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## An investigation of steric effects along a cyclopentadienyl substituent: a study by $^1\text{H}$ , $^{13}\text{C}$ and $^{29}\text{Si}$ NMR spectroscopy of bis(trimethylsilyl)cyclopentadienyl iron complexes

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### Abstract

The syntheses of a range of complexes,  $[(\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2)\text{Fe}(\text{CO})(\text{L})\text{I}]$ , ( $\text{L} = {}^t\text{BuNC}$ , 2,6- $\text{Me}_2\text{C}_6\text{H}_3\text{NC}$  (xylNC),  $\text{P}(\text{OMe})_3$ ,  $\text{PMe}_2\text{Ph}$ ,  $\text{P}(\text{O-}o\text{-tol})_3$ ,  $\text{PPh}_3$ ,  $\text{P}(m\text{-tol})_3$ ,  $\text{P}(p\text{-tol})_3$ , and  $\text{P}(\text{CH}_2\text{Ph})_3$ ) are reported. Three separate cyclopentadienyl ring proton resonances were observed in the NMR spectra of the iron complexes, and their assignments determined from NOE experiments ( $\text{L} = \text{P}(\text{OMe})_3$ ,  $\text{P}(\text{O-}o\text{-tol})_3$ ). The  $^{13}\text{C}$  NMR spectra were recorded and assignments made from a knowledge of the  $^1\text{H}$  spectra by use of CH correlated spectroscopy.  $^{29}\text{Si}$  and  $^{31}\text{P}$  NMR data were also obtained. Three-dimensional correlations were observed between separations of pairs of NMR resonances ( $^{29}\text{Si}$ ,  $^{13}\text{C}$  and  $^1\text{H}$ ) and (i) steric effects as measured by the Tolman cone angle,  $\theta$ , and (ii) electronic effects as measured by  $\nu_{\text{CO}}$ , the stretching frequency of the carbonyl group. The degree of correlation varied with the distance of the NMR-active nuclei from the iron atom (ring C and  $\text{Si}(\text{CH}_3)_3$  Si, C and H atoms), and the result is taken as an indication of the best region, in space, in which the Tolman cone angle concept is most appropriate. The best correlation occurred between the chemical shift difference of the two  $^{29}\text{Si}$  resonances and  $\theta$  and  $\nu(\text{CO})$  ( $R^2 = 0.96$ ,  $mse = 0.00640$ ). Conformational data obtained from the NOE spectra suggest that the Group 15 donor ligand resides close to a  $\text{SiMe}_3$  group and near the two adjacent ring protons. The steric demand of the two bulky  $\text{SiMe}_3$  groups hinders rotation of the  $\text{P}(\text{OMe})_3$  and  $\text{P}(\text{O-}o\text{-tol})_3$  ligands around the ring, resulting in a windscreen wiper motion of the ligand between the two  $\text{SiMe}_3$  groups.

### Introduction

In organometallic chemistry the cone-angle concept of ligand size, as initially proposed by Tolman for Group 15 donor ligands, is widely accepted as providing the best measure of ligand steric effects [1]. The concept has been extended to amines [2] and monosubstituted cyclopentadienyl ligands [3], and the limitations and advantages of the approach are well recognised [4].

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To explore the Tolman concept further, as well as to assess the steric parameters associated with cyclopentadienyl ligands, we have commenced a systematic NMR investigation of a series of half sandwich transition metal complexes containing multiply substituted cyclopentadienyl ligands. We report below an NMR study ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{29}\text{Si}$  and  $^{31}\text{P}$ ) of a series of  $[(\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2)\text{Fe}(\text{CO})(\text{L})\text{I}]$  ( $\text{L} = ^i\text{BuNC}$ ,  $2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC}$  (xylNC),  $\text{P}(\text{OMe})_3$ ,  $\text{PMe}_2\text{Ph}$ ,  $\text{P}(\textit{o}\text{-tol})_3$ ,  $\text{PPh}_3$ ,  $\text{P}(\textit{m}\text{-tol})_3$ ,  $\text{P}(\textit{p}\text{-tol})_3$  and  $\text{P}(\text{CH}_2\text{Ph})_3$ ) complexes, and the correlation of the NMR parameters with the steric size as well as the electronic nature of L. The use of the trimethylsilyl substituent provides the possibility for assessing ring properties by means of  $^{29}\text{Si}$  spectroscopy [5]. The bulky  $\text{SiMe}_3$  groups [6] should give rise to hindered rotation [7] as well as the possibility of assessing NMR parameters as a function of distance from the iron atom.

