

## Scalar $^{13}\text{C}$ , $^{19}\text{F}$ spin–spin couplings between carbonyl carbons and aromatic fluorine in chelate ( $\eta^6$ -fluorobenzyl)-diphenylphosphitodicarbonylchromium complexes

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### Abstract

The  $^{13}\text{C}$  NMR spectra of ( $\eta^6$ -2-, -3-, and -4-fluorobenzyl)diphenylphosphitodicarbonylchromiums have been recorded. An attempt to rationalize the  $^{13}\text{C}$ ,  $^{19}\text{F}$  couplings between carbonyl carbons and aromatic fluorine in regard to the stereochemistry was undertaken.

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### Introduction

A previous report which dealt with the scalar  $^{13}\text{C}$ ,  $^1\text{H}$  couplings between carbonyl carbons and aromatic protons in ( $\eta^6$ -arene)tricarbonylchromium complexes, also mentioned analogous  $^{13}\text{C}$ ,  $^{19}\text{F}$  coupling in ( $\eta^6$ -fluorobenzene)tricarbonylchromium [1]. In order to find out whether the  $^{13}\text{C}$ ,  $^{19}\text{F}$  couplings were useful in the study of the  $\text{Cr}(\text{CO})_3$  tripod conformation, the ( $\eta^6$ -2-, -3-, and -4-fluorobenzyl)diphenylphosphitodicarbonylchromium complexes, **1**, **2** and **3**, respectively, were prepared and their  $^{13}\text{C}$  NMR spectra were recorded. In **1**, **2** and **3** the relative conformation of the carbonyl groups and aromatic ring substituents is fixed and this was expected to lead to the stereochemical dependence of the investigated coupling.

### Results and Discussion

The  $^{13}\text{C}$  NMR signals in the aromatic carbons range were assigned to the relevant carbons on the basis of their chemical shifts,  $^{13}\text{C}$ ,  $^{19}\text{F}$  and  $^{13}\text{C}$ ,  $^{31}\text{P}$  coupling constants, and intensities (Table 1). A few points deserve comment. The solubilities of the investigated complexes are rather low so that the coupled, tertiary carbons have a poor signal-to-noise ratio. The complexes also decompose slowly in the solution and the presence of the paramagnetic impurities in the sample is unavoidable. This results in a broadening of the spectral lines. Thus these spectra do not allow small couplings (ca. 1 Hz) to be measured precisely. In spite of this fact, I was

Table 1

Chemical shifts (ppm) and  $J(^{13}\text{C}, ^{19}\text{F}$  or  $^{31}\text{P})$  values (Hz, in parentheses) for the investigated complexes

Complex	Carbons of complexed aromatic ring						
	1	2	3	4	5	6	CH <sub>2</sub>
1	102.7	142.0	78.5	81.4 <sup>b</sup>	88.5	82.0 <sup>b</sup>	61.2
	(15.7) (6.0) <sup>a</sup>	(263.3)	(22.1)	(5.9) (1.0) <sup>a</sup>	(0)	(-2) (-2) <sup>a</sup>	(12.3) <sup>a</sup>
2	113.0	74.6 <sup>b</sup>	142.5	74.0 <sup>b</sup>	85.2	83.8	67.4
	(5.5) (6.3) <sup>a</sup>	(20.5) (1.3) <sup>a</sup>	(265.0)	(20.6) (2.1) <sup>a</sup>	(7.5)	(0)	(10.9) <sup>a</sup>
3	111.0	83.2	78.5	137.3			66.7
	(5.2) <sup>a</sup>	(6.3)	(21.5)	(260.5) (2.2) <sup>a</sup>			(1.5) (11.0) <sup>a</sup>

