Journal of Organometallic Chemistry, *458* (1993) 119–124

JOM 23649

Application of scalar ^{13}C, ^{19}F couplings between carbonyl carbons and aromatic fluorine to investigation of conformation of chelate phosphitodicarbonylchromium and dicarbonyl(phosphine)chromium complexes of fluorobenzenes

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(Received January 13, 1993)

Abstract

The ^{13}C NMR spectra of chelate dicarbonyl-(η^6-2,5-difluorobenzyl)- and -[η^6-2-(2- or 4-fluorophenyl)ethyl]-diphenylphosphitochromiums as well as those of dicarbonyl(triphenylphosphine)chromium complexes of fluorobenzene and its *meta* and *para* substituted (Me and NMe_2) derivatives have been reported. Coupling constants between carbonyl carbons and aromatic fluorine were used for determining the chromium tripod conformation. It was found that in chelate complexes the conformation depends on the length of the arene–metal bridge, on the ability of the arene substituent to stabilize the eclipsed conformation and on the steric interaction between the phosphorus ligand and the ring substituent. The two latter factors appeared also to be of great relevance to conformational equilibrium considerations concerning dicarbonylphosphinechromium complexes.

1. Introduction

In my previous paper [1] the first observation of the coupling between carbonyl carbons and aromatic fluorine in the tricarbonylchromium complex of fluorobenzene was reported. Because there was some evidence that this coupling originates from the "through-space" interaction between the nuclei involved, we made several attempts to use it as a probe in the investigation of the structure and conformation of arenechromium complexes [2]. One of our studies [2a] dealt with chelate dicarbonyl(η^6-2, -3, and -4-fluorobenzyl)diphenylphosphitochromiums (complexes **1**, **2** and **3**). In those complexes a bridge linking the aromatic ligand and metal restricts the rotation about the Cr–arene bond and we therefore expected to draw some conclusions concerning the relation between the conformation of chromium tripod and the coupling investigated. Unfortunately the data available did not permit an unequivocal interpretation of the results. This prompted us to extend our investigation to other rationally designed model compounds. In this paper the ^{13}C NMR spectra of chelate dicarbonyl-(η^6-2,5-difluorobenzyl)- (**4**), -[η^6-2-(2-fluorophenyl)-ethyl]- (**5**), -[η^6-2-(4-fluorophenyl)ethyl]-diphenylphosphitochromium (**6**) and dicarbonyl(triphenylphosphine)chromium complexes of fluorobenzene (**7**), 3-fluorotoluene (**8**), 4-fluorotoluene (**9**), 3-fluoro-*N*,*N*-dimethylaniline (**10**) and 4-fluoro-*N*,*N*-dimethylaniline (**11**) (see Fig. 1) are reported and interpreted.

2. Experimental section

The complexes **4–6** [3a] and **7–11** [4] were prepared by previously published procedures. Their melting points are: **5**: 137–139°, **6**: 129–132°, **7–11**: gradually decompose starting from *ca.* 140°. Complex **4** was obtained as an oil and attempts to crystallise it failed. ^1H and ^{13}C NMR parameters of all compounds investigated are consistent with the described structures. Solutions 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 Varian XL-200 spectrometer (operating at 50.3 MHz). Waltz16 proton decoupling was applied throughout. Typical acquisition and processing parameters for the aromatic and (in parentheses) carbonyl regions are: pulse width 60° (70°), spectral width *ca.* 200 ppm (3000 Hz), acquisition time 1.5 s (5 s). The central line of the

0022-328X/93/$6.00

TABLE 1. ^{13}C chemical shifts (ppm) and $J(^{13}C, ^{19}F$ and $^{31}P)$ values (Hz) for chelate complexes investigated

