

Preliminary communication

## Scalar $^{13}\text{C}$ – $^{19}\text{F}$ spin–spin couplings between carbonyl carbons and aromatic fluorines in tricarbonylchromium complexes of biphenyl derivatives

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### Abstract

The  $^{13}\text{C}$  NMR spectra of the carbonyl carbons region of 2,2'-difluoro-6,6'-dimethylbiphenyl and 4,5-difluoro-9,10-dihydrophenanthrene tricarbonylchromium complexes are reported. The  $^{13}\text{C}$ – $^{19}\text{F}$  couplings between carbonyl carbons and aromatic fluorines were used to determine the structures of the investigated complexes.

The coupling between carbonyl carbons and aromatic fluorine in  $(\eta^6\text{-arene})\text{tri-carbonylchromium}$  complexes has been reported previously [1–3]. It has been established that the coupling is effective only when  $\text{C}_{\text{Ar}}\text{–F}$  and  $\text{Cr}\text{–CO}$  bonds are in eclipsed conformation [2]. This suggests the “through-space” transmission of nuclear spin information between atoms involved and gives the opportunity to use that coupling as a direct probe in the study of stereochemical problems. Recently, the discussed coupling was applied to the investigation of  $\text{Cr}(\text{CO})_3$  tripod conformation in *meta*- and *para*-substituted fluorobenzene complexes [3]. Here we report preliminary results of the measurements of carbon–fluorine couplings in complexed biphenyl systems.  $(\pm)\text{-(}R^*,R^*\text{)-}[(1,2,3,4,5,6\text{-}\eta)\text{-}2,2'\text{-difluoro-6,6'-dimethylbiphenyl}]\text{tricarbonylchromium}$  (**1**),  $(\pm)\text{-(}R^*,S^*\text{)-}[(1,2,3,4,5,6\text{-}\eta)\text{-}2,2'\text{-difluoro-6,6'-dimethylbiphenyl}]\text{tricarbonylchromium}$  (**2**), and  $(\pm)\text{-}[(1,2,3,4,4a,10a\text{-}\eta)\text{-}4,5\text{-dif-$

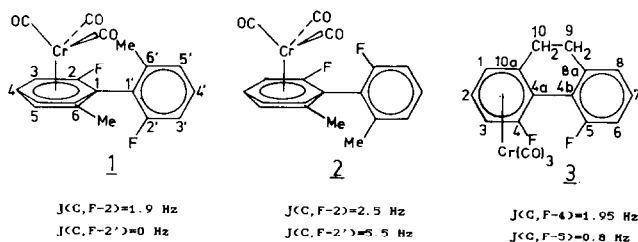
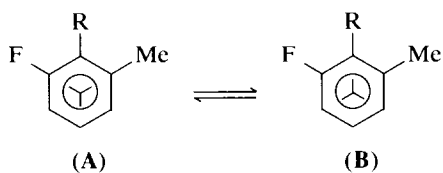


Fig. 1. Structures of complexes 1–3.

luorophenanthrene]tricarbonylchromium (**3**) (see Fig. 1) were prepared as described previously [4]. Their melting points are 170–173, 126–129 and 143–145 °C, respectively.

Solutions of the investigated complexes in  $\text{CDCl}_3$  were prepared under argon, degassed and sealed in 5 mm NMR tubes. The  $^{13}\text{C}$  NMR spectra were recorded with Bruker AM-500 (operating at 125.76 MHz) and Varian XL-300 (operating at 75.4 MHz) spectrometers. Acquisition and processing parameters were similar to those described previously [1–3]. Full  $^{13}\text{C}$  NMR data, consistent with the proposed structures, will be published elsewhere. 2,2'-Difluoro-6,6'-dimethylbiphenyl has been chosen as a model compound, as it has a high barrier to the rotation about the bond linking the rings. It enables, by use of chromatography, the separation of the diastereoisomeric complexes **1** and **2**, formed in the reaction of the above ligand with  $\text{Cr}(\text{CO})_6$ . Complexes **1** and **2** are stable in solid state as well as in solution, and, when left in  $\text{CDCl}_3$  solution for several months (at ca. 0 °C), none of them interconverts into the other. The carbonyl carbons of one of the complexes give a doublet ( $\delta = 232.20$  ppm) with  $J(\text{C}-\text{F}) = 1.9$  Hz whereas those of the other complex give a doublet of doublets ( $\delta = 231.96$  ppm) with  $J(\text{C}-\text{F}) = 2.5$  and 5.5 Hz. As it has been shown previously, the magnitude of the coupling constant between carbonyl carbons and fluorine attached to the complexed ring reflects the position of the following equilibrium:



Also, it has been found that the maximum value of the coupling constant only slightly exceeds the value observed for the *m*-fluoro-*N,N*-dimethylaniline complex (2.8 Hz [3]), and it is most unlikely to expect that coupling can be zero for any of above complexes, as two of the ring substituents, F-2 and Me-6, stabilize the rotamer in which  $\text{C}_{\text{Ar}}-\text{F}$  and  $\text{Cr}-\text{CO}$  bonds are eclipsed (type A). Therefore the coupling constants, equal to 1.9 Hz for one complex and 2.5 Hz for the other, were assumed to arise from the interaction of the carbonyl carbons and fluorine attached to the complexed ring. Thus, the couplings equal to 0 and 5.5 Hz must originate from interaction of the carbonyl carbons and the F-2' atom. It has been found for the arenetricarbonylchromium complexes [2,3] that “through-bond” interaction participate in the discussed couplings to a small extent, if any, and it should also be true for the C–F–2' interaction, as more bonds separate the coupled nuclei. Thus, one might expect that the interaction between carbonyl carbons and fluorine at uncomplexed ring has an overwhelmingly “through-space” character and its effectiveness depends on the spatial distance between nuclei involved. Therefore the magnitude of the  $J(\text{C}-\text{F}-2')$  coupling was decisive in elucidation of the structures of complexes **1** and **2**. Final attribution of the coupling constants to the relevant diastereoisomers is shown in Fig. 1. Assuming that the maximum value of  $J(\text{C}-\text{F}-2)$  coupling for rotamer A is 2.8 Hz (see above) and that this coupling is zero for rotamer B, the population of the rotamer B for complexes **1** and **2** can be estimated to be 30 and 10%, respectively. This shows that the

methyl group does in the case of complex **1**, probably because of its electrostatic repulsion with CO groups. From the reaction of 4,5-difluoro-9,10-dihydrophenanthrene with  $\text{Cr}(\text{CO})_6$ , only one complex has been separated and only one set of signals is observed in its  $^{13}\text{C}$  NMR spectrum at room temperature. Taking into account the low barrier of rotation about C-4ad–C-4b bond in the free ligand [5] it is reasonable to assume that the diastereoisomers, of analogous structures to **1** and **2**, interconvert rapidly at room temperature giving common, average NMR spectrum. In the carbonyl carbons region a doublet of doublets ( $\delta = 232.15$  ppm) with  $J(\text{C}-\text{F}) = 1.95$  and  $0.8$  Hz is observed. We conclude that the former value results from the interaction of the carbonyl carbon and fluorine at complexed ring, and that the latter is the coupling constant between carbonyl carbons and fluorine at the uncomplexed ring. However, one might assume that substituents (F-5 and  $\text{CH}_2$ -8a) of the uncomplexed ring, located in proximity to the appropriate substituents of complexed ring, disfavour the type **A** rotamer sterically, pronouncely reducing the coupling constant between carbonyl carbons and fluorine F-5 to  $0.8$  Hz.

For more detailed interpretation of the observations presented in this work the internuclear distances, based on the crystallographic data should be taken into account. We also expect to obtain valuable information from the tricarbonylchromium complexes of 4,5-difluorophenanthrene, as it is under our current investigation.

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