## Results and discussion

### *Synthesis of $[(\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2)\text{Fe}(\text{CO})_2\text{I}]_2$ , $[(\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2)\text{Fe}(\text{CO})_2\text{I}]$ and $[(\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2)\text{Fe}(\text{CO})(\text{L})\text{I}]$*

The published procedure for the synthesis of trimethylsilylcyclopentadiene [8] was found to produce the required monosubstituted compound along with a higher boiling fraction, identified as bis(trimethylsilyl)cyclopentadiene. This compound can also be obtained in a stepwise manner by treating  $\text{C}_5\text{H}_5\text{SiMe}_3$  with butyllithium followed by  $\text{SiMe}_3\text{Cl}$  [7]. A number of experiments were carried out to determine whether the amount of bis(trimethylsilyl)cyclopentadiene could be optimised in a 'one pot' reaction from sodium cyclopentadienide and trimethylchlorosilane. Two variables were used to optimise the amount of bis(trimethylsilyl)cyclopentadiene: order of reagent addition and reagent stoichiometry. In the first set of three experiments, 2, 3 and 4 equivalents of trimethylchlorosilane were added to a 1:2 mixture of sodium to cyclopentadiene. In this set of experiments the yield of trimethylsilylcyclopentadiene was optimal at 57% for the 2:1:4 stoichiometry ( $\text{Na}:\text{C}_5\text{H}_6:\text{SiMe}_3\text{Cl}$ ). In the next set of three experiments the order of addition was reversed (same stoichiometric ratios), giving an optimal 81% yield for the 2:1:2 stoichiometry. Since neither the order of addition nor stoichiometric adjustments gave > 85% yield of the bis(trimethylsilyl)cyclopentadiene, the two step method (see Experimental) is preferred for the synthesis of  $\text{C}_5\text{H}_4(\text{SiMe}_3)_2$ .

Treatment of the mixture of mono- and bis(trimethylsilyl)cyclopentadiene, provided by either the 'one pot' or two step methods, with  $\text{Fe}(\text{CO})_5$ , and subsequent reaction of the resulting dimer with elemental iodine, gave two products, identified as  $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Fe}(\text{CO})_2\text{I}]$  [3] and  $[(\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2)\text{Fe}(\text{CO})_2\text{I}]$  by IR (Table 1) and NMR spectroscopy (Tables 2–4). It is noteworthy that the product ratio was dependent on the source of bis(trimethylsilyl)cyclopentadiene used. For reaction of  $\text{Fe}(\text{CO})_5$  with the ligand prepared by the two step process, > 95:5 ratio of  $[(\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2)\text{Fe}(\text{CO})_2\text{I}]$  to  $[(\eta^5\text{-C}_5\text{H}_4(\text{SiMe}_3))\text{Fe}(\text{CO})_2\text{I}]$  was found. Use of the product from a 'one pot' synthesis led to a 1:1.4 ratio of mono- to bis- product. The mixture of  $[(\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2)\text{Fe}(\text{CO})_2\text{I}]$  and  $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Fe}(\text{CO})_2\text{I}]$  was easily separated on silica columns for use in later studies.

Reaction of  $[(\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2)\text{Fe}(\text{CO})_2\text{I}]$  with the ligand (L) was attempted under a variety of conditions, typically in the presence of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}]_2$  as catalyst [9]. Reaction conditions as well as product yields are given in Table 5.

Table 1

IR data for  $[(\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2)\text{Fe}(\text{CO})(\text{L})\text{I}]$  complexes

L	$\nu(\text{CO})/\text{cm}^{-1}$ <sup>a</sup>
<sup>t</sup> BuNC <sup>b</sup>	1974.0
xylNC <sup>c</sup>	1977.2
P(OMe) <sub>3</sub>	1948.9
PMe <sub>2</sub> Ph	1936.8
P( <i>o</i> -tol) <sub>3</sub>	1972.3
PPh <sub>3</sub>	1944.9
P( <i>m</i> -tol) <sub>3</sub>	1945.6
P( <i>p</i> -tol) <sub>3</sub>	1944.5
P(CH <sub>2</sub> Ph) <sub>3</sub>	1941.3
CO	2033.5, 1992.0

<sup>a</sup> Recorded in C<sub>6</sub>H<sub>6</sub> solution ( $\pm 0.5$  cm<sup>-1</sup>). <sup>b</sup>  $\nu(\text{CN}) = 2138.6$  cm<sup>-1</sup>. <sup>c</sup>  $\nu(\text{CN}) = 2115.0$  cm<sup>-1</sup>.

