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INDENYL AND FLUORENYL TRANSITION METAL COMPLEXES

VI *. ANALYSIS OF ^{13}C NMR SPECTRA OF SOME FLUORENECHROMIUM TRICARBONYLS

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Summary

Carbon-13 NMR spectra of the η^6-fluorenyl complexes (fluorene- (I), 3-methylfluorene- (II), and 6-methylfluorenechromium tricarbonyl (III) are described by the means of the "fingerprint" method, ^{13}C spin-lattice relaxation time measurements, and an additive calculation of carbon chemical shifts of the methyl-substituted complexes (II,III). This sequence of operations can be used to analyze ^{13}C NMR spectra of related polyaromatic transition metal complexes and their isomeric mixtures containing species of the same or different structural types.

The study of the reaction mechanisms typical of indenyl, fluorenyl and related polycyclic aromatic η^5- and η^6-transition metal complexes, including their rearrangements [1], requires reliable and rapid techniques for the determination of their structures.

Thus far, the ^1H NMR and IR spectroscopy methods have usually been applied. Both, however, have obvious shortcomings as the proton resonance signals and IR ν(CO) bands of compounds of different structural types tend to overlap. This considerably complicates qualitative and quantitative determination of their mixtures. Similar difficulties also arise in the case of intramolecular metallotropic rearrangements of η^1-cyclopentadienyl and η^1-indenyl compounds. It has been shown [2,3] that ^{13}C NMR is the most promising tool for examination of these systems. The literature data on its application to transition metal polyaromatic complexes are limited to the separation of ^{13}C resonances of coordinated and non-coordinated aromatic rings [4,5]. However, no complete

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* For part V see ref. 14.

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analysis of the ^{13}C NMR spectra observed was given in either of the works cited.

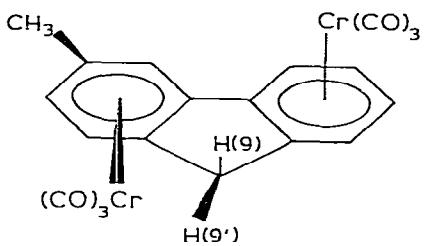
The present communication proposes a general method of ^{13}C resonances assignment for transition metal η^6-fluorenyl complexes. Its efficiency is demonstrated for fluorene- (I), 3-methylfluorene- (II), and 6-methylfluorenechromium tricarbonyl (III).

Experimental

The reactions were run under dry argon. Absolute solvents were used.

Fluorenechromium tricarbonyl (I) was synthesized and purified as described previously [1].

3-Methylfluorene- (II) and 6-methylfluorenechromium tricarbonyl (III). A mixture of 3-methylfluorene (2.6 g, 0.008 mol) and $(NH_3)_3Cr(CO)_3$ (2.7 g, 0.014 mol) in 50 ml dioxane was refluxed for 6 h. The mixture was then filtered, dioxane was distilled off under vacuum, the residue was dissolved in benzene/petroleum ether (1 : 1) and chromatographed (silica gel, L 100/160μ). The products isolated were recrystallized from methylene chloride/heptane. The most intense-coloured band gave 2.4 g (yield 52%) of a mixture of compounds II (45%) and III (55%) according to the ^1H NMR data (Table 1). Attempts at further separation of the mixture proved a failure. The product of lower mobility (a light-yellow band) was only poorly soluble in benzene, pyridine, and chloroform. The IR and ^1H NMR spectra of this product (isolated in a 60 mg yield) showed it to contain chromium tricarbonyl groups coordinated to both aromatic rings:



(IV)

TABLE 1

^1H NMR AND IR PARAMETERS OF THE COMPOUNDS STUDIED

No.	Compound	IR (cm^{-1}) [a] ν(CO)	^1H NMR (δ, ppm)				
			Aromatic rings		Five membered ring	CH_3	Solvent
			coordinated	non-coordinated			
II	η^6-3-$CH_3C_{13}H_9Cr(CO)_3$	1890, 1973	5.1—6.1	7.0—7.8	3.90	2.30	$CDCl_3$
III	η^6-6-$CH_3C_{13}H_9Cr(CO)_3$	1890, 1973	5.1—6.1	7.0—7.8	3.90	2.44	$CDCl_3$
IV	η^6-3-$CH_3C_{13}H_9(Cr(CO)_3)_2$	1903, 1965	5.4—6.6	—	4.00	2.30	C_6D_6

[a] All solutions in $CHCl_3$.