	Carbons of phenoxy rings							
	7,7'		8,8'		9,9'		10,10'	
1	151.9	151.5	122.0	121.1	129.4	129.3	124.5	124.2
	(10.4) <sup>a</sup>	(6.3) <sup>a</sup>	(4.1) <sup>a</sup>	(4.7) <sup>a</sup>			(0.9) <sup>a</sup>	
2	151.6	151.5	121.8	121.4	129.4	129.3	124.5	124.3
	(9.2) <sup>a</sup>	(8.3) <sup>a</sup>	(4.1) <sup>a</sup>	(4.4) <sup>a</sup>				
3	151.5		121.7		129.4		124.5	
	(8.4) <sup>a</sup>		(4.2) <sup>a</sup>					

<sup>a</sup>  $^{13}\text{C}$ ,  $^{31}\text{P}$  coupling constant. <sup>b</sup> Reverse assignment possible.

able to observe small couplings of carbon 4 in 3 and of carbons 2 and 4 in 2 with phosphorus in addition to the coupling of the benzylic carbon in 3 with fluorine (for carbon atom numbering see Fig. 1). It is impossible, on the basis of the data obtained, to distinguish unequivocally the signals from carbons 2 and 4 in 2 and those from carbons 4 and 6 in 1. In the latter case an additional problem arises since one of the signals assigned to these carbons is a broadened triplet with a more intense central line and line separation ca. 2 Hz. If this is caused by the couplings with the phosphorus and fluorine nuclei, the  $^3J(^{13}\text{C}, ^{19}\text{F})$  value should be unex-

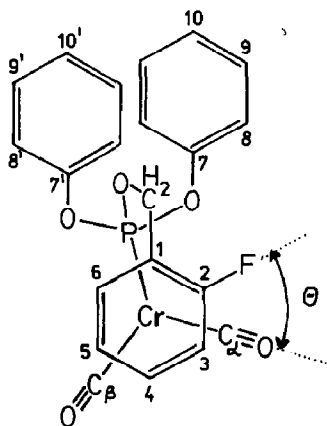
Fig. 1. Molecular structure showing carbon atom numbering and the angle  $\theta$ .

Table 2

Chemical shifts (ppm) and  $J(^{13}\text{C}, ^{19}\text{F}$  and  $^{31}\text{P})$  values (Hz) for carbonyl carbons in investigated complexes

Complex	Carbon	$\delta$	$^3J(^{13}\text{C}, ^{19}\text{F})$	$^2J(^{13}\text{C}, ^{31}\text{P})$
1	$\alpha$	233.5 <sup>a</sup>	2.1	29.0
	$\beta$	234.9 <sup>a</sup>	0	26.5
2	$\alpha$	233.5	6.8	26.5
	$\beta$	234.9	0	28.0
3	$\alpha, \beta$	233.6	0	26.9

<sup>a</sup> Reverse assignment possible (see text)

pectedly low (ca. 2 Hz) when compared with similar ones found for other cases. The phenoxy carbon signals, identified from their chemical shift values and higher intensities, indicate that both phenoxy groups in **1** and **2** are magnetically inequivalent. The data obtained do not allow the observed signals to be assigned to a particular aromatic ring.

The  $^{13}\text{C}$  NMR chemical shifts and coupling constant for the carbonyl carbons are listed in Table 2. In the *p*-fluoro substituted compound (**3**), the carbonyl carbons are magnetically equivalent and their signal is split into a doublet which has a large coupling constant owing to interaction with the phosphorus nucleus. Additional splitting, which would suggest carbonyl carbon-fluorine coupling, was not observed. The carbonyl part of the  $^{13}\text{C}$  NMR spectrum of **2** is shown in Fig. 2. The downfield signal is split into a doublet ( $J(\text{C},\text{P})$  28.0 Hz) whereas the upfield one consists of four lines from which two coupling constants can be found, viz.,  $J(\text{C},\text{P})$  26.5 Hz and  $J(\text{C},\text{F})$  6.8 Hz. A similar pattern is observed in the spectrum of **1** but in this case the carbon-fluorine coupling constant is markedly smaller (2.1 Hz). The obtained results clearly show that the  $^3J(^{13}\text{C}, ^{19}\text{F})$  coupling constant depends on the relative conformation of the  $\text{C}(\text{Ar})-\text{F}$  and  $\text{Cr}-\text{C}(\text{O})$  bonds. One possible interpretation of the presented data points to the most stable conformation of the  $\text{Cr}-\text{C}(\text{O})$  bonds being an eclipsed one. In complex **3**, where  $\theta$  (see Fig. 1) is  $60^\circ$ , the investigated coupling is zero. In complex **2** one of the two carbonyls is in the eclipsed conformation relative to the  $\text{C}(\text{Ar})-\text{F}$  bond ( $\theta$   $0^\circ$ ) and I believe that the

