

# NMR parameters as steric probes for arylcyclopentadienyl iron complexes

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## Abstract

The complexes  $[(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Fe}(\text{CO})(\text{L})\text{I}]$  ( $\text{L} = \text{PPh}_3, \text{P}(p\text{-C}_6\text{H}_4\text{Me})_3, \text{P}(p\text{-C}_6\text{H}_4\text{F})_3$ ) have been synthesised and characterised by IR and NMR spectroscopy. The difference in chemical shift separation between the cyclopentadienyl ring proton resonances flanking the methyl substituents,  $\Delta(\text{H}2\text{-H}5)$ , was found to be invariant with change in the *para* phosphine ligand substituent, suggesting that the measure is relatively free of electronic influences. A series of aryl substituted cyclopentadienyl complexes,  $[(\eta^5\text{-C}_5\text{H}_4\text{Ar})\text{Fe}(\text{CO})(\text{L})\text{I}]$  ( $\text{Ar} = \text{Ph}, p\text{-C}_6\text{H}_4\text{Me}, p\text{-C}_6\text{H}_4\text{tBu}, \text{L} = \text{P}(\text{OMe})_3, \text{PMe}_2\text{Ph}, \text{P}(\text{O}^i\text{Pr})_3, \text{P}(\text{O}-o\text{-tol})_3, \text{PPh}_3, \text{P}(\text{CH}_2\text{Ph})_3$ ) was also synthesised and characterised by IR and NMR spectroscopy. Again the parameter  $\Delta(\text{H}2\text{-H}5)$  was found to be invariant with change in the substituent on the cyclopentadienyl ring, suggesting that changes at a distance do not influence this steric measure. NOE different spectra recorded on  $[(\eta^5\text{-C}_5\text{H}_4\text{-}p\text{-C}_6\text{H}_4\text{Me})\text{Fe}(\text{CO})(\text{L})\text{I}]$  ( $\text{L} = \text{P}(\text{OMe})_3, \text{P}(\text{O}^i\text{Pr})_3$ ) indicate that the substituted cyclopentadienyl ring rotates freely about the Fe-ring centroid axis relative to the ligand set. NOE spectral data for  $\text{L} = \text{P}(\text{OMe})_3$  also reveal that the *p*-tolyl and  $\text{P}(\text{OMe})_3$  protons are close enough in space to give rise to a positive nuclear Overhauser effect. The relative size of the aryl ring is shown, by NMR spectroscopy, to lie between that of a methyl and a tert-butyl group.

**Key words** Iron complexes, Aryl complexes, Cyclopentadienyl complexes

## Introduction

Nuclear magnetic resonance spectroscopy provides one measure of assessing the steric demand of a cyclopentadienyl substituent [1]. In particular, earlier studies from our group on complexes of the type  $[(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Fe}(\text{CO})(\text{L})\text{I}]$  ( $\text{R} = \text{Me}, \text{tBu}; \text{L} = \text{phosphine, phosphite, isonitrile}$ ) have shown that  $\Delta(\text{H}2\text{-H}5)$ , the chemical shift separation of the cyclopentadienyl proton resonances on either side of the substituent R (the so-called 'ortho' resonances), not only varied proportionally with the size of the ligand L [2, 3], but was also influenced by the Me or tBu substituent on the ring. This relationship was studied in depth using a wide range of organometallic complexes in which L was kept constant and R was varied [1]. Clear evidence for the influence of the size of R on the chemical shift separation of the ortho cyclopentadienyl resonances was presented. However, a question arises as to the influence of electronic effects on the NMR parameter.

In order to investigate the electronic effect, a series of substituted cyclopentadienyl iron complexes,  $[(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Fe}(\text{CO})(\text{PAR}_3)\text{I}]$  ( $\text{Ar} = \text{Ph}, p\text{-C}_6\text{H}_4\text{F}, p\text{-C}_6\text{H}_4\text{Me}$ ), which contain substituents in the *para* positions of the phenyl rings attached to the phosphorus atom, was chosen for study. The substituents differ in electronic effect, but the steric effect of the *para* substituted ligands from the vantage point of the iron should be invariant. This steric effect can be measured by means of a Tolman cone angle  $\theta$  [4], (Fig. 1(a)) or a solid angle  $\Omega$  [5], (Fig. 1(b)). Although cone angles are the standard measure of size in organometallic chemistry, we have recently described some of the advantages in the use of solid angles as an alternative measure. The solid angle is the area of shadow cast when the ligand is projected from the apex onto the inside of a unit sphere. Details of the actual measurement of solid angles can be found elsewhere [5]. The differences in steric effect associated with the different *para* substituents on the phosphine ligand or the cyclopentadienyl ring aryl substituent can be differentiated using the solid angle approach.

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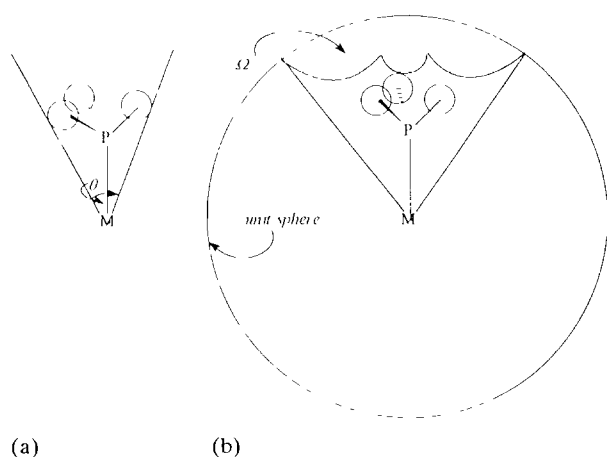


Fig. 1. Illustration of the difference between the cone angle,  $\theta$  and the solid angle  $\Omega$ . The maximum solid angle (i.e. when the ligand covers the unit sphere entirely) is  $4\pi$  steradians. To obtain the fraction of space occupied by the ligand,  $\Omega_s$ , the observed solid angle,  $\Omega$ , is divided by  $4\pi$ ,  $\Omega_s = \Omega/4\pi$ .

With the use of solid angles, the size of a ligand can be measured at any point along the ligand. This generates a radial profile, which is a graph of the variation of solid angle with distance along the ligand. The radial profile for a hypothetical  $PR_3$  ligand is shown in Fig. 2. For comparison, an example of a ligand profile, which is generated by rotation about the M–P bond, is shown in the same Figure. The radial profile provides a visual representation of the steric interaction between any two ligands attached to a common apex.

To investigate the sensitivity of the NMR measure with respect to distance, a series of aryl substituted cyclopentadienyl complexes,  $[(\eta^5-C_5H_4Ar)Fe(CO)(L)I]$  ( $Ar = Ph, p-C_6H_4Me, p-C_6H_4^tBu$ ;  $L = P(OMe)_3, PMe_2Ph, P(O^iPr)_3, p(O-o-tol)_3, PPh_3, P(CH_2Ph)_3$ ) was chosen for study. Each of the complexes was characterised and studied by IR and NMR spectroscopy to evaluate both steric and electronic effects associated with the Ar group. Substituents in the *para* position on the aryl ring attached to the cyclopentadienyl ring should have almost no steric effect from the perspective of the ring centroid (i.e.  $\theta_1$ , invariant; Fig. 3). From the perspective of the metal, subtleties in *para* substituents may be detected (i.e.  $\theta_2$ , Fig. 3) as mentioned above.

## Results and discussion

### Synthesis

The synthesis of complexes of the type  $[(\eta^5-C_5H_4R)Fe(CO)(L)I]$  ( $R = \text{alkyl}$ ,  $L = \text{phosphine, phosphite, isonitrile}$ ) is well documented [6]. For  $R = \text{aryl}$ , by contrast, only  $[(\eta^5-C_5H_4Ph)Fe(CO)_2]_2$ ,  $[(\eta^5-C_5H_4Ph)Fe(CO)_2I]$  and  $[(\eta^5-C_5H_4Ph)Fe(CO)\{P(OMe)_3\}I]$  have been prepared previously [7].

