

Fluorine-19 nuclear magnetic resonance studies of mixed bis(η^6 -arene)chromium(0) complexes

H. Ssekaalo*, J. J. Lagowski and C. M. Seymour**

Department of Chemistry, University of Texas, Austin, TX 78712 (U.S.A.)

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Abstract

^{19}F NMR studies have been conducted on mixed bis(η^6 -arene)chromium(0) complexes containing $(\text{CH}_3)_m$ ($m = 1, 2$ or 3) substituents in one of the partner arenes and CF_3 or F_n ($n = 1$ or 2) substituents in the other arene. There is deshielding of the ^{19}F in the $(\text{C}_6\text{H}_5)_m(\text{CH}_3)_m$ - $(\text{C}_6\text{H}_5\text{CF}_3)\text{Cr}$ complex (I) relative to that in $(\text{C}_6\text{H}_5)_2\text{Cr}$ (II). However, increased shielding of ^{19}F is observed in the $(\text{C}_6\text{H}_5)_m(\text{CH}_3)_m$ - $(\text{C}_6\text{H}_5)_n\text{F}_n$ Cr complex (III) relative to that in $(\text{C}_6\text{H}_5)_2\text{Cr}$ (IV). It appears that the fluorines in CF_3 take on a unique behaviour which is affected by a complex series of electron charge movements mainly due to more back-donation towards the $(\text{C}_6\text{H}_5)_m(\text{CH}_3)_m$ arene and relaying of effects of substituents of one arene on to those of the partner arene by the chromium centre. On the other hand, the upfield shift of the ^{19}F resonance in III, is rationalized partly on the basis of greater back-donation to the F_n -containing arene and electron-releasing effect of the $(\text{CH}_3)_m$ that is transmitted by the metal centre. Evidence from two different methyl proton chemical shifts in $(1,2,4\text{-C}_6\text{H}_3(\text{CH}_3)_3)(1,2\text{-C}_6\text{H}_4\text{F}_2)\text{Cr}$ suggests that the through space dipole interactions are an insignificant factor in the electron charge perturbations in these mixed-arene complexes.

Introduction

A limited number of studies on mixed bis(η^6 -arene)metal complexes of some transition metals, molybdenum [1] and chromium [2] in particular, in which fluorine is a substituent or a constituent of a substituent, have been carried out. In homo bis(fluoroarene)metal(0) complexes previously reported, there are large upfield shifts of ^{19}F NMR absorptions relative to the free arenes [3–5]. Wilburn and Skell [1] used fluorobenzene as one of the arenes in the majority of the mixed-arene complexes they studied. In all the mixed-arene complexes of chromium studied by McGlinchey and Tan [2], one of the partner arenes contained no fluorine.

In this work, we wish to report on the type of electronic perturbations taking place between mixed-arene complexes which contain substituents whose fluorine is not directly bonded to the benzene nucleus and those containing fluorine directly

bonded to the benzene nucleus. In the former case, trifluoromethylbenzene was used as one of the partner arenes while in the latter case, mono- or difluorobenzene was used. In either of these cases, the partner arene to the fluorine-containing arene, has electron-releasing substituents in the form of methyl or methyl-containing groups. This was done in view of the previous work in which electronic perturbations of the methyl protons of some of the systems herein reported were studied [6].

Experimental

The chemicals used in this work were all obtained from the Aldrich Chemical Company. The chromium metal, arenes, diethyl ether used as solvent for extracting the complexes, benzene- d_6 , and fluorotrichloromethane (CFCl_3), were all analytical grade and were used as such. However, the liquid chemicals were dried as described elsewhere [6].

The static metal vapour atom reactor for the reactions between chromium and the arenes, was similar to that used before [7, 8]. The five major outlets from the reactor vessel port to various

*Author to whom correspondence should be addressed. Present address: Department of Chemistry, Makerere University, P.O. Box 7062, Kampala, Uganda.

**Present address: IBM Research Division, Almaden Research Centre, San Jose, CA 95120, U.S.A.

flasks and pumping systems, are described elsewhere [6].

The procedure for the reactions was basically similar to that of Graves and Lagowski [9]. However, the modifications that were necessary to this procedure in order to make it more flexible and practicable for the reactions of this work, were described in the previous work [6] to which this is a follow-up.