Complex	Carbons of complexed aromatic ring [a]							
	1	2	3	4	5	6	CH_2	
4	100.95	139.98	75.41	71.25	138.13	69.73		61.05
J(C, F)	18.5, 7.5 [b]	264.8	25.1, 9.1	7.4, 24.1	261.3, 0	22.8, 3.5 [b]		0.7
J(C, P)	6.0 [b]	broadened	1.5	1.3	0	2.2 [b]		10.3
5	89.62	142.26	77.63	85.54	86.58	89.85	26.93	67.19
J(C, F)	13.8	260.8	22.1	7.3	0	4.1	0 [b]	0
J(C, P)	3.1	1.4	1.7	1.0	1.0	1.2	2.6 [b]	2.8
6	97.66	88.37	77.66	141.67			31.42	66.85
J(C, F)	0	6.9	21.0	260.9			0 [b]	0
J(C, P)	2.5	0	0	2.5			~ 1 [b]	3.2

	Carbons of phenoxy rings							
	7,7′		8,8′		9,9′		10,10′	
4	151.75	151.24	121.03	122.03	129.32	129.53	124.35	124.79
J(C, P)	10.9	7.0	4.7	4.1	0.8	1.3	1.2	1.5
5	151.75	151.58	121.62	122.58	129.32	129.20	124.10	124.56
J(C, P)	14.4	6.2	4.3	3.9	1.4	1.3	1.4	1.7
6	151.62		122.06		129.27		124.35	
J(C, P)	8.3		4.2		1.4		1.4	

[a] For enumeration of carbon atoms see Fig. 1. [b] Reverse assignment possible.

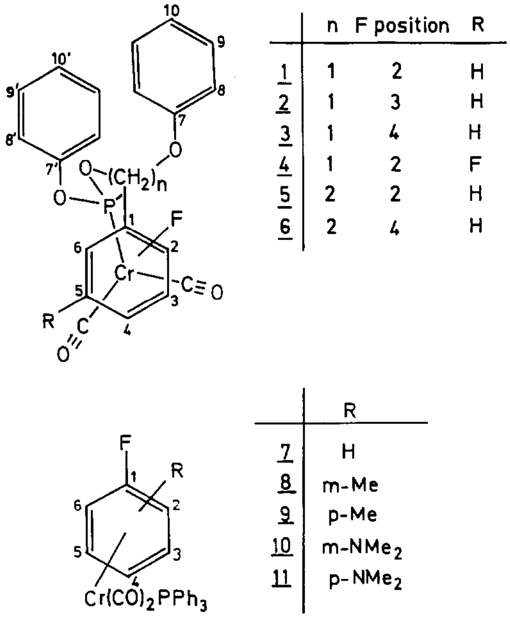
$CDCl_3$ triplet ($\delta = 77.0$ ppm) was used as the chemical shift reference. As found in the cases of complexes **1–3** [2a], the solutions of the complexes under investigation, especially those of **7–11**, gradually become turbid during recording of the spectrum as a result of decomposition. This, of course, dramatically decreases the resolu-

TABLE 2. ^{13}C chemical shifts (ppm) and $J(^{13}C, ^{19}F$ or $^{31}P)$ values (Hz, in parentheses) for aromatic carbons of (η^6-arene) dicarbonyl(phosphine)chromium complexes

Complex	Carbons of complexed aromatic ring [a,b]						
	1	2	3	4	5	6	CH_3
7	145.68	76.40	90.84	85.78			
	(259.7)	(20.5)	(7.6)	(0)			
8	145.64	75.53	102.20	86.05	91.19	76.43	20.47
	(260.0)	(19.7)	(7.1)	(0)	(7.1)	(20.6)	(0)
9	142.77	77.88	88.58	100.88			19.46
	(260.4)	(21.1)	(7.0)	(0)			(0)
10	147.42	61.77	130.78	69.95	90.62	72.47	39.67
	(257.4)	(22.9)	(8.1)	(0)	(7.3)	(20.9)	(0.9)
11	137.60	79.98	68.96	129.60			39.99
	(255.3)	(21.2)	(6.7)	(1.0)			(0)