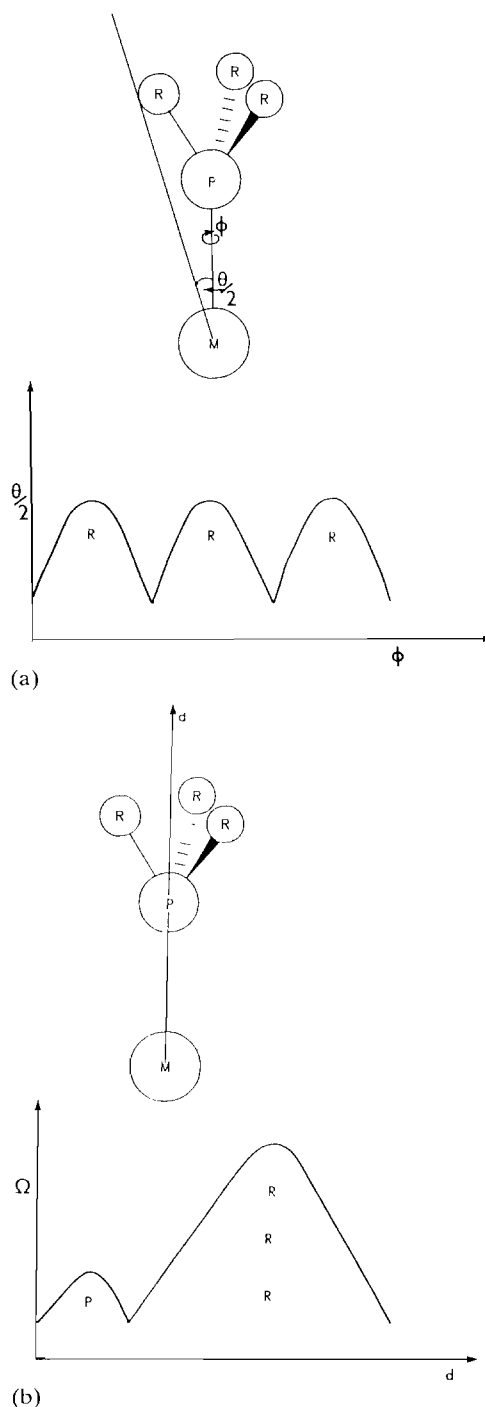


Fig 2 Schematic representation of the differences between (a) the ligand profile and (b) the radial profile for a hypothetical  $PR_3$  ligand

Two general strategies for the synthesis of substituted cyclopentadienyl metal complexes can be employed. These are: (i) modification of the ring followed by attachment to the metal or (ii) modification of the ring already attached to an organometallic system [6]. Both strategies have been described in the literature for the synthesis of aryl substituted cyclopentadienyl rings [8]

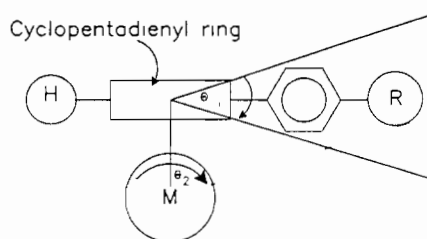
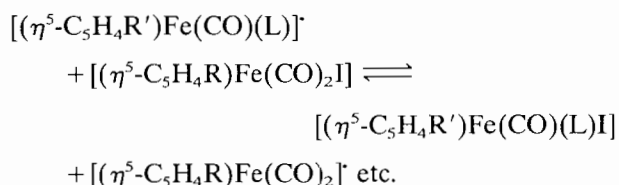
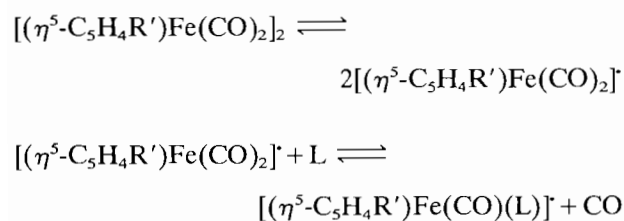


Fig. 3. Possible measures of steric size of a monosubstituted cyclopentadienyl ring (centroid and metal as apex of right circular cones).

In the present study, two variants of method (i) were employed for the synthesis of arylcyclopentadienes. The coupling reaction between iodobenzene and  $[(\eta^5\text{-C}_5\text{H}_5)\text{CuPBu}_3]$  was found to give poor yields of ligand, possibly owing to the extreme air sensitivity of the copper(I) species. A Grignard approach employing  $\text{ArMgBr}$  and cyclopent-2-en-1-one was thus attempted, and was found to give the required ligand in variable yield. A limitation of the Grignard approach is that it cannot be used for electron-withdrawing substituents on the arene ring. To test the generality of this methodology, a number of arylcyclopentadienes,  $\text{C}_5\text{H}_5\text{Ar}$  ( $\text{Ar} = \text{C}_6\text{H}_5$ ,  $p\text{-C}_6\text{H}_4\text{Me}$ ,  $o\text{-C}_6\text{H}_4\text{Me}$ ,  $p\text{-C}_6\text{H}_4^t\text{Bu}$ ,  $p\text{-C}_6\text{H}_4\text{OMe}$ ,  $\text{C}_6\text{H}_2\text{Me}_3$ ,  $\alpha\text{-naphthyl}$ ) was prepared. Only the  $p\text{-C}_6\text{H}_4\text{Me}$  and  $p\text{-C}_6\text{H}_4^t\text{Bu}$  cyclopentadienes were converted into the metal complex for this study, however, as these *para* substituents gave the same steric size as measured from the cyclopentadienyl ring centroid.

All iron complexes containing the arylcyclopentadienyl ligand were prepared by procedures well established in the literature [6]. The general synthetic strategy employed included formation of the diene by means of the Grignard reaction and elimination of water, reaction of the diene with either  $\text{Fe}(\text{CO})_5$  or  $\text{Fe}_2(\text{CO})_9$ , and cleavage of the resultant metal dimer with elemental iodine to give  $[(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Fe}(\text{CO})_2\text{I}]$ .

Thermal, photochemical and catalytic methods are known to induce replacement of CO in  $[(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Fe}(\text{CO})_2\text{I}]$  complexes by P-donor ligands [6]. In this study, dimers of the type  $[(\eta^5\text{-C}_5\text{H}_4\text{R}')\text{Fe}(\text{CO})_2]_2$ , used extensively by our research group, were used to catalyse some of the substitution reactions. The mechanism of the dimer-catalysed CO substitution reaction is still not known with certainty [9–11]. One possibility is shown below:



The free radical reaction suggests that  $[(\eta^5\text{-C}_5\text{H}_4\text{R}')\text{Fe}(\text{CO})(\text{L})\text{I}]$  as well as the expected  $[(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Fe}(\text{CO})(\text{L})\text{I}]$  should be formed. Both compounds were usually detected in the NMR spectra of the crude products for most reactions studied.

Electron-donating R groups are expected to slow down the substitution reaction by increasing the strength of the metal–carbonyl bond. The combination of an electron-donating R group and a highly nucleophilic ligand L can result in preferential metal–iodine bond cleavage under the reaction conditions. For example, strongly nucleophilic ligands like  $\text{PMe}_2\text{Ph}$  were found in this study to displace iodide from the metal in preference to the carbonyl group to yield salts,  $[(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Fe}(\text{CO})_2(\text{L})\text{I}]\text{I}$ . These salts were readily identified by NMR and IR spectroscopy, and by their insolubility in benzene and ready solubility in chloroform or dichloromethane. Conversion of the salts into the desired neutral complexes was achieved by reaction with trimethylamine *N*-oxide ( $\text{Me}_3\text{NO}$ ) [12].

#### Characterisation of the products

Selected spectroscopic and physical data for the compounds prepared in this study are given in Tables 1–4 and 7. The IR spectra of all the iron cyclopentadienyl complexes,  $[(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Fe}(\text{CO})_2]_2$ ,  $[(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Fe}(\text{CO})_2\text{I}]$  and  $[(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Fe}(\text{CO})(\text{L})\text{I}]$ , studied in this work revealed the expected number of  $\nu(\text{CO})$  absorption bands, the positions of which were influenced by both L and R groups. For  $[(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Fe}(\text{CO})(\text{L})\text{I}]$ , for example,  $\nu(\text{CO})$  varied by up to  $21.5\text{ cm}^{-1}$  for a constant R but variable L ( $\text{P}(O\text{-}o\text{-tol})_3$  versus  $\text{P}(O^i\text{Pr})_3$ , Table 1). However, the difference between  $\nu(\text{CO})$  values on keeping L constant and varying R from phenyl to *p*-tolyl was only  $1.1\text{ cm}^{-1}$ . Clearly the electron transfer effect is far greater for the L group than the R group for the complexes investigated.

