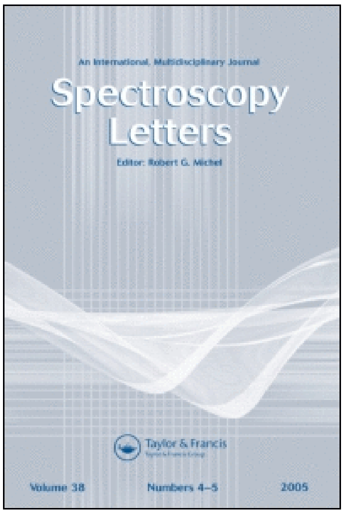

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^{13}C-NMR Spectra of Some π-(Arene)-Tricarbonylchromium(O) Complexes

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^{13}C-NMR SPECTRA OF SOME π-(ARENE)-TRICARBONYLCHROMIUM(O) COMPLEXES

KEY WORDS: π-(Arene)-tricarbonylchromium(o), ^{13}C-NMR spectra

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Many ^{13}C-NMR studies dedicated to the π-(Arene)-tricarbonylchromium(o) complexes are concerned with the origin of the large upfield shifts of the aromatic carbons on the coordination to the chromiumtricarbonyl group. This effect is not yet completely understood and various hypotheses have been formulated to justify it (1)(2)(3)(4).

As an experimental contribution to the subject we report the ^{13}C-NMR spectra of some π-(Arene)-tricarbonylchromium(o) complexes where the arene ligands are polycyclic aromatic hydrocarbons (condensed, uncondensed and with an alicyclic moiety).

The presence of either complexed and uncomplexed rings in the same molecule allows to test the ^{13}C chemical shift variations due to the chemical bond formation and also long range interactions as experienced by the other ring.

In the Table are reported the ^{13}C chemical shifts for free and complexed hydrocarbons. The peak assignments for the free arenes have been given elsewhere (5)(6)(7), while the attribution in the complexes has been determined with off-resonance experiments, undecoupled spectra and considering the relaxation times (8). Only few ambiguities arise for the assignment of some phenantrene complex resonances, but this is unimportant for the discussion; the chemical shift proposed for C-13 and C-14 resonances is more probable than the reversed one, which would cause for the C-13 resonance an upfield shift too large compared to the analogous quaternary carbon atoms in similar complexed hydrocarbons (e. g. Naphtalene).

The experimental results show that the ^{13}C shift produced by the metalcarbonyl group in the coordinated ring is scarcely affected by the structure of the rest of the ligand.

The average shift of the complexed ring is about 35 ppm upfield relative to the resonance in free arenes, while the corresponding shift in the uncomplexed moiety is noticeably smaller. This fact is a proof that there is no metal exchange between the ligand rings, at least at room temperature. Furthermore, each complex shows a single carbonyl resonance in the 232 ppm region: this result indicates that there is free rotation of the carbonyls, as found for other similar complexes (9).

In the uncoordinated rings the small variations are independent from the saturation of the carbon atoms and from the ring mobility and does not seem correlated with carbon-metal bond magnetic anisotropy, as previously suggested (4). Long range charge polarization effects may also be present.

Useful hints are derivable from the differences of the chemical shifts in the free ligand/benzene ($\Delta\delta_F = \delta_{ligand} - 128.6^*$) and π-(Arene) $Cr(CO)_3$/ π-(benzene) $Cr(CO)_3$ pairs ($\Delta\delta_c = \delta_{complex} - 92.4^*$ for the coordinated ring and $\Delta\delta'_c = \delta_{complex} - 128.6^*$ for the uncoordinated one). This result shows that $\Delta\delta_F$ and $\Delta\delta_c$ (or $\Delta\delta'_c$) are generally comparable in magnitude and sign. This agreement justifies the hypothesis that for the carbons of the complexed rings the main contribution to the chemical shift is the same of that observed in the π-(benzene)-tricarbonylchromium(o)/benzene pair, on which are superimposed terms related to the specific molecule. Further work is in progress on this subject (13).

