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Substituted cyclopentadienyl complexes

II *. ^{13}C NMR spectra of some [(η^5-C_5H_4Me)Fe(CO)(L)I] complexes

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Abstract

The $^{13}C\ \{^1H\}$ NMR spectra of a series of complexes [(η^5-C_5H_4Me)Fe(CO)(L)I] (L = t-BuNC, $P(OMe)_3$, PMe_3, PMe_2Ph, $PMePh_2$, PPh_3 and $P(C_6H_{11})_3$) have been recorded and the five cyclopentadienyl resonances assigned to ring carbon atoms by means of C–H correlated spectra. It has been observed that the C atoms *ortho* to the ring methyl group (C(2) and C(5)) as well as the quaternary C atom are always coupled to the ligand P atom. A correlation between the chemical shift difference Δ(C(2) – C(5)) and the Tolman cone angle, θ, has also been established.

Introduction

Recently we reported on the synthesis and proton NMR spectra of a series of [(η^5-C_5H_4Me)Fe(CO)(L)I] (**1**) complexes [1] and observed a correlation of the chemical shift difference between the protons *ortho* to the methyl ring substituent and the Tolman cone angle, θ, [2] of the ligand L. NMR studies on cyclopentadienylmetal complexes, e.g. substituted ferrocene derivatives, have indicated that a correlation also exists between ^{13}C and ^{1}H ring resonances [3]. This suggested to us that a similar correlation might exist between the ^{13}C chemical shifts and Tolman cone angle, θ, for complexes **1**. We also wished to establish whether information on the conformations of the ligand set relative to the cyclopentadiene ring could be obtained from the ^{13}C spectral data. Herein we report on our measurement and interpretation of the ^{13}C spectra of our complexes.

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Table 1

$^{13}C\ \{^1H\}$ NMR data for $[(\eta^5\text{-}C_5H_4Me)Fe(CO)(L)I]$ [a] complexes

L	Cyclopentadienyl ring [b,c]						Δ(C(2)−C(5))	Δ(C(3)−C(4))	(C(2)+C(5))/2	C(3)+C(4))/2	θ [d] (°)
	Me	C(1)	C(2)	C(3)	C(4)	C(5)					
CO	13.41	102.55	84.61	81.92	81.92	84.61	0	0	84.61	81.92	–
t-BuNC [f]	13.92	98.86	83.57	81.35	79.70	80.97	2.6	1.7	82.17	80.50	68 [e]
$P(OMe)_3$ [g]	13.84	98.55(2.6)	86.03(2.5)	82.16(0.2)	78.07	80.82(1.9)	5.2	4.1	83.42	80.10	107
PMe_3 [h]	14.32	94.17(2.5)	86.29(1.7)	79.00	77.14	79.57(1.5)	6.9	1.9	83.02	77.99	118
PMe_2Ph [i]	13.91	97.07	86.26(1.8)	81.85	78.16	80.75(1.9)	5.5	3.7	83.51	80.00	122
$PMePh_2$ [j]	13.82	97.70(2.8)	87.23(1.6)	82.65	78.03	79.84(1.5)	7.4	4.6	83.54	80.33	136
PPh_3	14.05	98.58(2.4)	88.88(1.8)	83.88	79.04	78.34(1.2)	10.5	4.8	83.61	81.46	145
$P(C_6H_{11})_3$ [k]	13.72	94.30(2.3)	88.70(2.0)	81.43	76.39(0.5)	75.55(0.8)	13.2	5.0	82.15	78.89	170

[a] Spectra recorded in C_6D_6. [b] δ in ppm relative to C_6D_6: J(P–C) in Hz. [c] Ring positions indicated in Fig. 1. [d] Tolman cone angle, θ; ref. 2. [e] Fan angle; ref. 9. [f] $(\mathit{C}H_3)_3CNC$ 30.42; $(CH_3)_3\mathit{C}NC$ 5.8; $(CH_3)_3CN\mathit{C}$, 201.67 ppm. [g] $P(O\mathit{C}H_3)_3$ 53.42(5.2) ppm. [h] $P(\mathit{C}H_3)_3$ 20.31(31.0) ppm. [i] $P(\mathit{C}H_3)_2Ph$ 19.56(34.7), 19.00(29.7) ppm. [j] PCH_3Ph_2 21.20(34.0) ppm. [k] $P(C_6H_{11})_3$ 39.33(17.5), 30.85(15.4), 28.01(9.4), 26.79 ppm.