As predicted, the dimers  $[(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Fe}(\text{CO})_2]_2$  and the unsubstituted iodo derivatives  $[(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Fe}(\text{CO})_2\text{I}]$  revealed only two closely spaced resonances for ring protons in the  $^1\text{H}$  NMR spectrum (Table 2). Up to four magnetically non-equivalent ring protons were detected in the  $^1\text{H}$  NMR spectra of  $[(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Fe}(\text{CO})(\text{L})\text{I}]$ . The NMR spectra of all complexes showed the characteristic number, chemical shift and intensity of peaks for the ligand, the ring and the substituent on the ring (Tables 2 and 3). NOE spectra were used

TABLE 1.  $\Omega_5$ ,  $\Delta(\text{H2-H5})$  (in ppm) and IR (in  $\text{cm}^{-1}$ ) data for  $[(\eta^5\text{-C}_5\text{H}_4\text{Ar})\text{Fe}(\text{CO})(\text{L})\text{I}]$  complexes<sup>a</sup>

Ar	L	$\Omega_5^b$	$\Delta(\text{H2-H5})$	$\nu(\text{CO})$
Ph	P(O- <i>o</i> -tol) <sub>3</sub>			1978.7
Ph	P(CH <sub>2</sub> Ph) <sub>3</sub>			1949.8
<i>p</i> -C <sub>6</sub> H <sub>4</sub> Me	P(OMe) <sub>3</sub>	0.225	0.66	1963.1
<i>p</i> -C <sub>6</sub> H <sub>4</sub> Me	PMe <sub>2</sub> Ph	0.274	0.52	1944.8
<i>p</i> -C <sub>6</sub> H <sub>4</sub> Me	P(O <sup><i>i</i></sup> Pr) <sub>3</sub>	0.319	0.80	1956.1
<i>p</i> -C <sub>6</sub> H <sub>4</sub> Me	P(O- <i>o</i> -tol) <sub>3</sub>	0.357	1.77	1977.6
<i>p</i> -C <sub>6</sub> H <sub>4</sub> Me	PPh <sub>3</sub>	0.286	1.37	1951.5
<i>p</i> -C <sub>6</sub> H <sub>4</sub> Me	P(CH <sub>2</sub> Ph) <sub>3</sub>	0.428	2.66	1948.7
Ph	CO			2034.2,
				1993.2
<i>p</i> -C <sub>6</sub> H <sub>4</sub> Me	CO			2032.0,
				1992.1

<sup>a</sup>Recorded in CH<sub>2</sub>Cl<sub>2</sub>. <sup>b</sup>Data refer to the Group 15 donor ligands, from ref 13

to assign the ring protons to the specific NMR resonances [2].

### NOE conformational analysis

NOE difference spectra were recorded on the  $[(\eta^5\text{-C}_5\text{H}_4\text{-}p\text{-C}_6\text{H}_5\text{Me})\text{Fe}(\text{CO})(\text{L})\text{I}]$  (L = P(OMe)<sub>3</sub> and P(O<sup>*i*</sup>Pr)<sub>3</sub>) complexes. As previously reported [14, 15], these spectra, together with appropriate CH correlated spectra, also facilitate the assignment of all peaks in all spectra of the relevant derivatives. Figure 4 shows the numbering scheme used in the analysis. By way of example, NOE spectra for  $[(\eta^5\text{-C}_5\text{H}_4\text{-}p\text{-C}_6\text{H}_5\text{Me})\text{Fe}(\text{CO})\{\text{P}(\text{OMe})_3\}\text{I}]$  are shown in Fig. 5. The assignment of the aromatic resonances was done by irradiating the resonance at 2.06 ppm (methyl group attached to po-

sition 8), which caused growth in the resonance at 6.95 ppm only (11%; Fig. 5(b)). Thus the resonance at 6.95 ppm can be assigned to positions 7 and 9. Irradiation of the peak at 6.95 ppm caused growth of the resonance at 7.38 ppm (16%, positions 6 and 10; Fig. 5(c)), and irradiation of the resonance at 7.38 ppm caused growth in the peak at 6.95 ppm (18.4%, positions 7 and 9; Fig. 5(d)).

Irradiation of the resonance at 7.38 ppm (Fig. 5(d)) also caused growth in resonances at 5.15 (20.5%) and 4.49 (18.4%) ppm, and hence permitted the assignment of the cyclopentadienyl ring protons 2 and 5 to these positions. The assignment of position 2 was verified by irradiation of the resonance in position 4, which showed growth for positions 5 (1.6%) and 3 (1.3%) but not 2 (Fig. 5(e)). This was further confirmed by independent irradiation of the other cyclopentadienyl ring resonances (Fig. 5(e)–(g)).

Free rotation of the substituted cyclopentadienyl ring about the ligand set was verified by irradiation of the protons in position 11 (P(OMe)<sub>3</sub> protons), which showed growth in all four cyclopentadienyl ring proton resonances (Fig. 5(h)). Most significant growth occurred in positions 3 and 5 (2.6%) and 4 (3.6%) rather than 2 (1.8%), suggesting the ligand is preferentially located on the side of the cyclopentadienyl ring away from the aryl group (Fig. 6). Of interest is the observation that irradiation of the P(OMe)<sub>3</sub> protons resulted in growth of *all* aryl ring protons. As expected, the effect was more pronounced for resonances corresponding to positions 6 and 10 than to positions 7 and 9 (Fig. 5(h)). The growth in the signal corresponding to position 8 (0.4%) was unexpected, but suggests that the aryl group

TABLE 2. <sup>1</sup>H NMR chemical shifts (in ppm) and coupling constants (in Hz) for  $[(\eta^5\text{-C}_5\text{H}_4\text{Ar})\text{Fe}(\text{CO})(\text{L})\text{I}]$  complexes<sup>a</sup>

Ar	L	H2	H3	H4	H5	<i>o</i> -Ar <sup>b</sup>	<i>m</i> -Ar <sup>b</sup>	CH <sub>3</sub>	L <sup>c</sup>	<sup>1</sup> J(H,H) <sup>d</sup>	<sup>3</sup> J(H,H) <sup>e</sup>	J(H,P)
Ph	P(O- <i>o</i> -tol) <sub>3</sub>	5.31	4.76	4.15	3.60	7.69	7.03		2.24, Me	7.94		
Ph	P(CH <sub>2</sub> Ph) <sub>3</sub>	5.26	4.55	3.30	2.49	7.47	7.16					
<i>p</i> -C <sub>6</sub> H <sub>4</sub> Me	P(OMe) <sub>3</sub>	5.15	4.53	4.38	4.49	7.38	6.95	2.06	3.36, Me	8.18	7.96	11.1 <sup>f</sup>
<i>p</i> -C <sub>6</sub> H <sub>4</sub> Me	PMe <sub>2</sub> Ph	4.61	4.25	4.23	4.09		6.88	2.08	1.41, Me		7.98	9.44
									1.63, Me			<sup>g</sup>
<i>p</i> -C <sub>6</sub> H <sub>4</sub> Me	P(O <sup><i>i</i></sup> Pr) <sub>3</sub>	5.23	4.91	4.53	4.43	7.47	7.06	2.16	1.17, Me	8.18	7.94	8.87 <sup>f</sup>
									4.84, CH			
<i>p</i> -C <sub>6</sub> H <sub>4</sub> Me	P(O- <i>o</i> -tol) <sub>3</sub>	5.33	4.79	4.16	3.56	7.72	7.11	2.04	2.24, Me	7.35		
<i>p</i> -C <sub>6</sub> H <sub>4</sub> Me	PPh <sub>3</sub>	5.26	4.55	4.02	3.91	7.40		2.08		8.13		
<i>p</i> -C <sub>6</sub> H <sub>4</sub> Me	P(CH <sub>2</sub> Ph) <sub>3</sub>	5.27	4.58	3.25	2.61			2.05				
<i>p</i> -C <sub>6</sub> H <sub>4</sub> Me	CO	4.62	4.27	4.62	4.27			2.13				
<i>p</i> -C <sub>6</sub> H <sub>4</sub> Me	dimer <sup>h</sup>	4.78	4.20	4.20	4.78	7.32	6.95	2.05				
<i>p</i> -C <sub>6</sub> H <sub>4</sub> <sup>1</sup> Bu	P(O- <i>o</i> -tol) <sub>3</sub>	5.35	4.74	4.18	3.66			1.17	2.23, Me			
<i>p</i> -C <sub>6</sub> H <sub>4</sub> <sup>1</sup> Bu	PPh <sub>3</sub>	5.22	4.54	4.11	4.00	7.31	6.96	1.15				
<i>p</i> -C <sub>6</sub> H <sub>4</sub> <sup>1</sup> Bu	CO	4.6	4.2	4.2	4.6	4.9	6.2	1.3				