The mass spectra of the compounds in each one of the mixtures were recorded on Bell and Howell 21-491 and Du Pont CEC 21-110B spectrometers for low- and high-resolution analysis, respectively. High-resolution mass spectrometry was used for the estimation of the elemental composition of each compound.

For the ^{19}F NMR spectroscopy, the samples were prepared in benzene- d_6 and sealed under vacuum. Earlier work [6] established that there is practically no arene exchange when the complexes are dissolved in other arenes at room temperatures and even up to 348 K. Therefore, there was no possibility of benzene- d_6 replacing any of the arenes in the complexes. The ^{19}F NMR spectra were recorded on a Bruker WH-90 spectrometer using CFCl_3 as an external reference.

Data for the methyl proton NMR using the same samples as for ^{19}F , were obtained in a manner similar to that reported before [6].

Results and discussion

The mass spectral data where $\text{C}_6\text{H}_5\text{CF}_3$ was a partner arene for competing with each of the $\text{C}_6\text{H}_{6-m}(\text{CH}_3)_m$ arenes for the chromium vapour atoms are reported elsewhere [6]. The same type of data where now $\text{C}_6\text{H}_{6-n}\text{F}_n$ (for $n = 1$ or 2) is the F-containing arene in the mixed-arene complexes are shown in Table 1. As has been pointed out by Ssekaalo *et al.* [6], all these data for high-resolution spectrometry indicate that the compounds in the mixtures retained their molecular integrity.

The ^{19}F NMR data for the products of the reactions are shown in Tables 2 and 3 for the CF_3 - and F_n -containing complexes, respectively. These values in chemical shifts are to the high field of CFCl_3 used as an external reference.

In Table 4 are shown the methyl proton NMR data for the products of the competition reactions from the $(\text{CH}_3)_m$ - and F_n -substituted arenes. These data should be compared with those from the $(\text{CH}_3)_m$ - and CF_3 -substituted arenes reported elsewhere [6]. In the $[\text{C}_6\text{H}_{6-m}(\text{CH}_3)_m](\text{C}_6\text{H}_5\text{CF}_3)\text{Cr}$ series of the mixed-arene complexes, the methyl proton electronic charge was perturbed in approximately equal strength on all

the methyl groups and invariably upfield relative to that in each respective homo-arene $(\text{C}_6\text{H}_{6-m}(\text{CH}_3)_m)_2\text{Cr}$ complex. On the other hand, data for the $(\text{C}_6\text{H}_{6-m}(\text{CH}_3)_m)(\text{C}_6\text{H}_{6-n}\text{F}_n)\text{Cr}$ series of the mixed-arene complexes, indicate that electronic charge perturbations on the methyl protons is irregular. In two of these latter complexes, the methyl protons are shielded to the same extent as those in the homo-arene complexes (reactions 1 and 2, Table 4). But in the other two mixed-arene complexes (reactions 3 and 4, Table 4), the methyl protons are shielded more than those in the homo-arene complexes. Further, the methyl protons in the $(1,2,4\text{-C}_6\text{H}_3(\text{CH}_3)_3)(1,2\text{-C}_6\text{H}_4\text{F}_2)\text{Cr}$ complex are not all equally shielded as shown by the two different chemical shifts, viz. 1.82 and 1.94 ppm.

For the $(\text{C}_6\text{H}_{6-m}(\text{CH}_3)_m)(\text{C}_6\text{H}_5\text{CF}_3)\text{Cr}$ series, the ^{19}F nucleus has been found to invariably absorb downfield relative to that in the $(\text{C}_6\text{H}_5\text{CF}_3)_2\text{Cr}$ complex. This is an apparently perplexing result because the CH_3 substituents are electron-releasing whereby we would have expected the ^{19}F nucleus to be more shielded by some more electron charge environment relayed via the chromium atom. It is worth pointing out that some unusual effects of the CF_3 group on bis(arene)chromium(0) complexes have also been noted by Radonovich *et al.* [10].