Both protons at C(9) were magnetically equivalent in the ^1H NMR spectrum of IV in benzene which indicated that the $Cr(CO)_3$ groups were positioned *trans* with respect to each other.

The proton NMR spectra were recorded on a Varian XL-100-15 instrument. The ^{13}C NMR spectra were obtained with a Varian CFT-20 spectrometer operated in the pulsed mode. Various modifications of double heteronuclear $^{13}C\{^1H\}$ resonance were used. ^{13}C spin-lattice relaxation time, T_1, was measured using the full [6] or reduced [7] progressive saturation techniques.

The IR spectra were recorded on an Carl Zeiss Jena UR-20 instrument.

Results and discussion

The number of ^{13}C NMR spectroscopic techniques and methods is now so large that the determination of even the most complicated organic species is merely a question of the choice of the operation sequence which is least time-consuming while providing reliable results. This is the most important question to be solved in studies of large series of structurally related compounds.

The assignment of the signals from the C(9) carbon of the five-membered fluorenyl fragment, the carbonyl groups and the methyl group in the spectra of the compounds studied (I—III) *, follows unambigously from their characteristic chemical shifts and through off-resonance decoupling. Moreover the latter technique makes it possible to identify the quarternary carbon atom signals, C(10)—C(13) (C(3) in II and C(6) in III). The problem is thus reduced to the choice of the means of analysis for the part of the spectra containing the aromatic ring carbon signals.

One of the most efficient methods used in the analysis of ^{13}C NMR spectra of 1,2-disubstituted benzenes and polyaromatic systems is the "fingerprint" method [8,9]. This technique is about three times more time consuming than the one based on measurements of routine ^{13}C NMR spectra under total proton decoupling. The visualization of the spectral information and the ease of interpreting it, however, provide a fair compensation for the time losses. For this reason, the first stage of our work included measurement of the ^{13}C monoresonance spectrum of fluorenechromium tricarbonyl. Characteristic signal splittings in that spectrum made it possible to assign the signals from the following pairs: C(1) and C(4), C(5) and C(8) ("α" carbon atoms) and C(2) and C(3), C(6) and C(7) ("β" carbon atoms).

Further refinement of the resonance signal assignments in the spectrum of I required measurements of spin lattice relaxation times, T_1, as spatial proximity of the five membered fluorenyl fragment protons to the C(1), C(8), C(10), and C(13) carbon atoms should decrease their T_1 times compared with C(4), C(5), C(11), and C(12), respectively, provided the dipole-dipole relaxation mechanism prevails. It should be noted that the distances from the aforementioned hydrogen atoms to C(2) and C(3) (and also C(6) and C(7)) being slightly different, the corresponding signals could not have been assigned at this stage of the analysis. The results obtained are listed in Table 2.

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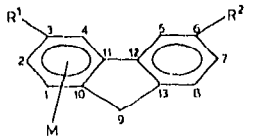
* A ^{13}C NMR spectrum of compound IV suitable for a detailed analysis could not be measured because of the small amount of the product isolated and its low stability. The preliminary results are, however, indicative of the absence of non-coordinated aromatic ring in this molecule.

TABLE 2

^{13}C CHEMICAL SHIFTS AND SPIN-LATTICE RELAXATION TIMES T_1 OF SOME FLUORENECHROMIUM TRICARBONYLS [a]



(I, R^1 = H, R^2 = H, M = $Cr(CO)_3$,
II, R^1 = CH_3, R^2 = H, M = $Cr(CO)_3$,
III, R^1 = H, R^2 = CH_3, M = $Cr(CO)_3$,
V, R^1 = CH_3, R^2 = H)

No.	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)	C(11)	C(12)	C(13)	CH_3	CO	Remarks
V	124.61	127.62	136.27	120.39	119.66	126.48	126.59	124.93	36.52	140.29	141.78	141.88	143.64	21.39		
I	90.13	91.44	90.61	86.23	119.90	127.23	128.35	124.91	36.66	112.70	110.75	138.45	141.88	—	233.06	
	(3.4 ± 0.2)	(3.4 ± 0.3)	(4.1 ± 0.3)	(5.1 ± 0.4)	(4.6 ± 0.2)	(3.3 ± 0.2)	(3.8 ± 0.3)	(3.7 ± 0.2)	—	—	—	—	—	—	—	*b*
	(3.7)	(4.2)	(4.0)	(5.4)	(4.9)	(3.6)	(4.0)	(3.9)	—	(24.0)	(45.0)	(49.0)	(31.0)	—	—	*c*
II	91.81	91.49	107.41	86.68	120.11	127.23	128.48	124.96	36.42	110.08	112.23	138.61	142.46	20.76	233.53	
	91.73	91.54	107.61	86.33	119.76	127.01	128.24	124.84	36.26	109.60	112.35	138.63	142.32	—	—	*d*
III	90.18	91.39	90.48	86.33	120.47	137.11	129.50	124.61	36.42	113.33	111.01	138.61	139.03	21.26	233.17	
	90.06	91.33	90.39	86.11	120.49	136.80	129.27	124.52	36.26	113.14	110.93	138.53	138.97	—	—	*d*