<sup>a</sup>Recorded from C<sub>6</sub>D<sub>6</sub> solution at 22 °C,  $\delta$  in ppm relative to TMS. <sup>b</sup>Aromatic resonances of the ring substituent, *o* and *m* relative to the cyclopentadienyl ring. <sup>c</sup>Aromatic resonances of the ligand not recorded. <sup>d</sup>Coupling constant <sup>1</sup>J(H,H) refers to the *ortho*-tolyl resonances (relative to the cyclopentadienyl ring), measured in Hz. <sup>e</sup>Coupling constant <sup>3</sup>J(H,H) refers to the *meta*-tolyl resonances (relative to the cyclopentadienyl ring), measured in Hz. <sup>f</sup><sup>3</sup>J(H,P) <sup>g</sup><sup>2</sup>J(H,P) <sup>h</sup> $[(\eta^5\text{-C}_5\text{H}_4\text{Ar})\text{Fe}(\text{CO})_2]$

TABLE 3  $^{13}\text{C}$  NMR chemical shifts (in ppm) and coupling constants (in Hz) for  $[(\eta^5\text{-C}_5\text{H}_4\text{Ar})\text{Fe}(\text{CO})(\text{L})\text{I}]$  complexes<sup>a</sup>

Ar	L	C1	C2	C3	C4	C5	CH3	L <sup>b</sup>	<sup>1</sup> J(P,C)	<sup>2</sup> J(C2,P)	<sup>2</sup> J(C3,P)
Ph	P(O- <i>o</i> -tol) <sub>3</sub>	100	85.6					17.3		5.3	
Ph	P(CH <sub>2</sub> Ph) <sub>3</sub>	98.8	83.8					36.0	19.93	2.9	
<i>p</i> -C <sub>6</sub> H <sub>4</sub> Me	P(OMe) <sub>3</sub>	97.1	84.0				21.2	36.0		2.7	
<i>p</i> -C <sub>6</sub> H <sub>4</sub> Me	PMe <sub>2</sub> Ph		82.2	79.3	82.2	79.9	21.2	17.9, Me 19.7, Me	29.14	1.7	1.1
<i>p</i> -C <sub>6</sub> H <sub>4</sub> Me	P(O <sup><i>i</i></sup> Pr) <sub>3</sub>		84.3	81.2	87.9	80.0	21.1	24.1, Me 71.0, CH		3.8	
<i>p</i> -C <sub>6</sub> H <sub>4</sub> Me	P(O- <i>o</i> -tol) <sub>3</sub>	101	85.2	85.9	80.9	77.5	21.2				3.3
<i>p</i> -C <sub>6</sub> H <sub>4</sub> Me	PPh <sub>3</sub>		86.0	85.1	79.4	71.9	21.3			2.5	
<i>p</i> -C <sub>6</sub> H <sub>4</sub> Me	P(CH <sub>2</sub> Ph) <sub>3</sub>		83.3	85.8	82.2	75.3	21.2	36.0	19.83	3.0	
<i>p</i> -C <sub>6</sub> H <sub>4</sub> Me	CO	100	84.0	82.5	84.0	82.5	21.7				
<i>p</i> -C <sub>6</sub> H <sub>4</sub> <sup>t</sup> Bu	P(O- <i>o</i> -tol) <sub>3</sub>	100	87.7	85.8	79.7	72.7	17.3	31.2, Me			5.14
<i>p</i> -C <sub>6</sub> H <sub>4</sub> <sup>t</sup> Bu	PPh <sub>3</sub>		86.0	85.3	82.1	76.7	31.3			2.52	

<sup>a</sup>Recorded from C<sub>6</sub>D<sub>6</sub> solution at 22 °C,  $\delta$  in ppm relative to TMS,  $J(\text{PC})$  in Hz <sup>b</sup>Ligand aromatic resonances not recorded.

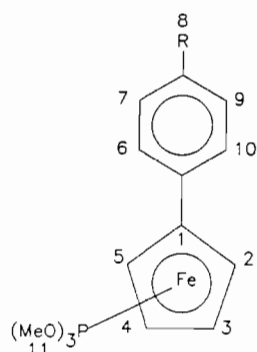


Fig. 4. Labelling system used in the NOE analysis. The cyclopentadienyl ring is viewed down the centroid-Fe axis. The CO and I ligands are not shown.

extends sufficiently far out in space to 'sense' the P(OMe)<sub>3</sub> ligand. Thus, even at the limit of the *p*-C<sub>6</sub>H<sub>4</sub>Me substituent, there is a small spatial interaction between the P(OMe)<sub>3</sub> ligand and the *p*-tolyl methyl protons. The radial profiles shown in Fig. 7 show that the interaction between the two ligands is indeed small. The complex  $[(\eta^5\text{-C}_5\text{H}_4\text{-}i\text{-}p\text{-C}_6\text{H}_5\text{Me})\text{Fe}(\text{CO})\{\text{P}(\text{O}^i\text{Pr})_3\}\text{I}]$  showed similar NOE effects with the same relative ordering of the resonance envelopes.

#### Relationship between $\Delta(\text{H}2\text{-H}5)$ and steric parameters

##### (a) Constant aryl group with varying ligand

In a previous publication we presented a relationship between NMR parameters, steric effects as measured by the Tolman cone angle  $\theta$  [4] and an electronic parameter,  $\nu(\text{CO})$  [1]. The aryl complexes show similar results. A correlation between  $\Delta(\text{H}2\text{-H}5)$ , the cone angle [4] and  $\nu(\text{CO})$  is observed for the  $[(\eta^5\text{-C}_5\text{H}_4\text{-}i\text{-}p\text{-C}_6\text{H}_5\text{Me})\text{Fe}(\text{CO})(\text{L})\text{I}]$  complexes ( $R^2=0.809$ , m.s.e. 0.128). The slope of the electronic parameter, as measured by  $\nu(\text{CO})$ , is not significantly different from zero ( $p=0.324$ ), suggesting that electronic factors do not play a dominant role in the correlation.

An attempt was also made to correlate the data with  $\Omega_s^*$ . Here a significant relationship between  $\Delta(\text{H}2\text{-H}5)$  and  $\Omega_s$  ( $R^2=0.746$ , m.s.e. 0.170 with all probability levels below 0.0805; Table 1) was observed\*\*. In an interactive outlier rejection analysis, the point corresponding to P(O<sup>*i*</sup>Pr)<sub>3</sub> was found to lie outside of one standard deviation, but within two (Fig. 8). Deleting this point gives an excellent correlation between  $\Delta(\text{H}2\text{-H}5)$  and  $\Omega_s$  ( $r=0.944$ , m.s.e. 0.110). This ligand is also the least symmetrical in the set studied and the solid angle for P(O<sup>*i*</sup>Pr)<sub>3</sub> should be closer to the value for PMe<sub>2</sub>Ph or P(OMe)<sub>3</sub>.

##### (b) Modification at the para position of the phosphine ligand

The question of whether the  $\Delta(\text{H}2\text{-H}5)$  measure is free of electronic effects in the aryl system has been investigated in a series of complexes  $[(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Fe}(\text{CO})(\text{L})\text{I}]$  in which the ligand L was varied. The ligands P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>, P(*p*-C<sub>6</sub>H<sub>4</sub>Me)<sub>3</sub> and P(*p*-C<sub>6</sub>H<sub>4</sub>F)<sub>3</sub> have different electronic effects but identical steric effects

\*In these studies a ligand (P-, N- or S-donor) was bound to a Cr(CO)<sub>5</sub> fragment and allowed to minimize in MM2. The solid angle was then measured in the minimum conformation. The choice of the Cr(CO)<sub>5</sub> fragment is extensively discussed in ref. 16. The value of the solid angle for P(O<sup>*i*</sup>Pr)<sub>3</sub> was measured assuming an averaging of conformation effects based on the Cr(CO)<sub>5</sub> fragment.

\*\*In the correlation between  $\Delta(\text{H}2\text{-H}5)$  and  $\theta$ , the electronic parameter  $\nu(\text{CO})$  cannot be convincingly rejected, because the mean square error increases when the variable is omitted ( $R^2=0.791$ , m.s.e. 0.140). The low probability level (0.324) is indicative of  $\Delta(\text{H}2\text{-H}5)$  not being significantly dependent on  $\nu(\text{CO})$ . However, if the solid angle  $\Omega_s$  replaces  $\theta$ , the rejection of  $\nu(\text{CO})$  becomes more significant. The relationship  $\Delta(\text{H}2\text{-H}5)=a\Omega_s+b\nu(\text{CO})+c$  shows the variables to be poorly correlated (0.671, m.s.e. 0.220) with  $\nu(\text{CO})$  not being significant (0.786). Rejecting  $\nu(\text{CO})$  improves both the correlation coefficient, mean square error and all significance levels ( $R^2=0.746$ , m.s.e. 0.170, probability levels <0.0805).