	Carbons of phosphine phenyl rings [c]			
	7	8	9	10
7	139.64	128.51	133.53	129.78
	(34.6)	(8.8)	(10.8)	(1.4)
8	139.11	127.88	132.94	129.02
	(34.1)	(8.9)	(10.8)	(1.4)
9	139.36	127.92	133.01	129.02
	(34.3)	(9.2)	(10.9)	(0)
10	139.57	127.67	132.91	128.7
	(32.5)	(8.8)	(10.8)	(1.9)
11	139.48	127.80	133.17	128.84
	(33.2)	(8.8)	(11.0)	(2.1)

[a] For enumeration of carbon atoms see Fig. 1. [b] In parentheses ^{13}C, ^{19}F coupling constants. [c] In parentheses ^{13}C, ^{31}P coupling constants.



	n	F position	R
1	1	2	H
2	1	3	H
3	1	4	H
4	1	2	F
5	2	2	H
6	2	4	H

	R
7	H
8	m-Me
9	p-Me
10	m-NMe$_2$
11	p-NMe$_2$

Fig. 1. Structure of complexes investigated and enumeration of carbon atoms.

tion. For each sample, the measuring time had to be adjusted to reach a compromise between satisfactory halfheight linewidth and the signal-to-noise ratio. For that reason the accuracy of determination of small coupling constants was limited and those around 1 Hz might in some cases escape detection.

3. Results and discussion

3.1. ^{13}C NMR spectra of the range of aromatic carbons

The ^{13}C chemical shifts and ^{13}C, ^{19}F and ^{13}C, ^{31}P coupling constants are listed in Tables 1 and 2. The ^{13}C NMR signals in the range of aromatic carbons were assigned to the relevant carbons on the basis of their chemical shifts, ^{13}C, ^{19}F coupling constants and intensities. ^{13}C, ^{19}F coupling constants are of the order of those usually encountered for fluoroarene derivatives. It is, however, worth noting the values of ^3J(C, F) between fluorine C2-F and carbon C6 in **4** (3.5 Hz) and in **5** (4.1 Hz). They are at least half those found for cases in which the carbon located between the fluorine bearing carbon and the observed one is substituted by hydrogen. This was also observed in complex **1** [2a] as well as in tricarbonylchromium complexes of 2-fluorotoluene and 2-fluorobenzyl alcohol [2b]. For some carbons of complexed aromatic rings in chelate complexes the ^{13}C, ^{31}P coupling is also manifested. For the carbons 1, bonded to the bridge, J(C, P) values are the largest and depend on the number of bridge bonds separating the observed nucleus from phosphorus. They are of the order of 6 Hz for complexes **1–4** and of 3 Hz for complexes **5** and **6**. It is difficult to judge which, "through-bond" or "through-space", mechanism of spin-spin interaction is responsible for that coupling and the participation of both of them cannot be excluded.

An interesting regularity has been found for C, P coupling concerning carbons C4. The signal of that carbon is split due to carbon-phosphorus interaction in all chelate complexes and the relevant coupling constant value depends on whether carbon C2 is substituted with fluorine (J(C4,P) ~ 2.2 Hz) or not (J(C4, P) ~ 1.1 Hz). Because C, P coupling constants for arene ligand carbons other than C1 do not depend on bridge length one might expect that in this case the P–Cr and Cr–Ar bonds are involved in the transmission of spin state information. Such a pathway is responsible for interaction between carbonyl carbons and aromatic protons in arenetricarbonylchromium complexes [1], between aromatic protons and phosphorus in arene(dicarbonyl)phosphine(or phosphite)chromiums [3] or between olefinic protons and phosphorus in diene(phosphine)carbonylchromiums [5].

Surprisingly, we did not encounter coupling of the kind under discussion in complexes **7–11**. As mentioned in the Experimental section the instability of those complexes in solution has the effect that a good resolution of the spectra is difficult to achieve. Despite that, J(C, F) and, in the case of the phenyl of phosphine, J(C, P) coupling constants of the order of 1–1.5 Hz were measured. Therefore one may conclude that the coupling constants of phosphorus-complexed arene carbons must be significantly less than 1 Hz. In a few cases an unambiguous assignment of the observed coupling to C, F or C, P interactions was difficult. For carbons 5 of **5** and 1 of **6** a zero value of coupling constant was ascribed to C, F interaction, as coupling between aromatic fluorine and carbon in position *para* was not observed in any of the investigated fluoroarene complexes. For carbons 1 and 6 of **4** both coupling constants are of a comparable magnitude and the larger value was arbitrarily assumed to be that of J(C, F). The lines of carbon 2 of **4** are markedly broadened but coupling constants due to the interaction with phosphorus cannot be determined.

