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Note on the solvent dependence of the ^{1}H-NMR coordination chemical shifts of tricarbonyl(η^6-[8]paracyclophane)chromium. A caveat concerning its interpretation *

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Abstract

The solvent dependence of the ^{1}H-NMR coordination chemical shifts of tricarbonyl(η^6-[8]paracyclophane)chromium (**1**) may act as an obstacle to their use as a probe in assessing the quenching of the aromatic ring current due to η^6-complexation.

Introduction

η^6-Complexation of arenes with transition metals induces large upfield shifts of the aromatic ^{1}H- and ^{13}C-NMR signals. The origin of this effect is still the subject of discussion and has been variously attributed to different factors such as the increase of electron density on the aromatic ring, metal–ligand anisotropy, rehybridization of the aromatic carbon atoms and weakening of the aromatic ring current [2–6]. To gain insight in the contribution of quenching of the ring current due to η^6-complexation, [*n*,*m*]- and [*n*]cyclophanes have been used as ligands, particularly by Elschenbroich's group [7–10]. The well-defined positions of the oligomethylene bridge protons in these compounds and the sensitivity of their ^{1}H-NMR chemical shifts to their location in the anisotropy cone of the benzene ring were used as probes to gauge the quenching of the aromatic ring current upon η^6-complexation. For example, in the case of bis(η^6-[10]paracyclophane)chromium, the ^{1}H-NMR coordination chemical shifts [δ(coord.) = δ(complex) − δ(ligand)] of the bridge protons α-, β-, γ-, δ- and ϵ-CH_2, respectively, changed sign after the β-CH_2 group (δ(coord.): α- and β-CH_2 < 0 ppm and γ-, δ- and ϵ-CH_2 > 0 ppm) [7]. The changes were rationalized by assuming a reduction of the aromatic ring

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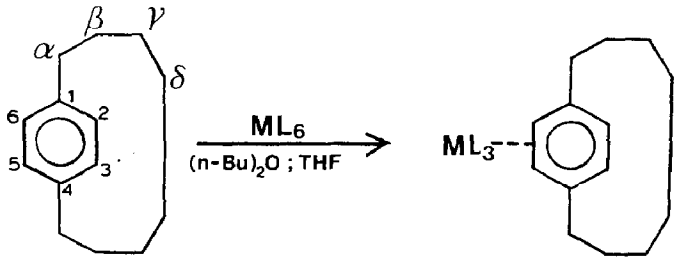

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Scheme 1. M = Cr; L = Co.

current due to η^6-complexation. Since δ(coord.) of the β-CH_2 groups was close to zero, the boundary between the shielding and deshielding region of the anisotropy cone was estimated to lie between the β- and γ-CH_2 groups.

We thought it of interest to see whether a similar effect applies to tricarbonyl(η^6-arene)chromium complexes [4,8]. Recently, we devised an easy route to tricarbonyl(η^6-[8]paracyclophane)chromium (**1**), which previously could be prepared only in low yield (4%) [4a]. Two developments brought considerable improvement. First, a short and efficient route to the ligand [8]paracyclophane (**2**) involving flash vacuum thermolysis in the final step, was devised [11]. Secondly, it was shown that compound **1** could be synthesized in 67% yield (after recrystallization) by treatment of the ligand **2** with 1.1 equivalents of $Cr(CO)_6$ in a refluxing mixture of di-n-butyl ether and tetrahydrofuran (see Scheme 1 and Experimental Section) [12]. We note that the synthesis of tricarbonyl(η^6-[6]paracyclophane)chromium (yield 3%) via a similar route has been reported recently [4b].) A reinvestigation of tricarbonyl(η^6-[8]-paracyclophane)chromium (**1**) by ^{1}H- and ^{13}C-NMR spectroscopy reveals that the ^{1}H-NMR coordination chemical shifts [δ(coord.) = δ(**1**) − δ(**2**)] show a strong solvent dependence as a consequence of specific solute–solvent interactions of the η^6-complex **1**.

Results and discussion

^{1}H-NMR data for compounds **1** and **2**, in $CDCl_3$ and C_6D_6, respectively, are presented in Table 1. From the ^{1}H-NMR data obtained in $CDCl_3$ as solvent, it appears as if the usual situation is encountered. A considerable upfield δ(coord.)