Table 2

<sup>1</sup>H NMR data for  $[(\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2)\text{Fe}(\text{CO})(\text{L})\text{I}]$  complexes <sup>a</sup>

L	$\delta$ H2	$\delta$ H4	$\delta$ H5	$\delta$ Si(CH <sub>3</sub> ) <sub>2</sub>	$\delta$ L <sup>b</sup>	$J(\text{P-H5})$	
<sup>t</sup> BuNC	4.94	4.52	4.56	0.342	0.326	1.01 (CH <sub>3</sub> )	
xylNC	5.12	4.59	4.65	0.342	0.296	2.29 (CH <sub>3</sub> ), 6.71 (Ar)	
P(OMe) <sub>3</sub>	5.01	4.37	4.79	0.429	0.268	3.38 (CH <sub>3</sub> )	3.90
PMe <sub>2</sub> Ph	5.01	2.72	4.07	0.323	0.309	1.86, 1.50 (CH <sub>3</sub> ), 7.35, 7.02 (Ar)	6.14
P( <i>o</i> -tol) <sub>3</sub>	5.48	2.78	4.72	0.482	0.306	2.42 (CH <sub>3</sub> ), 7.42 ( <i>o</i> -tol), 6.75 ( <i>m</i> , <i>p</i> -tol)	6.66
PPh <sub>3</sub>	5.05	2.79	4.08	0.383	0.331	7.81 ( <i>o</i> -Ph), 6.70 ( <i>m</i> , <i>p</i> -Ph)	5.07
P( <i>m</i> -tol) <sub>3</sub>	5.09	2.86	4.19	0.411	0.365	2.02 (CH <sub>3</sub> ), 7.80, 7.05, 6.84 (Ar)	5.23
P( <i>p</i> -tol) <sub>3</sub>	5.11	2.91	4.20	0.438	0.380	1.98 (CH <sub>3</sub> )	5.19
P(CH <sub>2</sub> Ph) <sub>3</sub>	5.21	2.66	4.17	0.416	0.294	3.67–3.45 (CH <sub>2</sub> ), 7.01 (Ar)	
CO	5.03	4.34	4.34	0.198	0.198		

<sup>a</sup> Recorded from a solution in C<sub>6</sub>D<sub>6</sub> at 22°C,  $\delta$  in ppm relative to TMS,  $J(\text{PH})$  in Hz. <sup>b</sup> Ar = aromatic.

Table 3a

<sup>13</sup>C NMR data for  $[(\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2)\text{Fe}(\text{CO})(\text{L})\text{I}]$  complexes <sup>a</sup>

L	$\delta$ C1	$\delta$ C2	$\delta$ C3	$\delta$ C4	$\delta$ C5	$\delta$ Si(CH <sub>3</sub> ) <sub>2</sub>	
<sup>t</sup> BuNC	85.50	101.5	84.76	90.49	91.26	0.171	0.171
xylNC	86.90	102.5	86.37	90.64	91.48	0.0735	0.0015
P(OMe) <sub>3</sub>	83.19	101.1	90.56	87.59	93.44	0.476	-0.067
PMe <sub>2</sub> Ph	96.64	96.36	89.09	77.11	93.80	0.771	-0.314
P( <i>o</i> -tol) <sub>3</sub>		104.6		76.83	91.91	0.548	-0.460
PPh <sub>3</sub>	100.3	94.74	88.24	79.93	95.64	0.698	-0.335
P( <i>m</i> -tol) <sub>3</sub>	99.93	95.16	88.23	78.60	96.13	0.757	-0.304
P( <i>p</i> -tol) <sub>3</sub>	99.95	95.23	88.11	78.78	95.91	0.791	-0.242
P(CH <sub>2</sub> Ph) <sub>3</sub>	94.04	101.7	85.45	77.29	91.63	1.032	-0.196
CO	90.32	104.1	90.32	92.35	92.35	-0.007	-0.007

<sup>a</sup> Recorded from C<sub>6</sub>D<sub>6</sub> solution at 22°C,  $\delta$  in ppm relative to TMS.