3.2. ^{13}C NMR spectra of the range of carbonyl carbons

Spectra of complexes **1–3** were reported in my previous paper [1]. An ambiguity was signalized there concerning the determination of which of two magnetically inequivalent carbonyl carbons of complex **1** is and which is not, coupled with fluorine. Two possible explanations of this problem were proposed. In the first one, a more or less strictly eclipsed conformation of the chromium tripod in all three complexes was assumed. One could then expect that carbon C_α does not interact with fluorine because the geometrical relation between those nuclei is identical to that in complex **3**, where the C(O), F coupling is not observed. This would lead to the conclusion that J(C(O), F) depends on the dihedral angle, θ, between planes defined respectively by coordinates of carbonyl carbon, chromium and arene centre (first plane) and by chromium, arene centre and fluorine (second plane, see Fig. 2) and reaches two maxima at $\theta = 0°$ (for C_α in **2**) and at $\theta = 180°$ (for C_β in **1**). The alternative explanation was based on the observation that in the crystalline phase the chromium tripod in the analogous 3,5-disubstituted complex is significantly twisted from its eclipsed conformation and on the assumption that the "through-space" mechanism dominates in the C(O)–F spin-spin interaction. (Our further investigations [2] have proven the latter assumption to be correct.) In such a case fluorine in **1** would interact with the C_α carbon rather than with C_β. The results obtained for compounds **4–6** (see Table 3) unequivocally solve this problem indicating the second approach to be correct.

To reveal the connection between the measured coupling constant and the conformation of the complex the following reasoning was applied. The observed J(C(O), F) value depends on the values of coupling constants and populations of conformers A and B shown in Fig. 2. Because in the discussed case the "through-space" mechanism of spin-spin interaction overwhelmingly dominates, the coupling constant for a particular conformer is proportional to the distance between the coupled nuclei. It seems justified in our qualitative discussion to assume that the most important factor governing the distance mentioned above is the angle θ which at the same time defines the conformation of the chromium tripod.

TABLE 3. Chemical shifts (ppm) and $J(^{13}C, ^{19}F$ and $^{31}P)$ values (Hz) for carbonyl carbons of complexes **1–6**

Complex	Carbon	δ	J(C, F)	J(C, P)
1 [a]	α	233.5	2.1	29.0
	β	234.9	0	26.5
2 [a]	α	233.5	6.8	26.5
	β	234.9	0	28.0
3 [a]	α, β	233.6	0	26.9
4	α	233.22	1.5	28.9
	β	232.84	6.3	25.3
5	α	233.97	4.6	30.6
	β	236.46	0	31.0
6	α, β	234.49	2.0	30.6

[a] From ref. 2a.

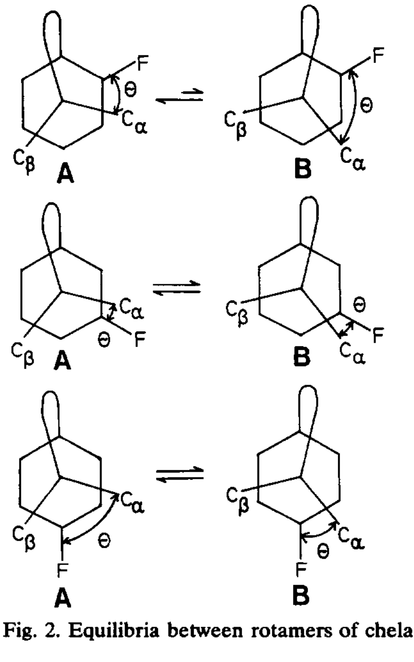


Fig. 2. Equilibria between rotamers of chelate complexes 1–6.