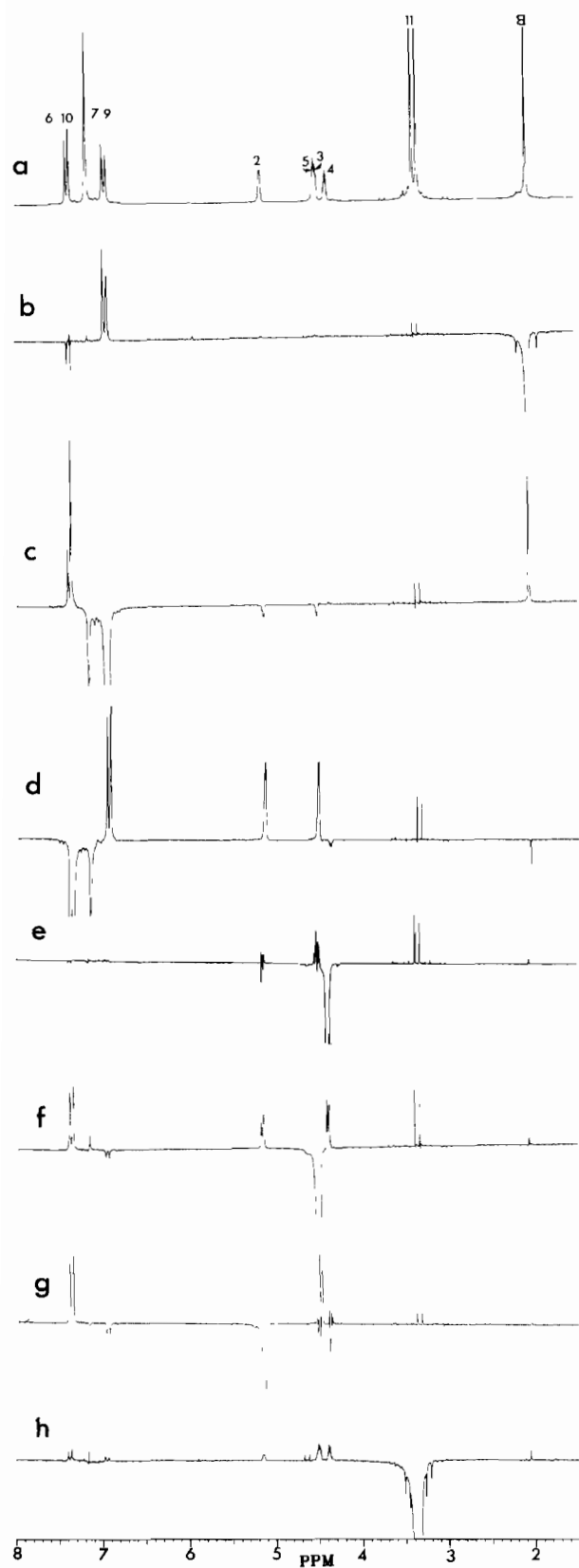


Fig. 5. NOE difference spectra of  $[(\eta^5\text{-C}_5\text{H}_4\text{-}p\text{-C}_6\text{H}_4\text{Me})\text{Fe}(\text{CO})\{\text{P}(\text{OMe})_3\}\text{I}]$ . (a) Reference spectrum, (b)–(h) defined in text

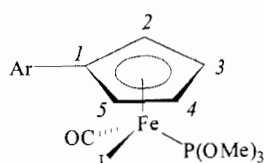


Fig. 6. Preferential location of the  $\text{P}(\text{OMe})_3$  ligand relative to the cyclopentadienyl ring as shown by the NOE experiment. Note that the ligand is situated nearly *trans* to the aryl group.

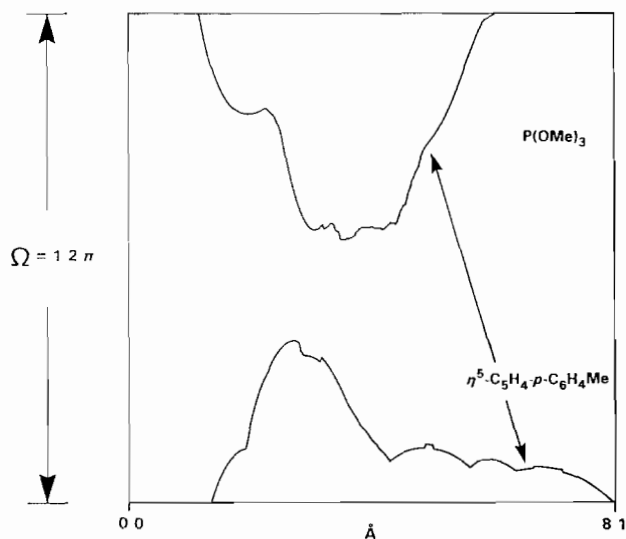


Fig. 7. Radial profiles of the  $\text{P}(\text{OMe})_3$  and  $\eta^5\text{-C}_5\text{H}_4\text{-}p\text{-tol}$  ligands. In the latter the *ipso* carbon atom of the cyclopentadienyl ring has been deleted for clarity (see method). The arrow indicates the area of small steric interaction between the  $\text{P}(\text{OMe})_3$  protons and the methyl group in the *para* position of the aryl ring.

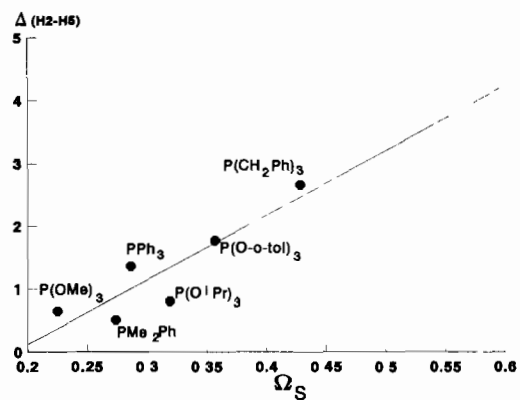


Fig. 8. Plot of  $\Delta(\text{H}2\text{-H}5)$  against  $\Omega_s$  for  $[(\eta^5\text{-C}_5\text{H}_4\text{-}p\text{-C}_6\text{H}_4\text{Me})\text{Fe}(\text{CO})(\text{L})\text{I}]$  complexes.

as determined from the metal (as measured by the Tolman cone angle [4] or solid angle [5]). As one moves away from the iron atom, however, the steric demand will change with distance from the apex. Radial profiles of the arylphosphine ligands are presented in Fig. 9 and, as can be observed, only at a distance of  $5.3 \text{ \AA}$  will the steric effects of these three ligands differ. In order to compare the substituent on the cyclopentadienyl

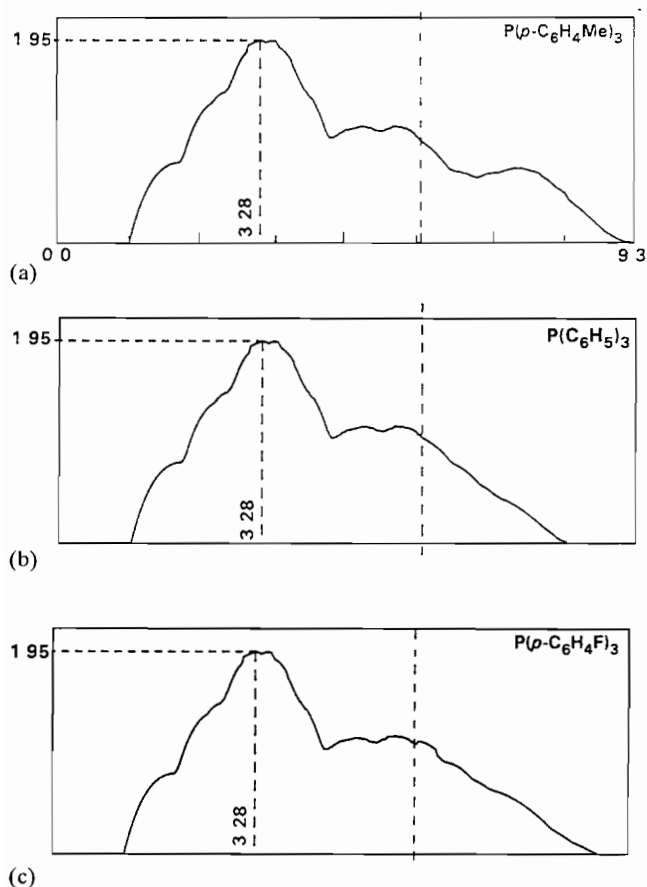


Fig. 9. Radial profiles of (a)  $P(p\text{-C}_6\text{H}_4\text{Me})_3$ , (b)  $P(\text{C}_6\text{H}_5)_3$  and (c)  $P(p\text{-C}_6\text{H}_4\text{F})_3$ . The dotted line indicates the radius (5.3 Å) at which the steric sizes of the three ligands become different.

