>p</i> -Difluorobenzene	7.02		5.48	
Fluorobenzene	6.97	7.25	5.38	5.38
<i>p</i> -Fluorotoluene	6.98	7.15	5.34	5.48
<i>p</i> -Fluoro- <i>N,N</i> -dimethylaniline	7.82	7.18	5.62	4.79

^a $\delta(4)_{\text{ligand}} = 7.05$ ppm; $\delta(4)_{\text{complex}} = 4.87$ ppm.

Table 4

Chemical shifts (ppm) and $J(^{13}\text{C}-^{19}\text{F})$ or $J(^{13}\text{C}-^1\text{H})^*$ values (Hz, in parentheses) for the investigated arene- $\text{Cr}(\text{CO})_2\text{CS}$ complexes

Ligand	Carbons						CO	CS
	1	2	3	4	5	6		
Benzene	98.08						230.59 (0.59)*	346.39 (0.66)*
Fluorobenzene	147.94 (269.7)	84.18 (19.4)	98.52 (7.3)	91.74 (0)			229.43 (1.7)	346.85 (2.4)
<i>o</i> -Fluorotoluene	145.68 (267.0)	100.75 (15.9)	99.56 (4.7)	92.98 (0)	96.30 (7.2)	85.04 (20.9)	230.26 (0.6)	229.98 (1.6)
								346.80 (2.4)

8) complexes. The x_A values 0.75, 0.60 and 0.28, obtained from eq. 3, for complexes **11**, **7** and **2**, respectively, are in excellent agreement with those calculated from the coupling constants.

It is stressed that calculated values of x_A and, even more so, of the coupling constants J_{ts} and J_{tb} should be treated as estimates only. Despite that the general conclusion can be drawn that the observed coupling constant depends mainly on the populations of the $\text{Cr}(\text{CO})_3$ conformers and can serve, at least in the qualitative sense, as a direct probe for monitoring the equilibrium between them.

Preliminary investigations have been undertaken on arenedicarbonylthiocarbonylchromium complexes in the hope of discovering the relative influence of the different chromium substituents on the rotamer populations. The data for $\text{Cr}(\text{CO})_2\text{CS}$ complexes of benzene, fluorobenzene and *o*-fluorotoluene are listed in Table 4. The coupling constant between thiocarbonyl carbon and aromatic protons, as well as fluorine, is of the same magnitude as that for carbonyl carbons. In the third complex the diastereotopic carbonyl carbons give separate signals which are split by fluorine with different coupling constants. The investigations are to be extended to other dicarbonylthiocarbonylchromium complexes as well as to dicarbonylphosphinechromium complexes for which the $^{13}\text{C}-^{31}\text{P}$ and $^{19}\text{F}-^{31}\text{P}$ coupling may provide additional information on the subject.

Acknowledgements

I express my appreciation to the Ministry of Education for supporting this work within the P/03/083/90-2 project, and to Professor J. Dabrowski of Max Planck Institute für Medizinische Forschung, Heidelberg, for the use of the 500 MHz spectrometer.

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