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^1H, ^{13}C NMR and Theoretical Studies on (Arene)tricarbonylchromium(0) Complexes

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^1H and ^{13}C NMR spectra of benzophenone-$Cr(CO)_3$ and fluorenone-$Cr(CO)_3$ have been recorded and fully assigned. Very large upfield coordination shifts of the resonances of the directly bonded rings are evident. A discussion on the nature of such shifts is made on the basis of the results of CNDO calculations on benzene-$Cr(CO)_3$.

Introduction

Kinetic experimental results about several arenes π-complexed with the $Cr(CO)_3$ group do not give a consistent picture about the electronic properties of this group. Some experimental findings show that the $Cr(CO)_3$ moiety behaves as an electron-withdrawing group [1, 2], whereas other evidence points to an electron-releasing function [3–5].

A great number of investigations have been performed by the NMR technique and the ^1H and ^{13}C results always show upfield shifts of the resonances of the aromatic nuclei upon coordination. Moreover a net increase of the ^{13}C–H coupling constants and a decrease of H–H coupling constants with respect to the free ligands are observed. The shielding found for proton nuclei (1–3 ppm) has been attributed both to magnetic anisotropy effect of the ring-metal bond [6, 7] and to quenching of the aromatic ring current [6]. Thoennes *et al.* [8] have analyzed qualitatively the various sources of complexation effects on ^{13}C shielding constants (25–40 ppm upfield shifts) and pointed to the leading role played by electronic effects, especially by metal → arene electron shift ("back donation").

In this paper we report further experimental data regarding ^1H and ^{13}C assignments of the spectra of benzophenone-$Cr(CO)_3$ and fluorenone-$Cr(CO)_3$. Furthermore, in order to quantify the role of "back donation" on the ^{13}C chemical shifts, we have performed electronic structure calculations in the CNDO scheme on benzene-$Cr(CO)_3$ – the simplest molecule of the series. In this respect, the calculated parameters (charges and bond orders) have been fitted to the chemical shift semiempirical relationships of the literature.

Experimental and Calculations

The arene-$Cr(CO)_3$ complexes were prepared in our laboratory following the standard methods described in the literature [2.9].

0.1 *M* and 1 *M* solutions in $CDCl_3$ (for ^1H and ^{13}C spectra respectively) were examined at room temperature with a Bruker WH 90FT instrument equipped with a BNC12 Nicolet computer. All solutions were degassed and tightly closed in a vacuum line.

The analysis of the ^1H spectra was performed by a modified version of the LAOCOON III program [10]. The ^{13}C resonances have been assigned on the basis of peak relative intensities and positions in decoupled spectra, analysis of coupled spectra and selective decoupling technique. Relaxation time measurements by the "inversion–recovery" method have been of assistance in some cases. These data will be reported in a successive paper. Furthermore the assignments have been in some cases checked theoretically by considerations of electronic structure with the aid of CNDO calculations.

The structural parameters used in the electronic structure calculations for benzene-$Cr(CO)_3$ were taken from X-ray data [11], with the assumption of a "staggered" conformation (Fig. 1) of the $Cr(CO)_3$ moiety with respect to the benzene ring. Clack's version [12] of the CNDO method for molecules containing transition elements was used in the present

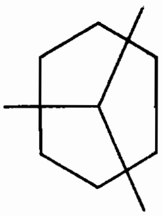

Figure 1. "Staggered" conformation of benzene-$Cr(CO)_3$.

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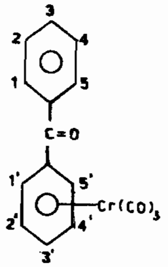
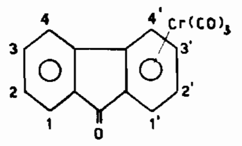
TABLE I. ^{1}H Chemical Shifts and Coupling Constants of (Arene) tricarbonylchromium(0) Complexes and the Parent Ligands[a].

		Parent[b]	Complex[b]	Difference[c]
Benzophenone	δ_1	7.81	7.77	+0.04
	δ_2	7.48	7.50	−0.02
	δ_3	7.59	7.59	0.00
	$\delta_{1'}$	7.81	6.03	+1.78
	$\delta_{2'}$	7.48	5.32	+2.16
	$\delta_{3'}$	7.59	5.62	+1.97
	J_{12}	7.85	7.75	+0.01
	J_{13}	1.41	1.35	+0.06
	J_{14}	0.55	0.63	−0.08
	J_{15}	1.80	1.82	−0.02
	J_{23}	7.56	7.45	+0.11
	J_{24}	1.14	1.12	+0.02
	$J_{1'2'}$	7.85	6.45	+1.40
	$J_{1'3'}$	1.41	0.79	+0.62
	$J_{1'4'}$	0.55	0.27	+0.28
	$J_{1'5'}$	1.80	0.90	+0.90
	$J_{2'3'}$	7.56	6.21	+1.35
	$J_{2'4'}$	1.14	0.81	+0.33
Fluorenone	δ_1	7.64	7.70	−0.06
	δ_2	7.28	7.39	−0.11
	δ_3	7.48	7.53	−0.05
	δ_4	7.49	7.44	+0.05
	$\delta_{1'}$	7.64	6.32	+1.32
	$\delta_{2'}$	7.28	5.30	+1.98
	$\delta_{3'}$	7.48	5.83	+1.64
	$\delta_{4'}$	7.49	5.74	+1.75
	J_{12}	7.40	7.56	−0.16
	J_{13}	1.09	1.12	−0.03
	J_{14}	0.77	0.62	+0.15
	J_{23}	7.62	7.50	+0.12
	J_{24}	0.90	0.98	−0.08
	J_{34}	7.49	7.35	+0.14
	$J_{1'2'}$	7.40	6.28	+1.12
	$J_{1'3'}$	1.09	0.76	+0.33
	$J_{1'4'}$	0.77	0.68	+0.09
	$J_{2'3'}$	7.62	6.23	+1.39
	$J_{2'4'}$	0.90	0.97	−0.07
	$J_{3'4'}$	7.49	6.23	+1.26