EXPERIMENTAL

The hydrocarbons were carefully purified commercial samples, and the complexes were prepared following the literature methods (14). The spectra were recorded at

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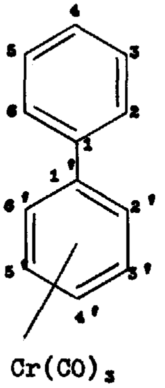
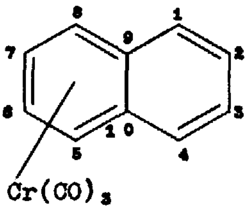
* $\delta_{benzene} = 128.6$ and $\delta_{(benzene)Cr(CO)_3} = 92.4$ ppm

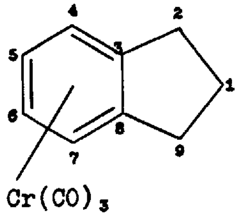
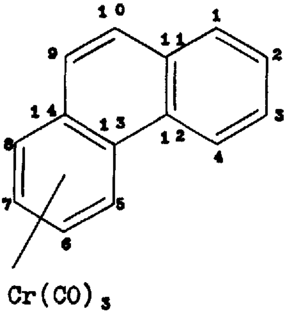
TABLE

^{13}C-NMR chemical shifts$^{(a)}$ of π-(arene)-tricarbonylchromium(o) complexes and of parent ligands

		Parent	Complex	$\Delta^{(b)}$
Diphenyl 	C_1	141.2	136.4	- 4.8
	$C_{2,6}$	127.1	127.0	- 0.1
	$C_{3,5}$	128.7	128.8	0.1
	C_4	127.1	129.0	1.9
	$C_{2'}$	141.2	110.6	-30.6
	$C_{2',6'}$	127.1	92.3	-34.8
	$C_{3',5'}$	128.7	92.7	-36.0
	$C_{4'}$	127.1	91.6	-35.5
	C≡O	-	232.4	-
Naphthalene 	$C_{1,4}$	127.9	128.7	0.8
	$C_{2,3}$	125.8	128.7	2.9
	$C_{5,8}$	127.9	92.5	-35.4
	$C_{6,7}$	125.8	20.8	-35.0
	$C_{9,10}$	133.4	105.7	-27.7
	C≡O	-	231.6	-

(continued...)

T A B L E (continued)

Indane 	C_1	25.7	24.0	- 1.7
	$C_{2,9}$	33.2	32.3	- 0.9
	$C_{3,8}$	144.2	114.5	-29.7
	$C_{4,7}$	124.4	90.1	-34.3
	$C_{5,6}$	126.0	91.8	-34.2
	C≡O	-	232.2	-
Phenantrene 	C_1	128.5	130.2	1.7
	C_2	126.5	125.6$^{(c)}$	-0.9
	C_3	126.5	128.2$^{(c)}$	1.7
	C_4	122.8	122.2	- 0.4
	C_5	122.8	86.1	-36.5
	C_6	126.5	89.7	-34.8
	C_7	126.5	89.7	-34.8
	C_8	128.5	92.0	-36.5
	C_9	126.9	128.4$^{(d)}$	1.5
	C_{10}	126.9	129.3$^{(d)}$	2.4
	C_{11}	132.0	131.9$^{(e)}$	- 0.1
	C_{12}	130.3	132.2$^{(e)}$	1.9
	C_{13}	130.3	96.5	-33.8
	C_{14}	132.0	103.0	-29.0
	C≡O	-	231.4	-

(a) ppm downfield from internal TMS; (b) $\Delta = \delta_{complex} - \delta_{free\ ligand}$; (c)(d)(e) the assignments can be reversed.

room temperature on 0.5M solutions (0.1M for complexed phenantrene) in anhydrous, oxygen free, $CDCl_3$ on a Bruker WH-90 spectrometer operating at 22.63 MHz in the pulsed Fourier Transform mode. The computer used (Nicolet BNC 12) allowed acquisition of 4096 output data points in the transformed spectra. Chemical shifts are reported in ppm downfield from internal tetramethylsilane.

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