Work by Domenicano and Vaciago [11] led them to conclude that the internal angle of the arene ring at the substituted carbon is $>120^\circ$ for a σ -electron-withdrawing substituent and $<120^\circ$ for a σ -electron-releasing substituent. In addition, they prescribed that π -bonding to the substituent tends to decrease this angle. The size of the internal arene angle at the CF_3 -substituted carbon in the homo bis(arene)chromium complexes studied by Eyring *et al.* [12], is about 120° . It is a fair assumption that the structures of our CF_3 -substituted mixed-arene complexes are not substantially different from those of Eyring *et al.* [12]. Then, it means that the size of the internal angle at the CF_3 -substituted carbon in these mixed-arene complexes of the present work, may be approximated to 120° . Therefore, according to the work of Domenicano and Vaciago [11], it follows that the CF_3 substituent in the complexes of Eyring *et al.* [12] and ours should not be appreciably electron-withdrawing. At the same time it can also be said that the CF_3 group does not appreciably release electron charge in these compounds. But according to the data of the present work, it can be argued that CF_3 may be a weak electron-releaser. Then, if the deshielding of the ^{19}F in the CF_3 -substituted mixed-arene complexes of this work (Table 2) is through the interatomic bond drift of the electron charge, it means that the consistent

TABLE 1. Mass spectral data^a for products of competition between arenes for chromium vapour atoms

Reaction number	Competing arene pair		Compounds predicted	HRMS ^b (m/o)	
	A	B		Calc.	Found
1	1,2-C ₆ H ₄ (CH ₃) ₂	C ₆ H ₅ F	(1,2-C ₆ H ₄ (CH ₃) ₂) ₂ Cr	264.0970	264.0976
			(1,2-C ₆ H ₄ (CH ₃) ₂)(C ₆ H ₅ F)Cr	254.0563	254.0567
			(C ₆ H ₅ F) ₂ Cr	244.0156	244.0164
2	1,2-C ₆ H ₄ (CH ₃) ₂	1,2-C ₆ H ₄ F ₂	(1,2-C ₆ H ₄ (CH ₃) ₂) ₂ Cr	264.0970	264.0978
			(1,2-C ₆ H ₄ (CH ₃) ₂)(1,2-C ₆ H ₄ F ₂)Cr	272.0469	272.0464
			(1,2-C ₆ H ₄ F ₂) ₂ Cr	279.9967	279.9973
3	1,2,4-C ₆ H ₃ (CH ₃) ₃	1,2-C ₆ H ₄ F ₂	(1,2,4-C ₆ H ₃ (CH ₃) ₃) ₂ Cr	292.3878	292.3865
			(1,2,4-C ₆ H ₃ (CH ₃) ₃)(1,2-C ₆ H ₄ F ₂)Cr	286.1922	286.1910
			(1,2-C ₆ H ₄ F ₂) ₂ Cr	279.9967	279.9979
4	1,2-C ₆ H ₄ (CH ₃) ₂	1,3-C ₆ H ₄ F ₂	(1,2-C ₆ H ₄ (CH ₃) ₂) ₂ Cr	264.0970	264.0952
			(1,2-C ₆ H ₄ (CH ₃) ₂)(1,3-C ₆ H ₄ F ₂)Cr	272.0469	272.0475
			(1,3-C ₆ H ₄ F ₂) ₂ Cr	279.9967	279.9962

^aSimilar data for C₆H_{6-m}(CH₃)_m/C₆H₅CF₃/Cr reactions are reported elsewhere [6]. ^bHRMS = high-resolution mass spectrometry.

TABLE 2. ¹⁹F NMR spectral data for homo- and mixed-arene chromium(0) complexes from C₆H_{6-m}(CH₃)_m/C₆H₅CF₃/Cr reactions

Complex		δ (CFCl ₃) (ppm)	Δ^a
Homo	Mixed ^b		
(C ₆ H ₅ CF ₃) ₂ Cr ^c		57.92	
	(1,2-C ₆ H ₄ (CH ₃) ₂)(C ₆ H ₅ CF ₃)Cr	56.71	-1.21
	(1,3-C ₆ H ₄ (CH ₃) ₂)(C ₆ H ₅ CF ₃)Cr	56.47	-1.45
	(1,4-C ₆ H ₄ (CH ₃) ₂)(C ₆ H ₅ CF ₃)Cr	56.47	-1.45
	(C ₆ H ₅ CH ₃)(C ₆ H ₅ CF ₃)Cr	56.75	-1.13
	(1,2,4-C ₆ H ₃ (CH ₃) ₃)(C ₆ H ₅ CF ₃)Cr	56.23	-1.69
	(C ₆ H ₅ C(CH ₃) ₃)(C ₆ H ₅ CF ₃)Cr	56.71	-1.21

^aShift of ¹⁹F absorption in mixed-arene complex from value of that in (C₆H₅CF₃)₂Cr. ^bFrom mixed-arene complexes which are components of the mixtures reported previously [6]. ^cIdentical chemical shift for the (C₆H₅CF₃)₂Cr component of each of the mixtures was obtained for all reactions.