Table 3b

<sup>13</sup>C NMR data for [(η<sup>5</sup>-C<sub>5</sub>H<sub>3</sub>(SiMe<sub>3</sub>)<sub>2</sub>)Fe(CO)(L)] complexes <sup>a</sup>

L	δ CO	δ L <sup>b</sup>	J(P-C2) <sup>a</sup>	J(P-C3) <sup>a</sup>
<sup>t</sup> BuNC	220.2	30.26 (CH <sub>3</sub> )		
xylNC	219.6	19.02 (CH <sub>3</sub> )		
P(OMe) <sub>3</sub>	220.8	53.66 (CH <sub>3</sub> )	3.05	
PMe <sub>2</sub> Ph	223.6	19.99–19.22 (CH <sub>3</sub> )	4.55	
P(O- <i>o</i> -tol) <sub>3</sub>	220.8	17.50 (CH <sub>3</sub> )	6.54	
PPh <sub>3</sub>	223.4		4.56	1.99
P( <i>m</i> -tol) <sub>3</sub>	223.8	21.48 (CH <sub>3</sub> )	4.59	
P( <i>p</i> -tol) <sub>3</sub>	223.4	21.21 (CH <sub>3</sub> )	4.82	
P(CH <sub>2</sub> Ph) <sub>3</sub>	222.2	38.06 (CH <sub>2</sub> )	3.68	2.39
CO				

<sup>a</sup> Recorded from C<sub>6</sub>D<sub>6</sub> solution at 22°C. δ in ppm relative to TMS, J(PC) in Hz. <sup>b</sup> Aromatic resonances not listed.

Table 4

<sup>31</sup>P and <sup>29</sup>Si NMR data for [(η<sup>5</sup>-C<sub>5</sub>H<sub>3</sub>(SiMe<sub>3</sub>)<sub>2</sub>)Fe(CO)(L)] complexes <sup>a</sup>

L	<sup>31</sup> P δ /ppm <sup>b</sup>	<sup>29</sup> Si δ /ppm <sup>c</sup>	δ (Si1-Si3)
<sup>t</sup> BuNC		-4.17	-4.25
xylNC		-4.12	-4.22
P(OMe) <sub>3</sub>	179.9	-3.51	-4.01
PMe <sub>2</sub> Ph	33.8	-3.68	-4.30
P(O- <i>o</i> -tol) <sub>3</sub>	164.9	-2.98	-3.66
PPh <sub>3</sub>	60.5	-3.40	-4.18
P( <i>m</i> -tol) <sub>3</sub>	62.2	-3.44	-4.23
P( <i>p</i> -tol) <sub>3</sub>	57.9	-2.97	-3.76
P(CH <sub>2</sub> Ph) <sub>3</sub>	57.3	-3.39	-4.33

<sup>a</sup> Recorded from solution in C<sub>6</sub>D<sub>6</sub>/C<sub>6</sub>H<sub>6</sub> at 22°C. <sup>b</sup> Chemical shift in ppm from 80% H<sub>3</sub>PO<sub>4</sub> (external standard). <sup>c</sup> Chemical shift in ppm from TMS (external standard).

Table 5

Quantities of materials used in the synthesis of [(η<sup>5</sup>-C<sub>5</sub>H<sub>3</sub>(SiMe<sub>3</sub>)<sub>2</sub>)Fe(CO)(L)] complexes

L	L (mmol)	complex <sup>a</sup> (mmol)	product yield <sup>b</sup>	
			(mmol)	(%)
<sup>t</sup> BuNC <sup>d</sup>	1.77	0.571	0.141	25
xylNC <sup>d</sup>	0.793	0.467	0.230	50
P(OMe) <sub>3</sub> <sup>c</sup>	2.52	0.467	0.248	53
PMe <sub>2</sub> Ph <sup>d</sup>	1.13	0.483	0.292	60
P(O- <i>o</i> -tol) <sub>3</sub> <sup>c</sup>	0.727	0.460	0.409	89
PPh <sub>3</sub> <sup>c</sup>	1.04	0.483	0.346	72
P( <i>m</i> -tol) <sub>3</sub> <sup>d</sup>	0.979	0.483	0.254	53
P( <i>p</i> -tol) <sub>3</sub> <sup>c</sup>	1.498	0.539	0.138	26
P(CH <sub>2</sub> Ph) <sub>3</sub> <sup>d</sup>	1.39	0.500	0.202	40

<sup>a</sup> [(η<sup>5</sup>-C<sub>5</sub>H<sub>3</sub>(SiMe<sub>3</sub>)<sub>2</sub>)Fe(CO)<sub>2</sub>I]. <sup>b</sup> Reaction time varied between 30 min and 18 h and was influenced by catalyst. <sup>c</sup> [(η<sup>5</sup>-C<sub>5</sub>H<sub>3</sub>)Fe(CO)<sub>2</sub>]<sub>2</sub> (5–10 mg) added as catalyst. <sup>d</sup> No catalyst added.

