Inorganica Chimica Acta, 219 (1994) 221–223

Note

^{1}H NMR analysis of some η^6-(substituted aryl phenylsulfonylacetonitrile)-η^5-cyclopentadienyliron cations

Alaa S. Abd-El-Aziz*, Paul Hazendonk, Christine R. de Denus and Harold M. Hutton
Department of Chemistry, University of Winnipeg, Winnipeg, Man., R3B 2E9 (Canada)

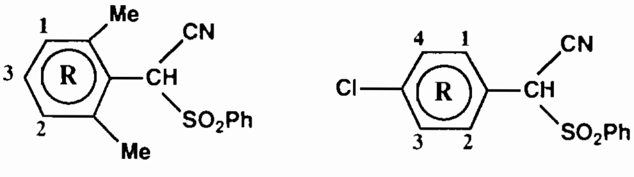
(Received October 26, 1993; revised January 14, 1994)

Abstract

A detailed ^{1}H NMR study of η^5-cyclopentadienyl-[η^6-(2,6-dimethylphenyl)phenylsulfonylacetonitrile]iron(II) and η^5-cyclopentadienyl-[η^6-(*p*-chlorophenyl)phenylsulfonylacetonitrile]iron(II) hexafluorophosphate salts (**Ia** and **IIa**) using difference nOe spectra and 2-D (COSY) techniques has shown that there is an enhanced restricted rotation about the arene–methine carbon bond with the formation of the complexes **Ia** and **IIa**.

Key words: Iron complexes; Arene complexes; Cyclopentadienyl complexes

Several NMR studies of η^6-arene-η^5-cyclopentadienyliron complexes including ^{1}H, ^{13}C and ^{19}F nuclei have been reported [1–5]. In this note we report the results of a detailed analysis of the ^{1}H NMR (Bruker 500 AMX spectrometer; chemical shifts were calculated from the solvent signals) spectra of the arene protons for η^5-cyclopentadienyl-[η^6-(2,6-dimethylphenyl)phenylsulfonylacetonitrile]iron(II) (**Ia**) and η^5-cyclopentadienyl-[η^6-(*p*-chlorophenyl)phenylsulfonylacetonitrile]iron(II) hexafluorophosphate salts (**IIa**) in comparison with their free arenes **Ib** and **IIb** (see Fig. 1). The synthesis of these compounds has already been reported [6].



Ia,b **IIa,b**

a: complex; R = CpFePF$_6$
b: uncomplexed arene

Fig. 1.

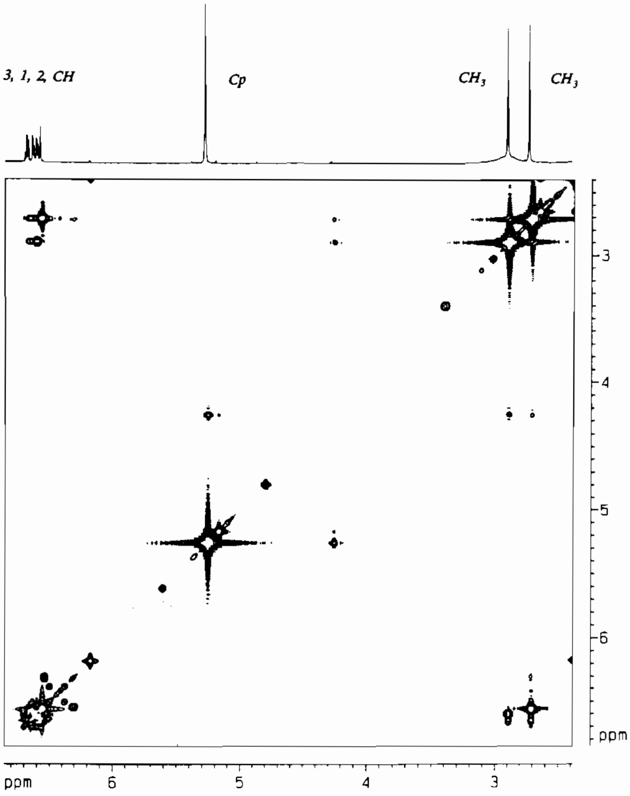


Fig. 2. The 1D and 2D COSY (optimized for long range coupling constants) ^{1}H NMR spectra of **Ia**.

The 1D and 2D NMR spectra of complexes **Ia** and **IIa** in acetone-d$_6$ are given in Figs. 2 and 3, respectively. The results of the ^{1}H NMR analyses of the arene protons of compounds **Ia**, **Ib**, **IIa** and **IIb** are given in Table 1. For both complexes there is a significant high field shift and a decrease in the coupling constants of the arene protons when the cyclopentadienyliron moiety is attached to the arene. The existence of long range coupling constants was determined from the 2D ^{1}H COSY and DQ-COSY experiments. The COSY and DQ-COSY of **Ia** (Fig. 2) and **Ib** show that there is a long range coupling between one of the arene methyl groups and the methine proton. For complex **IIa** (Fig. 3) and compound **IIb**, the methine proton interacts with both sides of the arene ring. There is an additional interaction between the methine and the *ortho* protons

---

*Author to whom correspondence should be addressed.