Table 1

^{1}H-NMR data for compounds **1** and **2** in $CDCl_3$ and C_6D_6, respectively

position [a]	$CDCl_3$			C_6D_6				
	δ(1)	δ(2) [b]	δ(coord.) [c]	δ(1)	δ(2)	δ(coord.) [c]	$\Delta\delta$(1) [d]	$\Delta\delta$(2) [d]
aromatic	5.34	7.13	−1.79	4.63	7.11	−2.48	−0.71	−0.02
α-CH_2	2.42	2.66	−0.24	1.90	2.63	−0.73	−0.52	−0.03
β-CH_2	1.67	1.47	0.20	1.23	1.49	−0.26	−0.44	0.02
γ-CH_2	1.23	0.91	0.32	0.82	1.01	−0.19	−0.41	0.10
δ-CH_2	0.80	0.19	0.61	0.49	0.38	0.11	−0.31	0.19

[a] Cf. Scheme 1. [b] Cf. ref 13. [c] δ(coord.) = δ(**1**) − δ(**2**); see text. [d] $\Delta\delta$(**1**) = δ(**1**,C_6D_6) − δ(**1**,$CDCl_3$) and $\Delta\delta$(**2**) = δ(**2**,C_6D_6) − δ(**2**,$CDCl_3$).

−1.79 ppm for the aromatic protons, a moderate δ(coord.) −0.24 ppm for the α-CH_2 protons and increasing downfield δ(coord.) 0.20, 0.32 and 0.61 ppm for the β-, γ- and δ-CH_2 protons, respectively, is calculated (Table 1). The change in sign of δ(coord.) between the α- and β-CH_2 groups for compound **1** seems at first sight to be in qualitative agreement with Elschenbroich's estimate of the boundary between the shielding (+) and deshielding (−) region of the anisotropy cone of the benzene ring in bis(η^6-[10]paracyclophane)chromium [7]. For the latter the zero cone falls between the β- and γ-CH_2 groups. This might be attributed to conformational differences; in [8]paracyclophane (**2**), the β-CH_2 groups will be more tied back towards the central axis of the benzene ring, and so be located in the shielding region of the anisotropy cone. This is corroborated by a study made by Haigh and Mallion [14], who described a procedure for the determination of proton positions in the anisotropy cone of benzene. Although it was originally developed for planar benzene, we expect it to be applicable for [8]paracyclophane (**2**). It should be realized that the deviation from planarity of the benzene ring in compound **2** is small (X-ray, 9.1° [15], MNDO 15.7° [16], MM 12.5° [17] and 9.0° [18], respectively; cf. also ref. 19 for a similar analysis of a [6]paracyclophane derivative). Transformation of the cartesian coordinates of the bridge protons of compound **2**, taken from an optimized MNDO geometry, into cylindrical coordinates expressed in units of benzene ring radii (1.39 Å) shows that the α-CH_2 groups are positioned in the deshielding region and the β-, γ- and δ-CH_2 groups in the shielding region of the anisotropy cone (Fig. 1A). Despite quantitative differences between δ(exp.) and δ(calc.) a good linear correlation (correlation coefficient 0.995) is found for the α-, β-, γ- and δ-CH_2 groups (δ 1.52 ppm of cyclooctane as ref. 7, Fig. 1B). (It should be noted that the Haigh and Mallion procedure tends to underestimate the amount of shielding cq. deshielding.) Therefore, the increasing downfield δ(coord.) of the CH_2 groups closer to the central axis of the benzene ring of compound **2** could be interpreted as evidence for weakening of the aromatic ring current in compound **1** due to η^6-complexation.

However, the corresponding data obtained in C_6D_6 lead to a different conclusion. Upfield δ(coord.) shifts are calculated up to the γ-CH_2 group and only for the δ-CH_2 groups is a downfield δ(coord.) shift found (Table 1). We must conclude that apparently the difference in outcome is a consequence of the solvent dependence of the ^{1}H-NMR spectra of compounds **1** and **2**. For the latter it is nearly negligible for the aromatic, α-CH_2 and β-CH_2 protons. Both the γ-CH_2 and δ-CH_2 protons show a downfield shift, which may be explained by "face to face" interactions between the bent benzene ring of compound **2** and C_6D_6. In contrast, a substantial upfield shift is observed for all protons of compound **1** (Table 1, $\Delta\delta$(**1**) and $\Delta\delta$(**2**), respectively). Specific complexation due to favourable interactions between compound **1** and C_6D_6 seems unlikely since we found a linear relation between δ(coord.) and ratios $CDCl_3$:C_6D_6. Recently, an investigation of solvent effects on ^{1}H-NMR coordination chemical shifts of tricarbonyl(η^6-benzene)chromium and some of its alkylated derivatives was reported [20]. In keeping with our results, in C_6D_6 upfield shifts of δ(coord.) were found. The values of δ(coord.) decreased with progressive alkyl substitution of the benzene ring. These observations were rationalized by invoking two competitive types of specific solute–solvent interactions; "face to face" (Type A) and benzene oriented with its six-fold axis in the plane of the coordinated benzene ring (Type B, Fig. 2). In the case of progressive alkyl substitu-