TABLE 3. ¹⁹F NMR spectral data for homo- and mixed-arene chromium(0) complexes from (C₆H_{6-m}(CH₃)_m/C₆H_{6-n}F_n)/Cr reactions

Complex		δ (CFCl ₃) (ppm)	Δ^a
Homo	Mixed		
(C ₆ H ₅ CF ₃) ₂ Cr		162.29	
(1,2-C ₆ H ₄ F ₂) ₂ Cr ^b	(1,2-C ₆ H ₄ (CH ₃) ₂)(C ₆ H ₅ F)Cr	167.74	5.45
		179.84	
	(1,2-C ₆ H ₄ (CH ₃) ₂)(1,2-C ₆ H ₄ F ₂)Cr	186.72	
(1,3-C ₆ H ₄ F ₂) ₂ Cr	(1,2,4-C ₆ H ₃ (CH ₃) ₃)(1,2-C ₆ H ₄ F ₂)Cr	187.69	7.85
		164.78	
	(1,2-C ₆ H ₄ (CH ₃) ₂)(1,3-C ₆ H ₄ F ₂)Cr	171.99	

^aShift of ¹⁹F absorption in mixed-arene complex from value of that in (C₆H_{6-n}F_n)₂Cr. ^bIdentical chemical shift for this component was obtained for reactions 2 and 3 (Table 1).

TABLE 4. Methyl proton NMR spectral data for products of competition between $C_6H_{6-m}(CH_3)_m$ and $C_6H_{6-n}F_n$ for chromium vapour atoms

Reaction number	Competing arene pair		δ (TMS) (ppm)	Type of complex δ is assigned to	
	A	B			
1	1,2- $C_6H_4(CH_3)_2$	C_6H_5F	2.01	(AA)Cr	(AB)Cr
2	1,2- $C_6H_4(CH_3)_2$	1,2- $C_6H_4F_2$	2.01	(AA)Cr	(AB)Cr
3	1,2,4- $C_6H_3(CH_3)_3$	1,2- $C_6H_4F_2$	1.82	(AB)Cr	
			1.94	(AB)Cr	
			1.99	(AA)Cr	
4	1,2- $C_6H_4(CH_3)_2$	1,3- $C_6H_4F_2$	1.95	(AB)Cr	
			2.01	(AA)Cr	

increased shielding of the methyl protons of these same compounds [6] may, to some extent, be attributed to the limited electron-releasing effect of the CF_3 such that it is relayed through the chromium centre. In fact there is also some work suggesting that CF_3 may be considered an electron-releasing group in the CF_3 -substituted arenes [13]. However, this conclusion was made in respect of free arenes in which the picture may be different from that in the metal-complexed arenes as has been indicated, for example, by Klabunde and Efner [14] that CF_3 is electron-withdrawing in the $(C_6H_4(CF_3)_2)_2Cr$ complex. Perhaps, we may tend more to say that a somewhat greater back-donation to the $C_6H_{6-m}(CH_3)_m$ ring may be the one influencing the electron charge drift away from the $C_6H_5CF_3$ ring and consequently more charge flow from the CF_3 , thus leading to a reduction of the electron charge in its fluorines.

In the case of the $(C_6H_{6-m}(CH_3)_m)(C_6H_{6-n}F_n)Cr$ series, there is an upfield shift of the ^{19}F absorption relative to that in the $(C_6H_{6-n}F_n)_2Cr$ complexes. This seems to be in agreement with the generally held view that the CH_3 group is an electron-releasing substituent. This line of argument is reinforced by a greater shielding of the ^{19}F nucleus when the number of CH_3 substituents is increased (Table 3). It is also possible that the increased shielding of ^{19}F may be due to a greater back-donation by the chromium centre stimulated by the direct bonding of the fluorines to the ring carbons.