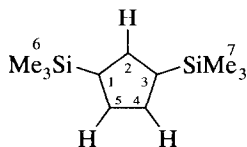


Fig. 1. Ring numbering scheme for  $[(\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2)\text{Fe}(\text{CO})(\text{L})\text{I}]$  complexes.

With the isonitrile ligands, both the presence of  $[(\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2)\text{Fe}(\text{CO})(\text{L})\text{I}]$  and  $[(\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2)\text{Fe}(\text{L})_2\text{I}]$  complexes were noted (IR, NMR spectroscopy). No attempt was made to study these disubstituted complexes.

### NMR study

(i) *Correlation of NMR spectra with molecular structure.* The NMR spectra ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{29}\text{Si}$ ,  $^{31}\text{P}$ ) of the  $[(\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2)\text{Fe}(\text{CO})_2\text{I}]$  complexes were recorded at room temperature and in every instance separate resonances for all atoms (correct numbers and relative intensities) were observed, confirming the structures of the new complexes. Thus in every instance the  $^1\text{H}$  NMR spectrum of the ring protons showed two  $\text{SiMe}_3$  resonances at *ca.* 0.3 ppm and three ring proton resonances (see Fig. 1 for ring numbering system).

For  $\text{L} = {}^t\text{BuNC}$  and  $\text{xyINC}$ , two of these ring proton resonances (H4 and H5) appeared as a doublet of AB quartets, while the other proton resonance, H2, appeared as a triplet ( $J(\text{HH}) = 1.4$  Hz for both  ${}^t\text{BuNC}$  and  $\text{xyINC}$ ). For  $\text{L} =$  phosphine/phosphite three well separated ring resonances were observed.

Assignments of the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral resonances of the ring atoms were achieved using NOE and CH correlated spectra recorded on appropriately chosen samples [10,11]. The NOE difference spectra for both the tri-*ortho*-tolylphosphite and trimethylphosphite derivatives were recorded and show analogous trends, thus allowing the unambiguous assignment of the ring protons for these and all other derivatives. This was made possible by the positions and shapes of the resonance envelopes. Thus, H2 was always the most downfield resonance. H5 typically comprised two envelopes due to P-H coupling (see Fig. 2a), the separations of the envelopes being dependent on the nature of the L group. This  $J(\text{P-H5})$  value varied between 3.8 Hz ( $\text{L} = \text{P}(\text{OMe})_3$ ) and 6.7 Hz ( $\text{L} = \text{P}(\text{O-}o\text{-tol})_3$ ). The  $J(\text{HH})$  coupling constants did not vary significantly with L group ( $J(\text{H2-H4})$  *ca.* 1.4 Hz;  $J(\text{H2-H5})$  *ca.* 2.5 Hz). An analysis of the NOE difference spectra for the  $\text{P}(\text{O-}o\text{-tol})_3$  derivative is given below.

For the tri-*ortho*-tolylphosphite complex (ligand cone angle  $141^\circ$  [1]) it is observed that irradiation of resonance 2 (Fig. 2c) results in small growth of both the methyl protons of the trimethylsilyl groups (0.8%) only, suggesting that this proton corresponds to ring position 2 (Fig. 1). This is confirmed by irradiation of resonances 5 and 4 (Fig. 2d, e) which only causes mutual resonance growth, but no growth of resonance 2. Similar results were found for the trimethylphosphite complex (ligand cone angle  $107^\circ$ ). The data suggest that the ligand size does not influence the relative positions of protons 2, 4 or 5. It is proposed that all other complexes have spectra with the same relative positioning of proton resonances, which is further confirmed, as mentioned above, by the relative shape of the resonances.