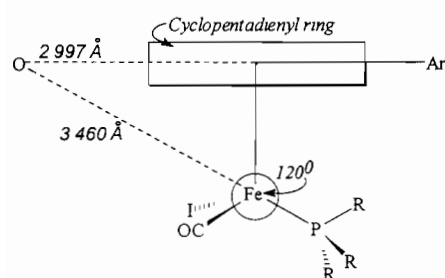


Fig. 10. Choice of apex for the sphere of variable radius  $[(\eta^5\text{-C}_5\text{H}_4\text{Ar})\text{Fe}(\text{CO})(\text{L})\text{I}]$  complexes.

ring meaningfully with the ligand set, L, an apex common to both L and R needs to be established. Because the substituent on the ring and the ligand are not directly attached to the metal, this apex needs to be outside of the molecule. To determine the location of the apex, the vector connecting the metal to the ligand is projected backwards until it intersects the vector connecting the substituent on the ring to the ring centroid (Fig. 10). The ring proton H2 and H5 are found at a distance of 2.29 Å using this common apex. Thus differences between aryl groups in the P ligand beyond 2.29 Å

should not influence the  $\Delta(\text{H2-H5})$  NMR data. Indeed only after a distance of 5.3 Å from the common apex do the various phosphine ligands show any steric differences (Fig. 9). Because  $\Delta(\text{H2-H5})$  is, indeed, invariant with change of phosphine (Table 4), we may conclude that  $\Delta(\text{H2-H5})$  is not affected by distance effects (or electronic parameters) in L to any significant extent.

(c) Variation of ring substituent with constant ligand

For complexes  $[(\eta^5\text{-C}_5\text{H}_4\text{Ar})\text{Fe}(\text{CO})(\text{L})\text{I}]$  in which Ar is varied but the ligand L is kept constant,  $\Delta(\text{H2-H5})$  will be affected by both electronic and distance influences from the Ar group. For this study, we have considered aromatic substituents modified in the *para* position (Ar = Ph, *p*- $\text{C}_6\text{H}_5\text{Me}$ , *p*- $\text{C}_6\text{H}_4\text{Bu}$ ). When L =  $P(\text{O-}o\text{-tol})_3$ , all  $\Delta(\text{H2-H5})$  values are similar (1.69–1.77 ppm). However, steric profiles for the three aryl substituents on the cyclopentadienyl rings are different (Fig. 11). This suggests that the interaction of the protons H2 and H5 with aryl groups occurs in a region where the aryl groups experience a similar steric demand, i.e. before 5.60 Å. Similar observations are noted for  $\Delta(\text{H2-H5})$  when L =  $P(\text{OMe})_3$ , for which the values are 0.78 ppm when Ar = Ph and 0.66 ppm when Ar = *p*- $\text{C}_6\text{H}_4\text{Me}$ . For L =  $P\text{Ph}_3$ , the values are 1.35 ppm when Ar = *p*- $\text{C}_6\text{H}_4\text{Me}$  and 1.22 ppm when Ar = *p*- $\text{C}_6\text{H}_4\text{Bu}$ . This, in particular, suggests that steric effects at a distance from the cyclopentadienyl ring centroid do not affect the  $\Delta(\text{H2-H5})$  parameter significantly. Clearly the aryl groups investigated also have different electronic effects, but the small variation in  $\nu(\text{CO})$  with change in aryl ring substituent ( $1.1\text{ cm}^{-1}$ ) suggests that the effects are small and do not significantly affect  $\Delta(\text{H2-H5})$ .

TABLE 4. Chemical shift differences,  $\Delta(\text{H2-H5})$  (in ppm) for  $[(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Fe}(\text{CO})(\text{L})\text{I}]$  complexes

R	L	$\Delta(\text{H2-H5})$
Me	$P\text{Ph}_3$	1.22
Me	$P(p\text{-C}_6\text{H}_4\text{Me})_3$	1.23
Me	$P(p\text{-C}_6\text{H}_4\text{F})_3$	1.22
Me	$P(\text{O-}o\text{-tol})_3$	1.24
Ph	$P(\text{OMe})_3$	0.78
Ph	$P(\text{O-}o\text{-tol})_3$	1.71
Ph	$P(\text{CH}_2\text{Ph})_3$	2.77
<i>p</i> - $\text{C}_6\text{H}_4\text{Me}$	$P(\text{OMe})_3$	0.66
<i>p</i> - $\text{C}_6\text{H}_4\text{Me}$	$P(\text{O-}o\text{-tol})_3$	1.77
<i>p</i> - $\text{C}_6\text{H}_4\text{Me}$	$P\text{Ph}_3$	1.35
<i>p</i> - $\text{C}_6\text{H}_4\text{Me}$	$P(\text{CH}_2\text{Ph})_3$	2.66
<i>p</i> - $\text{C}_6\text{H}_4\text{Bu}$	$P(\text{O-}o\text{-tol})_3$	1.69
<i>p</i> - $\text{C}_6\text{H}_4\text{Bu}$	$P\text{Ph}_3$	1.22
<i>i</i> -Bu	$P(\text{O-}o\text{-tol})_3$	2.38

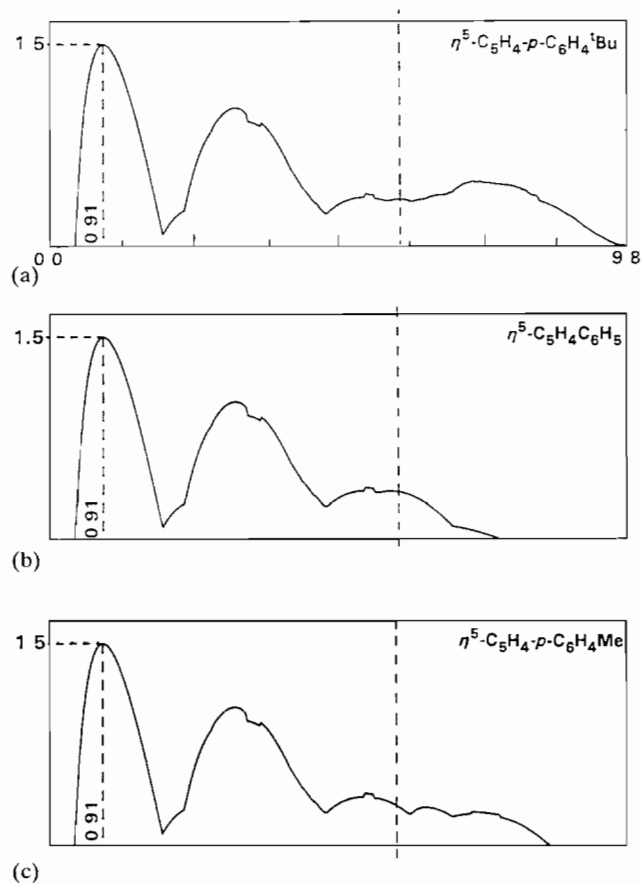


Fig. 11. Radial profile for (a)  $p$ -C<sub>6</sub>H<sub>4</sub>tBu, (b) C<sub>6</sub>H<sub>5</sub> and (c)  $p$ -C<sub>6</sub>H<sub>4</sub>Me. The dotted line indicates the radius (5.6 Å) at which the steric effects of the ligands become different.