If the fluorines in the $(C_6H_{6-m}(CH_3)_m)(C_6H_{6-n}F_n)Cr$ complexes do withdraw some electron charge from the nucleus of the arene, it would mean that their interatomic effect on the methyl protons would be felt via the chromium atom. The feeling of this effect would result in decreased shielding of these protons. That there is no such decrease (Table 4), appears to suggest that the fluorines have no effect on them. But if their effect on these protons was felt, but not observed, it means that back-donation to the $C_6H_{6-m}(CH_3)_m$ arene at least more than com-

pensates for the π -bond donation by the arene and the effect of the fluorines on them via the chromium centre. At this juncture, note should be taken of the fact that the methyl protons of the $(1,2,4 - C_6H_3(CH_3)_3) - (1,2 - C_6H_4F_2)Cr$ complex are not all equally shielded. From the size of the integrated curves below the respective absorption peaks, three of the protons absorb at 1.82 while the remaining six absorb at 1.94 ppm. It is reasonable to suggest that the latter resonance is due to protons from methyl groups *ortho* to each other since they are more likely to have the same electron charge environment. The difference in the absorption between the two sets of protons tends to indicate that back-donation, if it plays a significant role in perturbing their electron charge, may be affected through different orbital systems to either of these two sets.

The increased shielding of the ^{19}F nucleus in the mixed-arene compounds of the $(C_6H_{6-m}(CH_3)_m)(C_6H_{6-n}F_n)Cr$ type, is also exemplified by similar molybdenum compounds studied by Wilburn and Skell [1]. For example, ^{19}F in $(1,2 - C_6H_4(CH_3)_2)(C_6H_5F)Mo$, absorbs at 152.7 ppm relative to its absorption at 150.4 ppm in $(C_6H_5F)_2Mo$. In addition, there is a mixed-arene molybdenum complex $(C_6H_5CF_3)(C_6H_5F)Mo$ also studied by these investigations, that is of special interest in respect of the controversial role of the CF_3 substituent in relation to electron charge drift between its carbon and the ring carbon which should in turn affect the extent to which its fluorine nuclei are screened *vis-à-vis* the metal centre acting as a relay in influencing the effect of a substituent of one arene on a substituent of its partner arene. If it were an effective electron-releasing group in this complex, it would effect a noticeable increased shielding of the ^{19}F nucleus in the C_6H_5F arene. But, instead, it is the deshielding of this nucleus that is observed. On the other hand, the absorption resonance position of ^{19}F in CF_3 remains practically the same as that in $(C_6H_5CF_3)_2Mo$. It would be of interest if a study on a similar chromium complex was

conducted in order to find out how the chemical shifts of its fluorine nuclei compare with those of the molybdenum complexes.

It has been pointed out by Caldwell [15] and Khandkarova *et al.* [4] that van der Waals interactions between substituents is one of the factors that may contribute to the overall magnitude of chemical shifts of ^{19}F in uncomplexed and complexed arenes. Since there is free rotation of the complexed arene rings [16], we would expect all the protons on the methyl substituents of the $(1,2,4\text{-C}_6\text{H}_3(\text{CH}_3)_3)(1,2\text{-C}_6\text{H}_4\text{F}_2)\text{Cr}$ complex to be shielded equally if the van der Waals, i.e. the through space dipole, interactions between the methyl and fluorine groups were the major contributing factor in effecting increased shielding of these protons. This not being the case, it seems that the perturbation of the electron charge on the methyl protons, is a consequence of interatomic charge transmission whereby chromium plays the role of a relay between the two arenes. In any case, if the through space dipole interactions were significant, they would tend to deshield the protons rather than increasing their shielding.

The results of the present work, underscore the danger of interpreting the effect of a substituent of one arene on that of its partner arene in a simple manner. It is, therefore, reasonable at this stage of the development of this subject, to conclude modestly that the electron charge perturbations on the fluorine nuclei in the mixed-arene complexes herein studied, are a result of a rather complex mixture of unequal back-donation to either partner arene and the effects of substituents of one arene on those of the other partner arene such that these effects are felt by the substituents through interatomic bond systems of the metal and ligands themselves whereby the metal acts as a relay between the arenes. There is no evidence

suggesting that the through space dipole interactions are important in these perturbations.

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