The length of the bridge in complexes **1–4** is probably optimal to keep C(3 and 5)–R (R = H or F) and Cr–C(O) bonds in, more or less strictly, an eclipsed conformation provided the carbon C2 is not substituted. This would explain the lack of coupling in **3** and the large value of $J(C_\alpha$(O), F) in **2** (6.8 Hz). In complex **1** the repulsion between the bridge atoms and the C2 substituent decreases θ leading to the C_α–F spin-spin interaction. For the same reason the population of conformer A, which in the cases of **3** and probably of **2** is *ca.* 50%, is expected to be sufficiently high to treat the observed coupling constant value as approximating that for carbon C_α in this conformer. In complex **4** each of the carbonyl carbons gives a signal composed of four lines due to their interaction with phosphorus and one of fluorines. The smaller value of J(C(O), F) (1.5 Hz) has been ascribed to the C_α–F(C2) interaction and the larger (6.3 Hz) to the C_β–F(C5) interaction.

Each of these is smaller than the corresponding one in complexes **1** (2.1 Hz) and **2** (6.8 Hz). This is, I believe, a result of equilibrium between two forces affecting the chromium tripod conformation. From one side the fluorine at C5 stabilizes the eclipsed conformation in which $J(C_\beta$, F(C5)) reaches its maximum, whereas the value of $J(C_\alpha$, F(C2)) becomes negligibly small. From the other side the repulsion between fluorine at C2 and benzyl oxygen and phosphorus acts in an opposite direction decreasing the former and increasing the latter coupling constant. As expected, the observed J(C(O), F) for **5** and **6** are larger than those for **1** and **3**. When the bridge is longer, steric requirements force the chromium tripod to rotate out of the eclipsed conformation even if there is no fluorine at carbon C2. This is why the coupling is also observed in the 4-fluoro substituted complex **6** (J(C(O), F) = 2.0 Hz). Populations of rotamers A and B are here equal so the coupling constant for carbon C_β in **6A** (or carbon C_α in **6B**; see Fig. 2(c)) may be estimated to be 4.0 Hz. This is still smaller than that expected for carbon C_α in **5** (see Fig. 2a)) because even if a 100% population of rotamer A is assumed, the $J(C_\alpha(O), F)$ value could not be smaller than the one observed (4.6 Hz). Thus the angle θ in rotamer A must be smaller for **5** than for **6**.

This difference in tripod conformations originates from different C2 substituent-bridge atomic repulsions. It is worth noting that no evidence has been found for the "through-bond" mechanism of spin-spin interaction between carbonyl carbons and aromatic fluorines; fluorine nucleus affects exclusively the carbon signal of the carbonyl group located in its spatial proximity.

In Table 4 the data obtained for dicarbonyl(triphenylphosphine)chromium complexes, **7–11**, are collected. The first question which should be answered before more detailed interpretation of the results is which conformation of the freely rotating dicarbonylphosphinechromium moiety, eclipsed or staggered, is favoured. A predominance of any of those conformers will indicate a trade-off between electronic and steric factors. Hunter, Schlögl and co-workers [6] hypothesised on the basis of X-ray crystallography that a staggered conformation is favoured over an eclipsed one in solutions of dicarbonyl(triphenylphosphine)chromium complexes of polymethyl substituted arenes.

Some evidence presented below indicates that such a hypothesis cannot be adopted uncritically for compounds in which arenes bear the groups which strongly favour an eclipsed conformation of Cr–C(O) and C_{Ar}–R (R = Me, F or NMe_2) bonds, especially when the effects of both substituents themselves cumulate. Of two magnetically inequivalent carbonyl carbons of **10**, only one is coupled with fluorine and the observed coupling constant value, 6.9 Hz, is the largest of all measured in this series. This is very close to that found for the chelate complex **2** whose conformation, which is near to eclipsed, was deduced (see above). This suggests that complex **10** exists mostly, if not exclusively in conformation I (see Fig. 3(b)). The same conformation prevails also in the case of complex **8** but a lower observed coupling constant, 5.6 Hz, indicates that other conformations participate in the equilibrium more markedly than in **10**. This is because the capacity of the NMe_2 group for the stabilization of conformation I prevails over that of the methyl group. For both complexes of *meta* substituted fluorobenzenes, the second carbonyl carbon does not interact with fluorine. This means that the conformation in which $Cr–C_\beta(O)$ and C_{Ar}–F bonds are in the same plane is of little importance. The high energy of that conformation probably originates from the steric repulsion between triphenylphosphine and the *meta* substituent. On the basis of that observation, all conformations in which Cr–phosphine and C_{Ar}–substituent bonds are eclipsed have been excluded from consideration.