#### (d) Relative size of aryl substituents

If one assumes that  $\Delta(\text{H2-H5})$  is free of electronic effects, this parameter may be used to determine the relative size of the aryl group with the aid of the methodology presented previously [1]. Comparison of the  $\Delta(\text{H2-H5})$  values in Table 4 for  $[(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Fe}(\text{CO})(\text{L})\text{I}]$  (R = Me, Ph,  $p$ -C<sub>6</sub>H<sub>4</sub>Me,  $p$ -C<sub>6</sub>H<sub>4</sub>tBu and tBu; L = P(*o*-tol)<sub>3</sub>) gives information about the size of the aryl group relative to the methyl and tert-butyl groups, the trend showing that Me < Ph  $\sim$   $p$ -C<sub>6</sub>H<sub>4</sub>Me  $\sim$   $p$ -C<sub>6</sub>H<sub>4</sub>tBu < tBu. If the cyclopentadienyl and aryl rings were not rotating freely (as expected from extended delocalisation arguments) then the aryl ring would appear larger than a methyl group but smaller than a tert-butyl group ( $\Omega_s(\text{Me}) = 0.152$ ;  $\Omega_s(\text{Ph}) = 0.213$ ;  $\Omega_s(\text{tBu}) = 0.345$ ). However, if free rotation were to be observed, then the aryl group would appear larger than a tert-butyl group ( $\Omega_s(\text{tBu}) = 0.382^*$ ;  $\Omega_s(\text{Ph}) = 0.394$ ). The value of  $\Delta(\text{H2-H5})$  (L = P(*o*-tol)<sub>3</sub>) reveals that the NMR data for the phenyl group

\*These latter values are found by assuming that the aryl or tert-butyl groups undergo free rotation (see 'Experimental' for details of calculation)

(1.71 ppm) lies between the value for a methyl (1.24 ppm) and tert-butyl (2.38 ppm [3]) group. The same deduction can be made by consideration of the data for L = PPh<sub>3</sub>. We can thus conclude that either (i) the aryl group undergoes limited rotation relative to the cyclopentadienyl ring, or (ii) an average value of steric size is being detected which reflects rotation of the aryl ring without the generation of a complete solid cone. While we favour the first possibility, further information is required to differentiate between these two possibilities

## Conclusions

The NOE data obtained on complexes  $[(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Fe}(\text{CO})(\text{L})\text{I}]$  indicate that, while the biggest group R and L preferentially adopt an *anti* orientation (Fig. 6), the cyclopentadienyl ligand is still conformationally mobile. Furthermore, small but detectable NOE effects between L and R, even at the latter's most distant position, show the extent to which steric interactions can be manifested. Electronic influences resulting from varying these two groups did not change the readily measured parameter  $\Delta(\text{H2-H5})$  significantly. On the other hand, steric effects associated with the ligand L, quantified in terms of solid angles  $\Omega_s$ , were clearly important in a uniform series of complexes,  $[(\eta^5\text{-C}_5\text{H}_4\text{-}p\text{-C}_6\text{H}_5\text{Me})\text{Fe}(\text{CO})(\text{L})\text{I}]$ . However, for aryl substituents on either the cyclopentadienyl or phosphorus ligands,  $\Omega_s$  does not provide an adequate measure of their sizes, because interaction with H2 and H5 occurs in a region in which the steric profiles of the ligands are very similar. Rather, the steric effects at a distance need to be compared by the use of radial profiles to obtain a more complete picture of the role of steric effects in these complexes.

## Experimental

All ligands were obtained from commercial suppliers. The complexes  $[(\eta^5\text{-C}_5\text{H}_4\text{Ph})\text{Fe}(\text{CO})_2]_2$  and  $[(\eta^5\text{-C}_5\text{H}_4\text{Ph})\text{Fe}(\text{CO})_2\text{I}]$  were prepared by following a literature method [7]. All organometallic preparations were carried out under nitrogen using deoxygenated, dry, freshly distilled solvents. IR spectra were recorded on a Perkin-Elmer 580B IR spectrometer and NMR spectra on a Bruker AC200 NMR spectrometer operating at 200 MHz. NOE data were recorded as described previously [14].



*Synthesis of  $[(\eta^5\text{-C}_5\text{H}_4\text{Ar})\text{Fe}(\text{CO})_2]_2$ , Ar = Ph,  $p\text{-C}_6\text{H}_4\text{Me}$ ,  $p\text{-C}_6\text{H}_4\text{Bu}$ , by means of the Grignard Reaction*

Reaction of magnesium turnings (0.100 mol, Table 5) with dry bromoarene (0.11 mol, Table 5) in dry ether (50 ml) under an atmosphere of nitrogen at room temperature gave arylmagnesium bromide. After completion of the vigorous exothermic reaction, the reaction mixture was cooled to 0 °C and cyclopent-2-en-1-one (0.060 mol, Table 5) in ether (25 ml) was added dropwise under nitrogen. The mixture was then allowed to warm to room temperature. The white suspension was stirred for 1 h, and added to a mixture of ice and ether in a separating funnel. The organic layer was separated and washed with saturated aqueous ammonium chloride solution. The combined aqueous layers were further extracted with ether (2 × 20 ml) and the combined organic fractions dried ( $\text{MgSO}_4$ ) and filtered. Ether was removed *in vacuo*. An IR spectrum of the crude material revealed it to be predominantly 1-arylcyclopent-2-en-1-ol. The crude product was distilled under reduced pressure (~1 mm Hg) in a bulb-to-bulb apparatus to give the desired arylcyclopentadiene.

Iron nonacarbonyl (~10 g, 0.030 mol) was added to freshly distilled arylcyclopentadiene in toluene. This reaction mixture was heated to 60 °C under nitrogen for 1 h during which time the reaction mixture turned deep red. The reaction mixture was filtered through celite under nitrogen, and the toluene and unreacted  $\text{Fe}(\text{CO})_5$  were removed *in vacuo*. IR spectroscopy showed the presence of a bridging carbonyl peak. These products were used in the following reactions without further purification.

*Synthesis of  $[(\eta^5\text{-C}_5\text{H}_4\text{Ar})\text{Fe}(\text{CO})_2\text{I}]$ , Ar = Ph,  $p\text{-C}_6\text{H}_4\text{Me}$ ,  $p\text{-C}_6\text{H}_4\text{Bu}$*

A deoxygenated solution of excess iodine in dichloromethane was added at room temperature with stirring to the crude  $[(\eta^5\text{-C}_5\text{H}_4\text{Ar})\text{Fe}(\text{CO})_2]_2$  dissolved in freshly distilled, dry, deoxygenated dichloromethane. The reaction was monitored by IR spectroscopy by the disappearance of the bridging CO peak. Excess iodine was removed by pouring the mixture into aqueous

TABLE 5. Quantities of materials used in the synthesis of  $[(\eta^5\text{-C}_5\text{H}_4\text{Ar})\text{Fe}(\text{CO})_2]_2$  complexes<sup>a</sup>

Ar	Mg		ArBr		Ketone <sup>b</sup>	
	(g)	(mol)	(g)	(mol)	(g)	(mol)
Ph	2 450	0 100	17.25	0.110	4.998	0.0608
$p\text{-C}_6\text{H}_4\text{Me}$	2.598	0.106	19 18	0.112	4.998	0.0608
$p\text{-C}_6\text{H}_4\text{Bu}$	1.545	0.0636	11.06	0.0519	4.998	0 0608

<sup>a</sup>The yield of product was ~26% <sup>b</sup>Cyclopent-2-en-1-one

sodium thiosulfate solution (2 g in 150 ml) The organic layer was separated, and the aqueous layer extracted with  $\text{CH}_2\text{Cl}_2$  until almost clear. The combined organic layers were dried ( $\text{MgSO}_4$ ) and filtered and the solvent was removed *in vacuo* to yield the desired product (~77%).

*Synthesis of  $[(\eta^5\text{-C}_5\text{H}_4\text{Ar})\text{Fe}(\text{CO})(\text{L})\text{I}]$ , Ar = Ph,  $p\text{-C}_6\text{H}_4\text{Me}$ ,  $p\text{-C}_6\text{H}_4\text{Bu}$ ; L =  $\text{P}(\text{OMe})_3$ ,  $\text{PMe}_2\text{Ph}$ ,  $\text{P}(\text{O}^i\text{Pr})_3$ ,  $\text{P}(\text{O-}o\text{-tol})_3$ ,  $\text{PPh}_3$ ,  $\text{P}(\text{CH}_2\text{Ph})_3$*

The  $[(\eta^5\text{-C}_5\text{H}_4\text{Ar})\text{Fe}(\text{CO})_2\text{I}]$  complex (~0.500 mmol, Table 6) was dissolved in freshly distilled, deoxygenated, dry benzene (60 ml) under nitrogen. The ligand L (~0.600 mmol, Table 6) was added under nitrogen together with catalyst (Table 6). The solution was heated under reflux, and progress of the reaction was monitored by IR spectroscopy or TLC (50:50 benzene/hexane eluent). After completion of the reaction, the solvent was removed under reduced pressure and the product was purified by column chromatography (50:50 benzene/hexane eluent). The complexes,  $[(\eta^5\text{-C}_5\text{H}_4\text{Ar})\text{Fe}(\text{CO})(\text{L})\text{I}]$  were characterised by IR and NMR spectroscopy (Tables 1, 2 and 3).