Experimental

All compounds were prepared as reported previously [1]. NMR spectra were recorded on a Bruker AC 200 NMR spectrometer. C–H correlated spectra were obtained by routine procedures [4].

Results and discussion

The starting material $[(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Fe(CO)}_2\text{I}]$ used in this study contains an achiral Fe atom, and consequently three resonances are associated with the ring carbon atoms in the ^{13}C NMR spectrum (C(2) and C(5) as well as C(3) and C(4) are equivalent, Fig. 1). The signal from the quaternary carbon atom C(1) carrying the methyl substituent is readily assigned from its downfield position (102.55 ppm) and its weak intensity [5]. The resonance at 84.61 ppm (Table 1) is assigned to C(2) (and C(5)) since the C ring atoms *ortho* to C(1), which carry an electron-donating group, appears downfield of the C ring atoms *meta* to C(1) [6] (also see below).

$[(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Fe(CO)}_2\text{I}]$ can be made chiral by either replacing the Me group by a chiral group [7] or replacing a CO group by another ligand. In both instances all five ring C atoms become non-equivalent and this is confirmed by the ^{13}C data for the chiral complexes $[(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Fe(CO)(L)I}]$ (L = t-BuNC, P(OMe)_3, PMe_3, PMe_2Ph, PMePh_2, PPh_3, $\text{P(C}_6\text{H}_{11})_3$) given in Table 1.

Although the C(1) resonance is readily identified from its chemical shift and weak intensity, identification of the resonances C(2)–C(5) is non-trivial. However, since the ring proton resonances have already been assigned from NOE difference spectra [1], C–H correlated (XHCORR) spectra were used to assign the ^{13}C ring resonances. An example, for L = PMePh_2, is shown in Fig. 2.

From the data listed in Table 1 the following generalisations can be made:

(*i*) C(2) is always downfield and coupled to the PR_3 ligand [8]. Presumably this criterion can be used for assigning ^{13}C spectra of other complexes of **1**.

(*ii*) C(5) has a variable position but is always coupled to PR_3 although the J(P–C) coupling is more variable than observed for C(2).

(*iii*) The average position of the *ortho* ring atoms (C(2) + C(5)) is downfield from the averaged positions of the *meta* (C(3) + C(4)) ring atoms. This is consistent with results obtained for achiral systems [6].

(*iv*) No trends are discernible which relate either the positions or J(P–C) coupling of C(3) and C(4) to ligand cone angles.

(*v*) The C ring methyl resonance is hardly affected by variations of L.

Assignment of the ring carbon resonances allows for the determination of Δ(C(2) − C(5)) and Δ(C(3) − C(4)) (Table 1). It is clear that Δ(C(2) − C(5)) varies

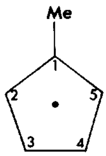

Fig. 1. Labelling scheme for the ring carbon atoms.