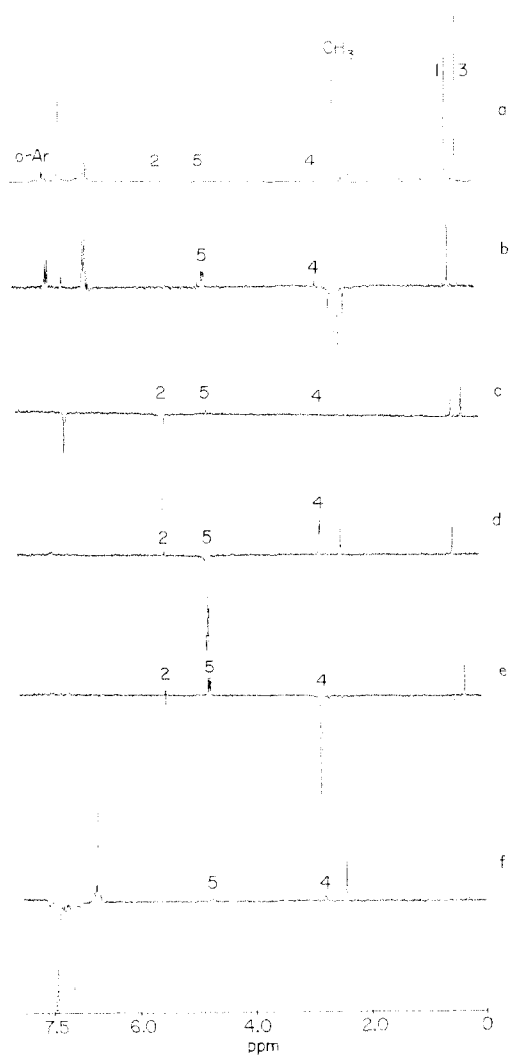


Fig. 2. Selected NOE data for  $[(\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2)\text{Fe}(\text{CO})\text{X}(\text{P}(\text{O-}o\text{-tol})_3)_1]$ . (a) No irradiation, (b) irradiation of *ortho* tolyl  $\text{CH}_3$  protons, (c) irradiation of H2, (d) irradiation of H5, (e) irradiation of H4, (f) irradiation of *ortho* tolyl aromatic protons.

CH correlated spectroscopy permitted assignment of the  $^{13}\text{C}$  spectra of the new complexes. Since all the  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectra contain analogous resonance positions and shapes, it was only necessary to record the spectra of two complexes in order to assign the spectra for the full series of complexes. This was achieved for  $\text{L} = \text{PMe}_2\text{Ph}$  and  $\text{xylNC}$ . The  $^{13}\text{C}$  NMR spectra of  $[(\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2)\text{Fe}(\text{CO})_2\text{L}]$  consisted of three ring resonances at  $\delta = 104$  ppm (intensity ratio 1),  $\delta = 92$  ppm (weak intensity; quaternary C atom) and  $\delta = 90$  ppm (intensity ratio 2). The data could readily be assigned to ring positions C2, C1/C3 and C4/C5 (Fig. 1). Introduction of chirality into the molecule by substitution of a CO ligand on iron,

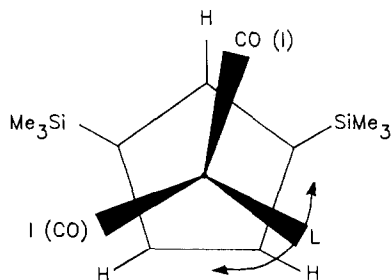


Fig. 3. Preferred conformations of the ligand set about the Fe–Centroid Axis for L = P(OMe)<sub>3</sub> and P(O-*o*-tol)<sub>3</sub>.

resulted in the presence of five C ring resonances in the <sup>13</sup>C NMR spectrum. For L = <sup>1</sup>BuNC and xylNC, C1 and C3 can readily be detected by their weak intensity and C2 by its positions at *ca.* 100 ppm. Resonances C4 and C5, thus correspond to the remaining two resonances at *ca.* 90 ppm. For L = group 15 donor ligand, two of the C atoms show coupling to phosphorus. From the CH correlated spectra, these were shown to correspond to C2 and C3. Assignment of all ring carbon resonances thus proved straightforward.