[a] 0.1 *M* solutions in CDCl$_3$. [b] Chemical shifts in ppm from TMS and coupling constants in Hz. [c] Positive values indicate upfield shifts.

work. On employing the STO basis set with Burns' exponents [13] together with Clack's semi-empirical parameters no convergence on the energy was obtained. However, with the Slater usual exponents the convergence was reached with the following semiempirical values obtained by rough parametrization:

$$\beta^{o}_{3d} = -24.0 \text{ eV} \qquad \beta^{o}_{4sp} = -12.5 \text{ eV}.$$

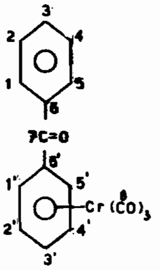
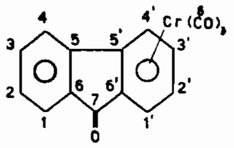
Results and Discussion

NMR Data

Proton chemical shifts and coupling constants for both free and complexed arenes are reported in Table I. An analysis of the ^{1}H spectrum of benzophenone in CCl$_4$ is reported in the literature [14] and with minor variations our results are comparable. The ^{1}H spectrum of fluorenone shows a concentration dependent behaviour. The relative chemical shifts of protons at positions 3 and 4 (see Table I – nearly degenerate in 0.1 *M* solution – are reversed when the concentration of the sample is increased to 1 *M*, indicating probably solvent–solute interaction.

The ^{1}H parameters of fluorenone can be compared to those reported for fluorene [15] in the same solvent. A downfield shift of about 0.2 ppm of all resonances but that of proton 3 (see Table I) is present in fluorenone, owing to both magnetic anisotropy

TABLE II. ^{13}C Chemical Shifts and ^{13}C–H Coupling Constants of (Arene)tricarbonylchromium(0) Complexes and the Parent Ligands[a].

		Chemical Shifts[b]			Coupling Constants[c]	
		Parent	Complex	Difference[d]	Parent	Complex
Benzophenone[f]	C_1	129.9	128.6	+ 1.3	162	155
	C_2	128.1	128.6	– 0.5	163	155
	C_3	132.3	132.4	– 0.1	161	159
	C_6	137.4	136.5	+ 0.9		
	C_7	196.2	193.3	+ 2.9		
	$C_{1'}$	129.9	95.8	+34.1	162	175
	$C_{2'}$	128.1	89.6	+38.5	163	178
	$C_{3'}$	132.3	94.8	+37.5	161	173
	$C_{6'}$	137.4	96.3	+31.1		
	C_8		230.1			
Fluorenone	C_1	129.1	130.4	– 1.3	162	161
	C_2	124.3	124.3	0.0	156	173
	C_3	137.4	134.3	+ 3.1	161	161
	C_4	120.3	120.8	– 0.5	159	161
	C_5	(134.2)[e]	(133.9)	+ 0.3		
	C_6	(144.4)	(141.9)	+ 2.5		
	C_7	193.9	189.6	+ 4.3		
	$C_{1'}$	129.1	91.6	+37.5	162	170
	$C_{2'}$	124.3	87.2	+37.1	156	179
	$C_{3'}$	137.4	94.0	+43.4	161	173
	$C_{4'}$	120.3	83.7	+36.6	159	182
	$C_{5'}$	(134.2)	(92.3)	+41.9		
	$C_{6'}$	(144.4)	(107.6)	+36.8		
	C_8		229.8			

[a] 1 *M* solutions in $CDCl_3$. [b] Values in ppm from TMS. [c] Values in Hz. [d] Positive values indicate upfield shifts. [e] Values in parentheses cannot be unambiguously assigned. [f] Chemical shifts of benzophenone-$Cr(CO)_3$ are very similar to that reported in ref. 24.

and electronic effects of the carbonyl group coplanar with the aromatic rings.

As a consequence of complexation with the $Cr(CO)_3$ moiety, the directly bonded ring shows in both complexes all its resonances shifted upfield to a different extent, ranging from 1.3 to 2.2 ppm (Table I), whereas the other ring appears to be virtually unmodified. Coupling constants display a noticeable decrease only in the bonded ring. It is noteworthy that in 0.1 *M* solution also the relative chemical shifts of the 3 and 4 protons of both rings of complexed fluorenone are inverted with respect to the parent arene.