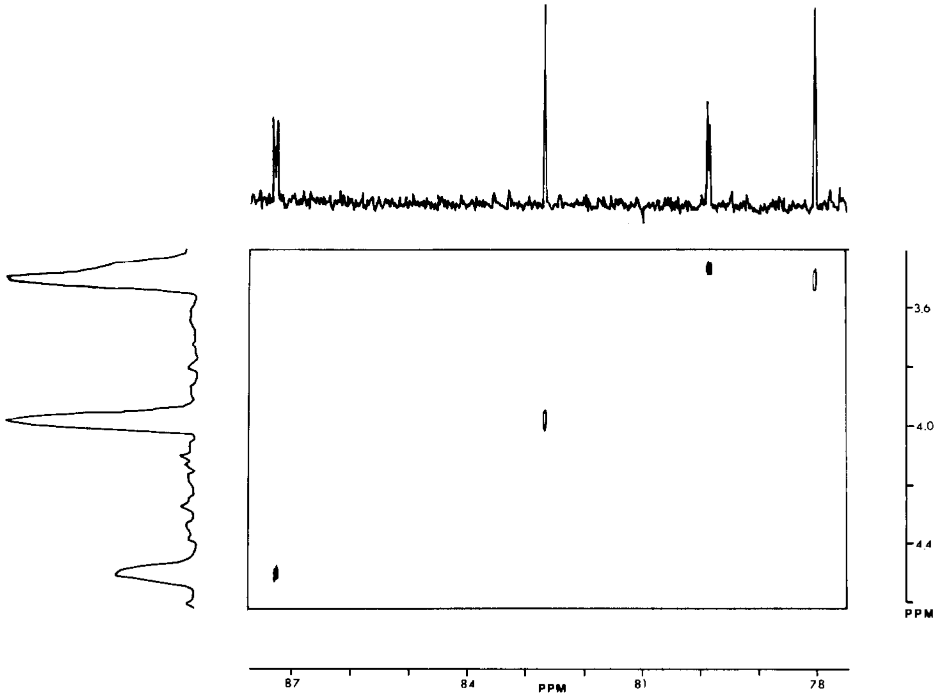

Fig. 2. C–H correlated spectrum for $[(\eta^5\text{-}C_5H_4Me)Fe(CO)(PMePh_2)I]$.

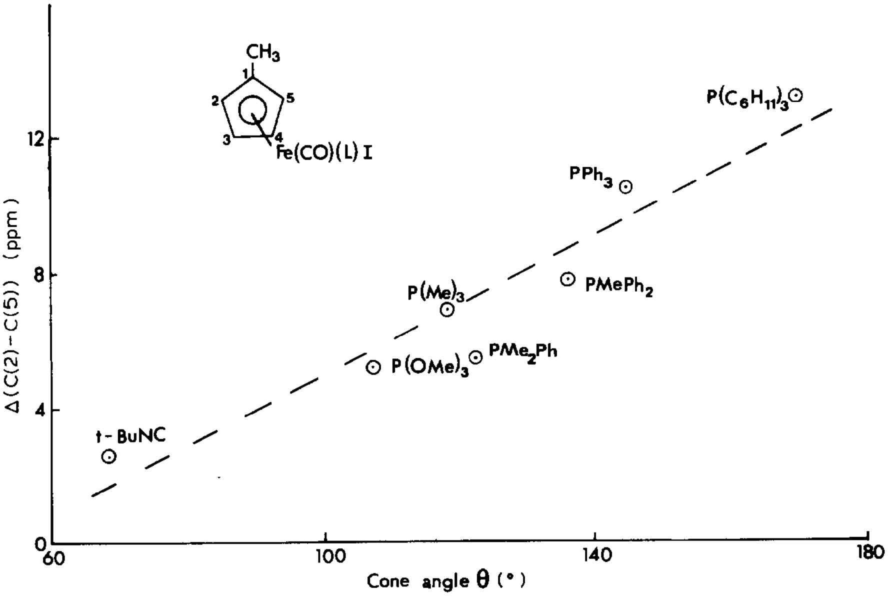

Fig. 3. Plot of Tolman cone angle, θ, against $\Delta(C(2)-C(5))$ for the $[(\eta^5\text{-}C_5H_4Me)Fe(CO)(L)I]$ complexes

with the isocyanide fan angle [9] or Tolman cone angle, θ, [2] (Fig. 3), and that $\Delta(C(2) - C(5)) > \Delta(C(3) - C(4))$. Similar observations were made for the ring proton resonances and presumably the same factors are responsible for both observations.

Originally we had thought that the observation of a larger ^{31}P coupling to H(3) and H(4) (than to H(2) and H(5)) implied restricted rotation of the ligand set relative to the ring [1]. However the $^{13}C-^{31}P$ coupling data show coupling only to C(1), C(2) and C(5). It is noteworthy that $^{13}C-^{31}P$ coupling has been observed for the quarternary ring atom in $[(i\text{-}PrC_5H_4)Rh(PPh_3)I_2]$, and that this coupling was suggested to arise from the ring acting as an allyl-ene ligand [10]. Although the same situation may occur in our complexes we have no physical data to support this proposal. The resolution of this problem must await structural data, and consequently our ^{13}C NMR results at present give no conformational information.

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