SSDI 0020-1693(94)03830-H

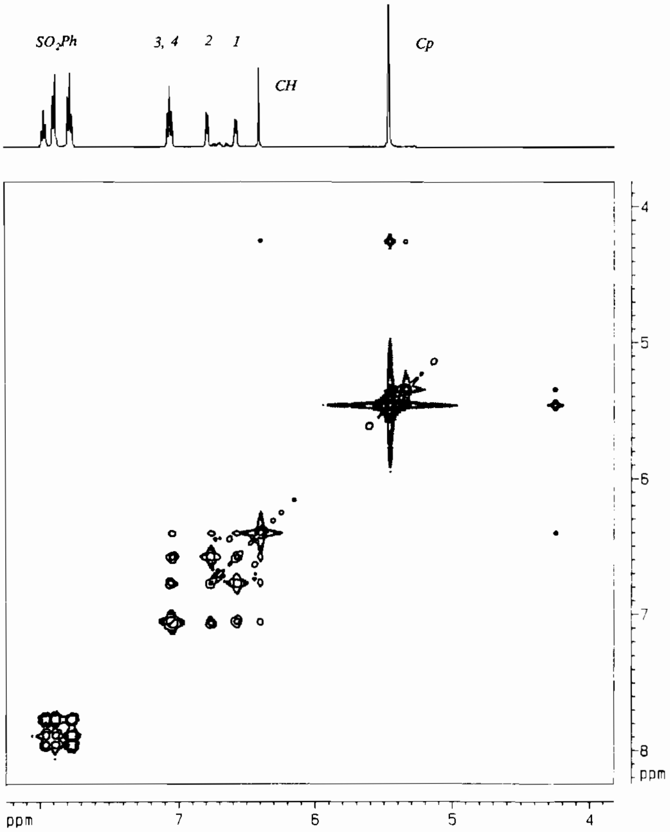


Fig. 3. The 1D and 2D COSY (optimized for long range coupling constants) ^{1}H NMR spectra of **IIa**.

of the phenylsulfonyl group of compound **IIb**, which indicates through space coupling.

A temperature study of the proton spectrum of compound **Ib** in DMSO-d$_6$ showed that there is restricted rotation about the arene–methine bond, resulting in the interchange of protons H(1) and H(2) as well as the two methyl groups. The spectrum of **Ia** in DMSO-d$_6$ resulted in broad lines and the temperature study was inconclusive, although we would expect a similar restricted rotation. The evidence of preferential coupling between the protons on one side of the arene ring and the methine proton, as observed with the COSY experiments, is consistent with this rotational barrier, resulting in a conformer where the methine interacts preferentially with one side of the arene ring [7]. The spectra of the arene protons of compound **IIb** between 20 and 60 °C indicate that there is no rotational barrier about the arene–methine bond. This is consistent with the COSY spectrum for **IIb** where the methine interacts with both *ortho* and *meta* protons and there is no preferential orientation.

The interactions between the methine proton and the arene ring, for compounds **Ia,b** and **IIa,b** were also studied by the proton difference nOe technique since it is a more sensitive measure for comparison of the magnitudes of interacting protons. The difference nOe spectra for **Ia** and **Ib**, with the methine proton saturated, are given in Figure 4. For both **Ia** and **Ib** the high field methyl has a larger nOe than that at lower field. Comparing the difference nOe integrals for **Ia** and **Ib** we find that the relative nOe values between the two methyl groups in compound **Ib** (9.3%:3.6%) and the complex **Ia** (8.8%:0.3%) both indicate that there is a preferential interaction between the methine proton and one of the *ortho* methyl groups. For the complex, with its larger molecular weight, the difference nOe due to the preferred interaction is reduced slightly but the nOe ratio between the two methyl resonances is significantly increased indicating that there is an increase in preferential orientation due to an increased rotational barrier. This effect decreases with an increase in temperature so it is a temperature dependent rate process.