[a] ^{13}C chemical shifts are given in ppm from TMS with accuracy ±0.05 ppm. Relaxation times T_1 (s) were measured with progressive saturation technique [b] and their reduced version [c] and are given in parentheses. [d] The results of the additive calculation.

Measurement of spin-lattice relaxation times is still applied rather infrequently to assign ^{13}C NMR signals, though the methodological aspects of this approach have received a good deal of attention in the literature. The reason for that may be the considerable time expenditure inherent in experiments of this type. The latter are justified if the compound under investigation may be expected to exhibit significant differences in spin-lattice relaxation times of certain carbon atoms owing to some particular features of the supposed structure (arising from its symmetry, specificity of intramolecular dipole—dipole interactions, etc.) while other methods fail to provide a reliable assignment of ^{13}C NMR resonance signals. As relative T_1 values are only of interest within this approach, the problem of systematic errors does not arise and fast procedures may be applied, which considerably reduce time expenditure [7].

The analysis of ^{13}C NMR spectra of mixtures of compounds II and III which, as stated, could be not separated * was based on the results obtained for I and 3-methylfluorene (V), chosen as model compounds and studied by the same techniques as 4-methylfluorene [11]. The data obtained (Table 2) can be used to suggest an additive scheme for the calculation of the ^{13}C NMR resonances in methyl-substituted fluorenechromium tricarbonyls II and III. The additive calculations showed that with compound III where the chromium tricarbonyl group is linked with the non-methylated aromatic ring, a good agreement between the experimental and calculated chemical shifts is observed (viz., $|\delta^i_{calc.} - \delta^i_{exp.}| = \Delta\delta^i \leqslant 0.3$ ppm), whereas with II, the calculation error for the coordinated aromatic ring carbon atoms amounts to 6 ppm. Comparison of the ^{13}C NMR chemical shifts of benzene, toluene, *m*-xylene, mesitylene, durene, hexamethylbenzene and their chromium tricarbonyl complexes (see the data cited in refs. 12 and 13) showed that the screening action of the organometallic group on the aromatic ring carbon atoms decreases with the number of methyl groups in the molecule. Additive calculation of ^{13}C chemical shifts for compound II taking into considera tion the latter effect gave $\Delta\delta^i \leqslant 0.4$ ppm (see Table 2).

The data obtained may thus be interpreted as follows. The assignment of the fluorenechromium tricarbonyl ^{13}C NMR signals was made by the "fingerprint" technique and comparative analysis of spin-lattice relaxation times of its ^{13}C nuclei. This stage requires comparatively large experimental time expenditures. At the same time, this technique provides the possibility of rapidly obtaining the most important data on the compound under study, which is the parent in the series under consideration.

The scheme of additive calculation of ^{13}C chemical shifts suggested facilitates signal assignment in ^{13}C NMR spectra of the mixture of fluorenechromium tricarbonyls II and III. At this stage, the assignment of the C(2) and C(3), C(6) and C(7) signals in the spectrum of I was refined **. Similar additive calculations may be performed for other alkyl-substituted fluorenechromiumtricarbonyls. The application of the "fingerprint" technique and relaxation time, T_1, measurements are then only required to resolve ambiguities.

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* The task is complicated by the fact that the isomers are isolated from the reaction mixture in approximately equal amounts though it has been suggested earlier that the organometallic group should preferably attach to the aromatic ring having a higher electron density [10].

** The variant of the C(2) and C(3) (C(6) and C(7)) signal assignment chosen was that which gave the minimum $\Sigma\Delta\delta^i$ value in the calculations of carbon-13 chemical shifts for II and III.

We can see no serious objections to the application of the sequence of methods suggested here to analysis of ^{13}C NMR spectra of both individual fluorene complexes and related polyaromatic systems containing transition metals and isomer mixtures containing species of the same or different structure types (e.g. η^6- and η^5-complexes).

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