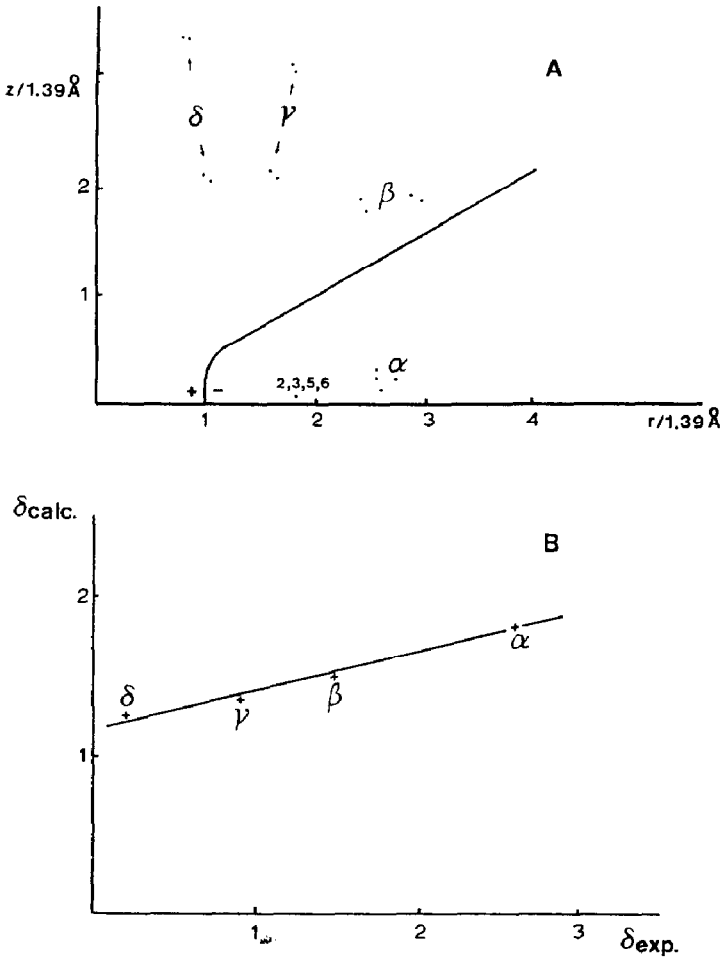

Fig. 1. Estimated positions of the bridge protons of [8]paracyclophane (**2**) in the shielding (+) and deshielding (−) region of the anisotropy cone of the benzene ring (A) and a comparison between δ(exp.) and δ(calc.) of these protons (B). δ(calc.) = 1.52 + Δδ; Δδ is obtained from the tables reported in ref. 14 with the use of the cylindrical coordinates of the bridge protons. δ 1.52 of cyclooctane is taken as reference [7].

tion, Type B interactions will be sterically inhibited, while Type A interactions will be less affected. For compound **1** Type A interactions are less probable owing to the presence of the oligomethylene bridge on one side of the aromatic ring. Thus, Type

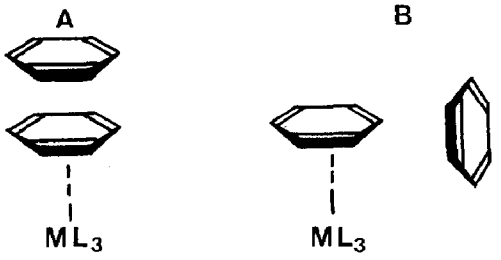

Fig. 2. Type A and Type B solute–solvent C_6D_6) interactions.