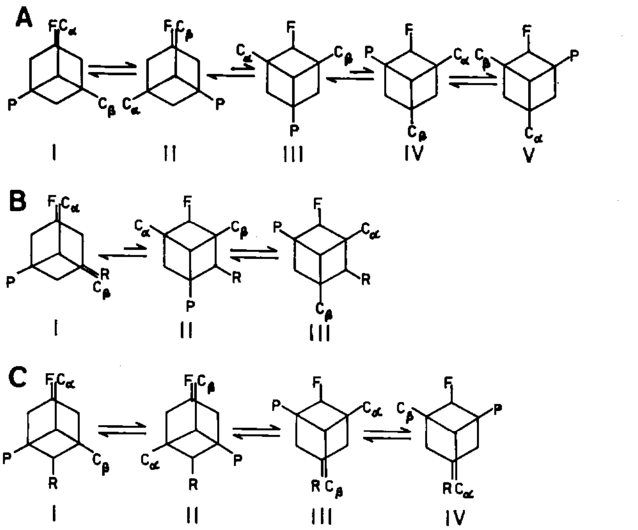


Fig. 3. Equilibria between most stable chromium tripod rotamers for dicarbonyl(triphenylphosphine)chromium complexes 7–11.

TABLE 4. Chemical shifts (ppm) and $J(^{13}C, ^{19}F$ and $^{31}P)$ values (Hz) for carbonyl carbons of complexes 7–11

Complex	Carbon	δ	J(C, F)	J(C, P)
7	α, β	240.4	2.9	20.2
8	α	239.2	5.6	19.9
	β	240.5	0	20.1
9	α, β	240.0	1.7	20.3
10	α	241.6	6.9	19.4
	β	242.1	0	18.7
11	α, β	241.6	0.7	20.2

For complexes of *para* substituted fluorobenzenes the observed coupling constants are smaller. This becomes understandable if one notices that each arene substituent stabilizes different conformations (see Fig. 3(c). For complex **9** the observed coupling constant, 1.7 Hz, is about a quarter of that for **10**. This would suggest that all rotamers shown in Fig. 3(c)) are equally populated. Because the fluorine substituent stabilizes the eclipsed conformation more effectively than the methyl group, one could expect conformations I and II to be more populated. However, taking into account the size of substituents, the steric interaction between the methyl group and phosphine moiety may diminish the population of conformation I and II more than the fluorine-phosphine interaction does in the case of conformations III and IV.

In complex **11** both factors act in the same direction. The dimethylamine group is larger and stabilizes the eclipsed conformation considerably better than fluorine. Consequently the population of conformers III and IV is *ca.* 90% and the observed coupling constant is lowered to 0.7 Hz. In the fluorobenzene complex (**7**) the relatively large value of the observed coupling constant (2.9 Hz) indicates a high population (*ca.* 40%) of conformer I (or II; see Fig. 3(a)). It seems that for steric reasons the fractions of conformations IV and V are negligibly small. The observations reported above appear to be internally consistent indicating that when steric interaction allows, the dicarbonyl(phosphine)chromium tripod may adopt the eclipsed or more correctly eclipsed like conformation (where θ is near but not necessary equal to zero), especially when there is a stabilizing substituent at the arene ring.

Acknowledgments

I express my appreciation to the State Committee of Scientific Research for supporting this work within the PB 185/2/91 project.

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