*Formation of  $[(\eta^5\text{-C}_5\text{H}_4\text{-}p\text{-C}_6\text{H}_5\text{Me})\text{Fe}(\text{CO})(\text{PMe}_2\text{Ph})\text{I}]$  from  $[(\eta^5\text{-C}_5\text{H}_4\text{-}p\text{-C}_6\text{H}_5\text{Me})\text{Fe}(\text{CO})_2(\text{PMe}_2\text{Ph})\text{I}]$*

The thermal reaction between  $[(\eta^5\text{-C}_5\text{H}_4\text{-}p\text{-C}_6\text{H}_5\text{Me})\text{Fe}(\text{CO})_2\text{I}]$  and  $\text{PMe}_2\text{Ph}$  did not yield  $[(\eta^5\text{-C}_5\text{H}_4\text{-}p\text{-C}_6\text{H}_5\text{Me})\text{Fe}(\text{CO})(\text{PMe}_2\text{Ph})\text{I}]$  (24 h), but rather a yellow precipitate. This precipitate,  $[(\eta^5\text{-C}_5\text{H}_4\text{-}p\text{-C}_6\text{H}_5\text{Me})\text{Fe}(\text{CO})_2(\text{PMe}_2\text{Ph})\text{I}]$  (163 mg, 0.342 mmol), was separated by filtration and dissolved in deoxygenated

TABLE 6 Quantities of materials used in the synthesis of  $[(\eta^5\text{-C}_5\text{H}_4\text{Ar})\text{Fe}(\text{CO})(\text{L})\text{I}]$  complexes<sup>a</sup>

Ar	L	Complex <sup>b</sup>		L <sup>c</sup>	
		(mg)	(mmol)	(mg)	(mmol)
Ph	$\text{P}(\text{O-}o\text{-tol})_3$	208	0.547	208	0 590
Ph	$\text{P}(\text{CH}_2\text{Ph})_3$	206	0 526	201	0 660
$p\text{-C}_6\text{H}_4\text{Me}$	$\text{P}(\text{OMe})_3^d$	243	0.617	85	0 685
$p\text{-C}_6\text{H}_4\text{Me}$	$\text{PMe}_2\text{Ph}^e$	404	1.03	234	1.70
$p\text{-C}_6\text{H}_4\text{Me}$	$\text{P}(\text{O}^i\text{Pr})_3$	398	1.01	331	1.59
$p\text{-C}_6\text{H}_4\text{Me}$	$\text{P}(\text{O-}o\text{-tol})_3$	226	0.574	212	0 602
$p\text{-C}_6\text{H}_4\text{Me}$	$\text{PPh}_3^d$	226	0 574	182	0 694
$p\text{-C}_6\text{H}_4\text{Me}$	$\text{P}(\text{CH}_2\text{Ph})_3$	211	0 536	188	0.618
$p\text{-C}_6\text{H}_4\text{Bu}$	$\text{P}(\text{O-}o\text{-tol})_3$	517	1.19	515	2 65
$p\text{-C}_6\text{H}_4\text{Bu}$	$\text{PPh}_3^f$	510	1 17	406	1 55

<sup>a</sup>The yield of  $[(\eta^5\text{-C}_5\text{H}_4\text{Ar})\text{Fe}(\text{CO})(\text{L})\text{I}]$  varied between 9 and 39%. Reaction times were between 1 and 12 h. <sup>b</sup> $[(\eta^5\text{-C}_5\text{H}_4\text{Ar})\text{Fe}(\text{CO})_2\text{I}]$ . <sup>c</sup>The ligand <sup>d</sup> $[(\eta^5\text{-C}_5\text{H}_4\text{-}p\text{-C}_6\text{H}_4\text{Me})\text{Fe}(\text{CO})_2]_2$  used as catalyst. <sup>e</sup>Only  $[(\eta^5\text{-C}_5\text{H}_4\text{-}p\text{-C}_6\text{H}_4\text{Me})\text{Fe}(\text{CO})_2\text{-PMe}_2\text{Ph}]\text{I}$  was isolated. This was converted into the desired complex by reaction with trimethylamine-*N*-oxide (0 040 g, 0 533 mmol) in  $\text{CH}_2\text{Cl}_2$ . <sup>f</sup> $[(\eta^5\text{-C}_5\text{H}_4\text{-}p\text{-C}_6\text{H}_4\text{Bu})\text{Fe}(\text{CO})_2]_2$  used as catalyst

CH<sub>2</sub>Cl<sub>2</sub>. The CH<sub>2</sub>Cl<sub>2</sub> was removed under vacuum, and replaced by benzene containing dry trimethylamine-*N*-oxide (0.040 g, 0.533 mmol). The reaction mixture was heated under reflux for 2 h, during which time the precipitate partially dissolved. The crude product from the reaction was subjected to column chromatography (50:50 benzene/hexane then 50:50 benzene/ether as eluents). Pure [(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>-*p*-C<sub>6</sub>H<sub>5</sub>Me)Fe(CO)(PMe<sub>2</sub>Ph)-I] (123 mg, 0.274 mmol, 80%) was eluted as the major product from the column and characterised by IR and NMR spectroscopy.

*Synthesis of [(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>Me)Fe(CO)(L)I], L = PPh<sub>3</sub>, P(*p*-C<sub>6</sub>H<sub>4</sub>Me)<sub>3</sub>, P(*p*-C<sub>6</sub>H<sub>4</sub>F)<sub>3</sub>*

The [(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>Me)Fe(CO)<sub>2</sub>I] complex (1 mmol) and L (1.1 mmol) were added to benzene (10 ml) and the solution heated to reflux. The catalyst, [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>]<sub>2</sub> (10 mg), was added to the reaction mixture and the progress of reaction was monitored by IR spectroscopy. After the disappearance of the ν(CO) peaks assigned to the starting material, the reaction mixture was heated for a further 15 min. After cooling, the reaction mixture was filtered through a cellulose column (benzene) and a yellow precipitate remained on the column. The benzene was removed *in vacuo* and the desired product, [(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>Me)Fe(CO)(L)I], purified by column chromatography (benzene as eluent) and crystallised from either hexane or toluene/hexane mixtures (20–70% yield). The product was characterised by IR and NMR spectroscopy (Table 7).

For L = PPh<sub>3</sub>, the yellow precipitate was collected from the cellulose column by eluting with CH<sub>2</sub>Cl<sub>2</sub>, and identified as [(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>Me)Fe(CO)<sub>2</sub>PPh<sub>3</sub>I] by IR and NMR spectroscopy. This product was crystallised from CH<sub>2</sub>Cl<sub>2</sub>/ether/hexane (30–60% yield). IR: ν(CO) (CH<sub>2</sub>Cl<sub>2</sub>) 2046, 2002 cm<sup>-1</sup>. NMR: δ (relative to TMS, CDCl<sub>3</sub>) 5.28 (H3, H4); 5.42 (H2, H5); 2.16 (Me) ppm.

#### Measurement of solid angle profiles

All solid angle profiles were measured by the methodology presented previously [15]. For the ligands, an M–P bond distance of 2.28 Å was chosen. For the arylcyclopentadienes, the apex was taken from the ring

TABLE 7 Melting point (in °C), IR (in cm<sup>-1</sup>) and <sup>1</sup>H NMR chemical shifts (in ppm) for [(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>Me)Fe(CO)(L)I] complexes

L	m.p. <sup>a</sup>	ν(CO) <sup>b</sup>	Me <sup>c</sup>	H2 <sup>c</sup>	H3 <sup>c</sup>	H4 <sup>c</sup>	H5 <sup>c</sup>
PPh <sub>3</sub>	150–52	1960, 1950	1.93	4.63	4.12	3.49	3.41
P( <i>p</i> -C <sub>6</sub> H <sub>4</sub> Me) <sub>3</sub>	132–134	1948	1.97	4.70	4.24	3.60	3.47
P( <i>p</i> -C <sub>6</sub> H <sub>4</sub> F) <sub>3</sub>	133–135	1953	1.91	4.55	3.99	3.35	3.35

<sup>a</sup>Uncorrected. <sup>b</sup>Recorded in hexane. All absorption are strong. <sup>c</sup>Recorded in C<sub>6</sub>D<sub>6</sub>, δ relative to TMS

centroid (i.e. 1.20 Å from the *ipso* carbon of the cyclopentadienyl ring). The C<sub>*ipso*</sub>–C<sub>*ipso*</sub> distance was chosen to be 1.406 Å (the distance in biphenyl). The two rings were also assumed to be coplanar. Solid angles for the methyl, phenyl and tert-butyl groups were measured at an arbitrary distance of 2.00 Å from the quaternary carbon atom. Solid angles for freely rotating phenyl and tert-butyl groups were obtained from the linear angle measured in maximum conformation using ALCHEMY [17]. These solid angles were converted into linear angles using eqn. (1), where θ/2 is the semi-vertex angle measured from ALCHEMY.

$$\Omega = 2\pi \left[ 1 - \cos\left(\frac{\theta}{2}\right) \right] \quad (1)$$

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