Table 2

^{13}C-NMR Data of compound **1** and **2** in $CDCl_3$ and C_6D_6, respectively

position [a]	**1**, $CDCl_3$		**1**, C_6D_6		**2** [b], $CDCl_3$	
	δ	$^1J_{(CH)}$	δ	$^1J_{(CH)}$	δ	$^1J_{(CH)}$
1,4	118.4	–	117.8	–	140.5	–
2,3,5,6	91.8	171.7	91.5	167.0	129.9	151.0
α-CH_2	33.6	131.9	33.3	132.6	35.8	125.7
β-CH_2	31.7	129.2	31.6	128.7	31.5	127.2
γ-CH_2	25.8	127.1	25.8	126.1	26.0	126.5
δ-CH_2	31.5	124.2	31.4	123.3	30.1	124.6
CO	233		235		–	

[a] Cf. Scheme 1. [b] Cf. ref. 13.

B interactions are expected to predominate, and this is consistent with the experimentally observed upfield shifts (Table 1; $\Delta\delta(1)$). The solvent dependence of δ(coord.) of tricarbonyl(η^6-[8]paracyclophane)chromium (**1**) obviously represents a limitation on the application of δ(coord.) as measure of the degree of quenching of the aromatic ring current. Opposite trends are found in different solvents, especially for the intermediate positions of the oligomethylene bridge.

We should point out that the scant data in the literature are in nearly quantitative agreement with our results in the sense that in C_6D_6, δ(coord.) is approximately -2.5 ppm for the aromatic protons and -0.65 ppm for the benzylic ones; the corresponding values in non-interacting solvents ($CDCl_3$, C_6D_{12}) are -1.8 ppm and -0.2 ppm [4,20,21].

Finally, we note that the observed solvent dependence of the ^{1}H-NMR δ(coord.) of tricarbonyl(η^6-[8]paracyclophane)chromium (**1**) is hardly discernable in the ^{13}C-NMR spectra (Table 2). This supports the view that the observed anomalies are not reflecting changes in the η^6-complex, such as charge distribution, but rather in solute–solvent interactions (*vide supra*). Although recently the ^{13}C chemical shifts in $CDCl_3$ of compound **1** were reported, the ^{13}C chemical shifts of the β- and δ-CH_2 groups were not assigned unambiguously and an incomplete set of ^1J(CH) coupling constants was presented [22]. Selective decoupling experiments led to the assignment shown in Table 2. The increase in ^1J(CH) of the aromatic C–H bonds upon η^6-complexation has been directly related to the coordination effect and rationalized in terms of an increase in *s*-character [23]. Remarkably, a small increase, of 6.2 Hz, for ^1J(CH) is found also for the α-CH_2 groups. If this is also caused by an increase in *s*-character, it indicates a decrease of the C–C(α)–C(β) valence angle. Unfortunately, an X-ray structure determination has not been carried out for compound **1**. However, a comparison of the C–C(α)–C(β) valence angle of [2,2]paracyclophane and its mono-η^6-tricarbonylchromium complex, for which X-ray structural data are available, confirm this interpretation (C–C(α)–C(β); [2,2]paracyclophane 113.7° [24] and tricarbonyl(η^6-[2,2]paracyclophane)chromium 110.9° [25]); see also ref. 26.

Conclusion

The strong solvent dependence of the ^{1}H-NMR coordination chemical shifts of tricarbonyl(η^6-[8]paracyclophane)chromium (**1**) limits their use in assessing the

degree of quenching of the aromatic ring current due to η^6-complexation. Erroneous conclusions may be reached if solute–solvent interactions are not taken into account; aromatic solvents may be particularly suspect in this regard.

Experimental

The ^{1}H-NMR spectra were recorded on a Bruker WH 90 spectrometer operating at 90 MHz with tetramethylsilane (TMS δ 0.00 ppm) as internal standard. The ^{13}C-NMR spectra were recorded on a Bruker WM 250 operating at 62.89 MHz with the solvent as internal standard.

Tricarbonyl(η^6-[8]paracyclophane)chromium (1)

A solution of [8]paracyclophane (**2**, 0.07 g, 0.37 mmol) [11,12], $Cr(CO)_6$ (0.09 g, 0.40 mmol) in a mixture of dry di-n-butylether (3 ml) and dry tetrahydrofuran (0.4 ml) was heated under reflux under nitrogen for 48 h, then cooled to room temperature. The solvents were evaporated off under reduced pressure and the residue was purified by column chromatography (Al_2O_3, eluent dry benzene) under nitrogen. Evaporation of the solvent gave compound **1** as yellow crystals (0.08 g, 25 mmol, 67%, m.p. 149 °C (decomposition) [4a]). For ^{1}H- and ^{13}C-NMR data see Tables 1 and 2.

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