

Preliminary communication

NMR spectra of organometallic compounds: use of a lanthanide shift reagent

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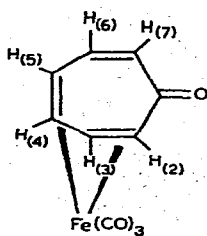
Paramagnetic lanthanide complexes have found wide application in NMR studies to date. We are not however aware of any reports concerning their use with organometallic compounds. We are currently investigating the potential of such complexes in this context and would like briefly to report preliminary work on certain compounds of iron.

Absorptions in the PMR spectra of the compounds (I)–(III) were assigned initially by spin decoupling experiments. Details are given in Table 1 for CDCl_3 solutions. Each solution was then saturated as far as possible with $\text{Eu}(\text{TMHD})_3^{2,*}$ and the spectra re-run. The relative chemical shift changes so observed (Δ_i = change in shift of i -th proton on complexing with $\text{Eu}(\text{TMHD})_3$ /smallest such shift observed for the molecule) are also quoted in Table 1. No concentrations were measured since our object was solely to investigate the suitability of the method for rapid routine application.

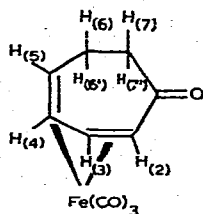
The magnitude of the shift changes observed for the carbonyl containing molecules (I) and (II) are small as might be expected, the carbonyl function being a relatively weak Lewis base generally. (Shifts of the same approximate magnitude were observed for tropone under the same conditions). For the hydroxyl containing compound (III) however larger shifts might have been expected, since other work with compounds having hydroxyl functions suggests relatively strong complexes are formed¹ with $\text{Eu}(\text{TMHD})_3$ leading to large shifts. The values observed here might well reflect steric inhibition to approach by the europium complex due to the presence of the iron tricarbonyl group, leading to weaker complexation with europium and correspondingly smaller shifts.

Nevertheless, the relative shifts observed clearly confirm the assignments obtained by spin decoupling, and in particular allow ready assignment of the site of methyl substitution at C(1) of (III). The method is of obvious value therefore in studies of organometallic compounds having sites of Lewis basicity. We propose to investigate the potential of the method further and determine if possible the mechanism by which the shifts are propagated, there is a possibility that contact effects may be transmitted through delocalised π -systems of this type in addition to the normally predominant pseudocontact shifts^{3–5}.

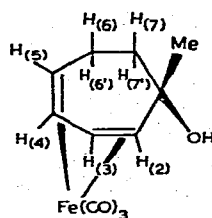
*TMHD = 2,2,6,6-tetramethylheptanedionato.



(I)



(II)



(III)

TABLE 1

Compound	Proton	δ^a	Δ^b
I	H(2)	3.13	4.6
	H(3)	6.37	1.3
	H(4)	6.37	1.3
	H(5)	2.73	1.0
	H(6)	6.56	1.3
	H(7)	5.03	4.3

(Max. shift change observed for H(2) = 27.5 cps)

II	H(2)	3.05	6.0
	H(3)	5.92	1.5
	H(4)	5.56	1.0
	H(5)	3.33	1.0
	H(6), H(6') ^c	2.63	1.5
	H(7), H(7') ^c	2.00	6.5

(Max. shift change observed for H(7), H(7') = 13.0 cps)

III	H(2)	2.87	2.7
	H(3)	5.29	1.1
	H(4)	5.29	1.1
	H(5)	3.13	1.0
	H(6), H(6') ^c	2.00	1.3
	H(7), H(7') ^c	1.26	2.0
	OH	1.67	16.4
	Me	1.31	2.7

(Max. shift change observed for -OH = 57.5 cps)

^a Spectra were recorded at 60.004 Mcps on a Perkin-Elmer R 10 spectrometer operating at 33.3°. Shifts were measured relative to internal TMS. Quoted values are in absence of shift reagent. ^b Δ is defined in the text. Addition of Eu(TMHD)₃ shifted resonances downfield of the normal resonance position in every case. ^c Shifts quoted for these complex patterns are approximate. Shift changes on addition of Eu(TMHD)₃ were however determined with about the same accuracy as for the other values quoted.

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