In Table II we detail the ^{13}C chemical shifts and ^{13}C–H coupling constants. The ^{13}C spectrum of benzophenone has been given by Nelson *et al.* [16] and our assignments are in agreement. The assignment of the resonances of the junction carbon atoms of fluorenone (C_5 and C_6, see Table II) is not straightforward. Unfortunately the measurement of relaxation time T_1, which amounts to 91.0 and 85.4 seconds respectively for resonances at 134.2 and 144.4 ppm, does not allow to add any proof to the assignment proposed in Table II on the basis of considerations on electronic structure.

The ^{13}C spectra of complexed molecules show the usual pattern, *i.e.*, a large upfield shift for the resonances of the complexed ring. It is noteworthy that the shift values in our compounds are very high (up to 43 ppm) compared with those reported for this class of complexes.

Theoretical Results

The results of electronic structure calculations on benzene-$Cr(CO)_3$ are collected in Table III which gives the orbital charges and relevant bond orders for free and complexed benzene. The results warrant some comments: a) The complexed benzene ring is charged positively (+0.102) according to an overall withdrawing effect of the $Cr(CO)_3$ moiety; b) On

TABLE III. CNDO Orbital Charges and Relevant Bond Orders for Benzene and Benzene-$Cr(CO)_3$.

Orbital Charges		Benzene	Benzene-$Cr(CO)_3$
Carbon (ring)	2s	1.009	0.947
	$2p_\sigma$	1.986	1.934
	$2p_\pi$	1.000	1.081
	total charge	+0.005	+0.038
Hydrogen	1s	1.005	1.021
	total charge	−0.005	−0.021
Chromium	4s		0.214
	$4p(a_1)$		0.218
	4p(e)		0.412
	$3d(a_1)$		1.142
	3d(e)		3.510
	total charge		+0.504
Carbon (carbonyl)	2s		1.419
	2p		2.468
	total charge		+0.113
Oxygen	2s		1.673
	2p		4.642
	total charge		−0.315

Bond Orders		Benzene	Benzene-$Cr(CO)_3$
Carbon–Carbon	2s–2s	0.337	0.305
	$2s–2p_\sigma$	0.663	0.650
	$2p_\pi–2p_\pi$ (*cis*)	0.667	0.499
	$2p_\pi–2p_\pi$ (*trans*)		0.629
Carbon–Hydrogen	2s–1s	0.491	0.524
	$2p_\sigma–1s$	0.816	0.827

complexation there is an electronic population increase on the ring carbon $2p_\pi$ orbitals (1.000 → 1.081) showing the presence of "back donation" (Metal → π^*), while a net decrease in the electronic population of the ring σ framework is present; c) Ring π bond orders are decreased in the complex with respect to free benzene and depend on whether the bonds are *cis* or *trans* [11] with respect to the $Cr(CO)_3$ group (Fig. 1), with the *cis* bond orders being lower than the *trans* ones. The average bond order for the "quasi-free" rotation of the $Cr(CO)_3$ moiety amounts to 0.564 against 0.667 in benzene.

A comparison of our results with the *ab initio* calculations [17] of the literature indicates a very good agreement, while a full comparison with the GTO–CNDO/2 results of Saillard *et al.* [18] is not possible because these latter authors have not reported bond orders.

Employing the empirical relationship [19]

$$\Delta\sigma_H = 10.6\ \Delta Q_\pi$$

which correlates the relative chemical shift of aromatic protons to the ring carbon $2p_\pi$ electronic population, we obtained an 0.86 ppm upfield coordination shift against the experimental value of 1.9 ppm [20]. It is likely that in this case a determining role is played by the ring–metal bond anisotropy due to the well known importance of remote nonbonding effects on proton chemical shifts [8].

The π bond order (p_π) change brought about by complexation may explain the experimental decrease of the protonic *ortho* coupling constants. In fact the following empirical relationship [21]

$$J_{ortho} = 12.7\ p_\pi - 1.1$$

gives an *ortho* coupling of 7.38 Hz for free benzene, while for the complex it yields 6.06 Hz, in good agreement with the experimental trend reported in Table I.

The expression obtained by Alger, Grant and Paul [22] for the paramagnetic term of the ^{13}C chemical shift for sp^2 hybridized carbons

$$\Delta\sigma_C = 100\Delta Q_\pi + 67\ \Delta Q_\sigma - 76\ \Delta P_\pi$$

correlates the chemical shift of aromatic hydrocarbons with the π and σ electronic populations (Q_π and Q_σ) and with the total π bond order ($P_\pi = 2\ p_\pi$). With the aid of data in Table III it is easy to calculate a total ^{13}C upfield shift for benzene-$Cr(CO)_3$ of about 16 ppm (the experimental value being 36 ppm [23]). This result may be considered satisfactory, given the approximations used throughout the calculations. We can state that a large part of the experimental ^{13}C upfield shift can be explained by effects arising from the competition between "donation" (Ligand → Metal) and "back donation" (Metal → Ligand).

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