For compound **IIb** the ortho protons have the same chemical shift and with equal interaction with the methine protons, the measured difference nOe (5.8%) would indicate a 2.9% contribution for each proton. In comparison, the *ortho* protons in complex **IIa** have different chemical shifts and the nOe integrals (2.6%: 1.0%) show preferential interaction when the cyclo-

TABLE 1. NMR analysis of the arene protons in compounds **Ia,b** and **IIa,b**

	Arene chemical shifts[a] (ppm from TMS, ±0.01)				Arene coupling constants[a] (Hz, ±0.05)					
	δ_1	δ_2	δ_3	CH$_3$	J_{12}		J_{13}		J_{23}	
Ia	6.63	6.60	6.68	2.91, 2.74	[b]		6.25		6.34	
Ib	7.19	7.16	7.28	2.66, 2.40	[b]		7.57		7.57	
	δ_1	δ_2	δ_3	δ_4	J_{12}	J_{13}	J_{14}	J_{23}	J_{24}	J_{34}
IIa	6.59	6.81	7.08	7.06	1.85	[b]	6.24	6.74	[b]	1.36
IIb	7.40	7.40	7.51	7.51	2.29	[b]	8.48	8.48	[b]	2.27

[a] Labelling as designated in Fig. 1. [b] Coupling constant <0.04 Hz.

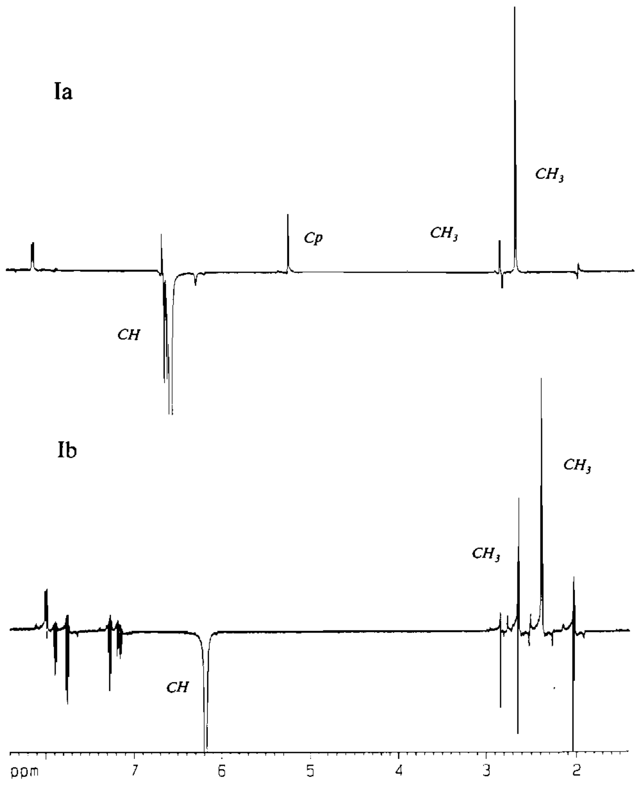


Fig. 4. The difference nOe spectra for **Ia** and **Ib** with irradiation of the methine proton.

pentadienyliron is complexed to the arene ring. In the determination of the nOe for **IIa** there was the possibility of some saturation transfer to the one *ortho* proton since its chemical shift is close to that of the methine which is being saturated. With a decrease in the saturation power the difference nOe values (0.7%, ~0%) qualitatively confirmed that there is a difference between these measured integrals, although the relative error is larger due to a decrease in the signal to noise of the spectrum.

From the results of the COSY and difference nOe experiments we conclude that the restricted rotation due to the *ortho* methyl substituents in **Ia,b** results in a preferred rotational conformer that interacts preferentially to one side of the arene ring. Complexation of the cyclopentadienyliron moiety to the arene ring **Ia**, **IIa** also affects the rotational motion, even for the *para* chloro complex **IIa** where there is no observable restricted rotation under the conditions used. If we compare those molecules where there is some hindrance to the rotational motion about the arene–methine carbon bond (**Ia**, **Ib**, **IIa**) the α-asymmetric carbon substituents affect the chemical shifts on either side of the arene differently at both the *ortho* and *meta* positions. With an insignificant rotational barrier (**IIb**) the effect of the α-asymmetric carbon on the chemical shifts is not observable.

Acknowledgements

Financial support by the Natural Science and Engineering Research Council of Canada and the University of Winnipeg is gratefully acknowledged.

References

1 I.U. Khand, P.L. Pauson and W.E. Watts, *J. Chem. Soc. C*, (1968) 2257.
2 I.U. Khand, P.L. Pauson and W.E. Watts, *J. Chem. Soc. C*, (1968) 2261.
3 A.N. Nesmeyanov, I.F. Leshchova, Y.A. Ustynyuk, Ye.I. Sirotkina, I.N. Bolesova, L.S. Isayeva and N.A. Vol'kenau, *J. Organomet. Chem.*, *22* (1970) 689.
4 A.A. Koridze, N.M. Astakhova and P.V. Petrovskii, *J. Organomet. Chem.*, *254* (1983) 345.
5 B.R. Steele, R.G. Sutherland and C.C. Lee, *J. Chem. Soc., Dalton Trans.*, (1981) 529.
6 A.S. Abd-El-Aziz and C.R. de Denus, *J. Chem. Soc., Perkin Trans. II*, (1993) 293.
7 T. Schaefer and R. Laatikainen, *Can. J. Chem.*, *61* (1983) 2785.