(ii) *NOE conformational analysis.* The NOE spectra also allow for the identification of the preferred solution conformers of  $[(\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2)\text{Fe}(\text{CO})(\text{L})\text{I}]$  [11]. We have, thus, determined the conformers from this information for L = P(OMe)<sub>3</sub> and P(O-*o*-tol)<sub>3</sub>. In the complex,  $[(\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2)\text{Fe}(\text{CO})\text{P}(\text{O-}o\text{-tol})_3\text{I}]$  irradiation of the ligand *ortho* proton aromatic resonance (Fig. 2f) results in growth of the downfield trimethylsilyl proton resonance (position 1 in Fig. 2; 0.5%) as well as the cyclopentadienyl ring proton resonance corresponding to positions 4 and 5 (3%), but no growth for proton 2. Irradiation of the *ortho* methyl proton of the phosphite ligand (Fig. 2b) results in significant growth in the signals for proton H5 and the downfield trimethylsilyl resonances. Irradiation of proton H2 (Fig. 2c), H5 (Fig. 2d) and H4 (Fig. 2e) confirms this result, as does irradiation of the trimethylsilyl resonances (not shown). It is thus proposed that the favoured conformation in solution is that shown in Fig. 3. Note that the data suggest a preferred conformation of the aromatic rings of the P(O-*o*-tol)<sub>3</sub> group, where the aromatic *ortho* proton is closer to H4 and the *ortho* methyl proton closer to H5. Further, the considerable barrier to free ring rotation (at room temperature) is apparent, presumably, because of the steric interaction between the P(O-*o*-tol)<sub>3</sub> ligand and the SiMe<sub>3</sub> groups. A ‘windscreen wiper’ type motion is thus proposed, with the P(O-*o*-tol)<sub>3</sub> ligand residing close to ring positions 3, 4 and 5, with access to position 2 not being favoured. To explore this phenomenon further, the NOE spectra of another complex containing a smaller ligand (P(OMe)<sub>3</sub>) was investigated. For the trimethylphosphite derivative, irradiation of the ligand methyl proton resonances results in equal growth in ring resonances 4 and 5 (2.5%), both trimethylsilyl resonances (0.2%), but, noticeably, no growth in ring proton resonance 2. This result was confirmed by irradiation of protons 2, 4, 5 and SiMe<sub>3</sub> protons which gave corresponding growth patterns for the P(OMe)<sub>3</sub> resonance. Thus restricted rotation about the Fe–ring centroid axis also occurs for the trimethylphosphite derivative with a preferred conformation for this complex as shown in Fig. 3.

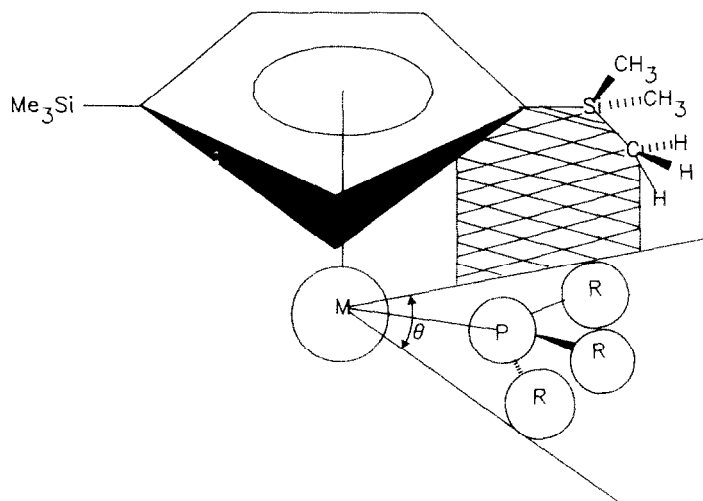


Fig. 4. Diagrammatic representation of the region in space (indicated area) in which a generalised Tolman cone angle for a  $PR_3$  ligand is found to be meaningful for complexes of the type  $[(\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2)\text{Fe}(\text{CO})(\text{PR}_3)]$ .

(iii) *Correlation between NMR parameters and steric and electronic parameters.*

One assumption associated with the Tolman cone angle is that the cone extends infinitely out in space from the apex. The limit in space is, however, defined by the length of the individual ligands (Fig. 4). By choosing a probe that extends further out in space than the individual ligands, this limit of the Tolman cone can, in principle, be established.

We have chosen to determine this by means of a multi-nuclear NMR approach, using the  $\text{SiMe}_3$  substituent on the cyclopentadienyl ring as a probe. From previous studies we have determined that a correlation exists between the *ortho* cyclopentadienyl ring protons and the steric and electronic parameters associated with the cyclopentadienyl substituents, which was shown to take the form  $\Delta = aE + b\theta + c$ , where  $\Delta$  is the chemical shift separation between the relevant two resonances,  $E$  is an electronic parameter,  $\theta$  is the measure of steric size and  $a$ ,  $b$ ,  $c$  are empirical constants [3]. The steric correlation was proposed to result from the presence of the apparent geminal *ortho* ring protons which are in close proximity to the stereogenic metal atom [3,12]. Addition of two substituents in a 1, 3 arrangement provides a situation in which a range of *geminal* groupings are generated, e.g.  $\text{SiMe}_3$  groups in positions 1 and 3, ring protons in positions 1 and 4 (or 5) and ring proton positions 4 and 5. Further, the series of *geminal* atoms are situated at various distances from the iron centre in the  $\text{SiMe}_3$  group (*viz.* Cl, Si, C, H atoms).