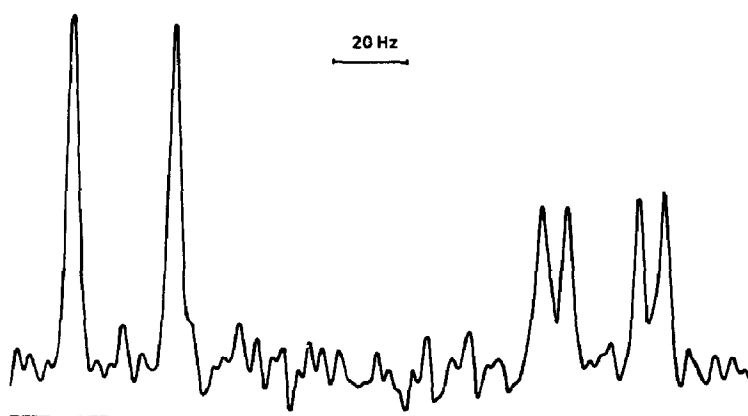


Fig. 2. The  $^{13}\text{C}$  NMR spectrum of the carbonyl carbons in complex **2**.

fluorine nucleus interacts only with the carbon of that carbonyl group. It seems reasonable to assume that the through-space mechanism plays an important role in that coupling. In complex **1** the fluorine nucleus is probably coupled to the carbon of the anti-eclipsed carbonyl group ( $\theta$  180°) since the coupling constant for  $\theta$  60° in **3** was found to be zero. On the other hand X-ray crystallography of the 3,5-dimethyl substituted complex of this type indicates that the conformation of the Cr(CO)<sub>2</sub>P tripod is not eclipsed [2]. From the crystallographic data for that complex, I calculated the distances between the carbonyl carbon and the aromatic carbons 2 and 3; the difference between these is only 0.11 Å. If this conformation prevails in solution, which is especially reasonable for **1** in view of the fluorine-benzyl oxygen or -phosphorus repulsion, the carbonyl carbon-fluorine distance in **1** could not be much longer than that in **2** and should be short enough for weak through-space carbon-fluorine nuclear interaction. Thus, as in **2**, the fluorine nucleus affects the signal of the carbonyl group located in proximity to that substituent.

It is impossible to determine which interpretation is correct from the data presented here. This problem should be resolved when the <sup>13</sup>C NMR spectrum of the 2,5-difluoro substituted analogous complex becomes known; the preparation of this compound has just been undertaken.

## Experimental

The complexes were prepared by previously published procedures [3] and their elemental analysis and <sup>13</sup>C NMR parameters are consistent with described structures. Melting point of **2** is 91–93°C. Complexes **1** and **3** begin to decompose at ca. 130 and 100°C, respectively. Solutions of the investigated complexes (0.05 M) in CDCl<sub>3</sub> were prepared under argon, degassed and sealed in 5 mm NMR tubes. The <sup>13</sup>C NMR spectra were recorded with Bruker AM-500 (operating at 125.76 MHz) and Varian XL-300 (operating at 75.4 MHz) instruments. Waltz16 proton decoupling was applied throughout. Typical acquisition and processing parameters: for the aromatic region – pulse width 60°, spectral width 100 ppm, acquisition time 4.7 s, digital resolution ca. 0.2 Hz/point, number of scans 1000; for the carbonyl region – pulse width 70°, spectral width 500 Hz, acquisition time 8 s, digital resolution ca. 0.1 Hz/point, number of scans 500. The central line of the CDCl<sub>3</sub> triplet ( $\delta$  77.0 ppm) was used as the chemical shift reference.

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