Focusing on ring positions, 1 and 3, a modest correlation between  $\Delta(\text{Cl-C3})$  and  $\theta$  ( $R^2 = 0.67$ ,  $mse = 7.31$ ) is observed, which improves significantly with the addition of an electronic parameter,  $\nu(\text{CO})$  ( $R^2 = 0.92$ ,  $mse = 7.14$ ). In this latter case, the most statistically correct model conforms to the relation  $\Delta(\text{Cl-C3}) = a \cdot \theta + b \cdot \nu(\text{CO}) + O$ , with all probability levels being significant to  $> 93\%$ . However, moving one atomic position away, to the silicon atoms, an excellent correlation between  $\Delta(\text{Si1-Si3})$  and  $\theta$  ( $R^2 = 0.90$ ,  $mse = 0.000918$ ) is found, which is signifi-



cantly improved by the inclusion of the electronic parameter,  $\nu(\text{CO})(R^2 = 0.96, mse = 0.00410)$ . Moving yet another atomic position from the silicon, a good correlation between  $\Delta(\text{C6-C7})$  and  $\theta$  ( $R^2 = 0.83, mse = 0.0361$ ) is observed, which is improved upon the inclusion of  $\nu(\text{CO})(R^2 = 0.89, mse = 0.0242)$ . Continuing this analysis, by moving yet another atomic position from the carbon atoms, no appreciable correlation between  $\Delta(\text{H6-H7})$  and  $\theta$  ( $R^2 = 0.68, mse = 0.00335$ ) is found and no correlation found with the addition of  $\nu(\text{CO})$ . Thus, we propose, that the atoms defining the limit of the Tolman cone are in close proximity, on average, to atoms Si and C1, C3 (Fig. 4). Ring atoms falling outside this range (e.g. H6) result in variable steric interaction with L.

Examination of the other *geminal* arrangements also shows differing correlation coefficients. In this instance, the data provide further information about the preferred conformations of the L group, but do not provide any additional information on the ligand cone length.

## Experimental

All phosphine, phosphite and isonitrile ligands were obtained from commercial sources and used without further purification. 1,3-Bis(trimethylsilyl)cyclopentadiene was synthesised from trimethylsilylcyclopentadiene by the published procedure [7]. All operations were performed under nitrogen in a well-ventilated fume cupboard, using freshly distilled, dry, deoxygenated solvents. Silica was used for column chromatography with benzene/hexane (50:50) as eluent unless otherwise stated. All column separations were performed under nitrogen, and the required fractions were collected under nitrogen. IR spectra were recorded on a Bruker IFS88 FTIR spectrometer in benzene. NMR spectra were recorded on a Bruker AC-200 spectrometer in  $\text{C}_6\text{D}_6$  or  $\text{C}_6\text{H}_6/\text{C}_6\text{D}_6$  solutions.

Silicon-29 NMR spectra were obtained by the INEPT [13] method. The delay time in the INEPT pulse sequence was optimised at  $\Delta$  (equivalent to  $1/(4J)$ ) = 0.114 s using measurements taken from an approximately 3M solution of  $\text{C}_5\text{H}_5\text{SiMe}_3$  in  $\text{CDCl}_3$ . Between 8000–14000 transients were recorded from each sample, using a spectral width of 4000 Hz and acquisition time of 1.02 s; digital resolution was 0.49 Hz/pt after zero-filling. Silicon-29 and phosphorus-31 NMR data are summarised in Table 4.

### Synthesis of $[(\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2)\text{Fe}(\text{CO})_2]_2$

Impure 1,3-bis(trimethylsilyl)cyclopentadiene [14] (3.887 g) was placed in a two-necked round-bottom flask with iron pentacarbonyl (19 g) and the stirred mixture was heated under nitrogen at  $150^\circ$  for 18 h. The excess of iron pentacarbonyl was removed *in vacuo* and the crude product dissolved in benzene. A bridging carbonyl peak in the IR spectrum indicated the presence of  $[(\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2)\text{Fe}(\text{CO})_2]_2$  and  $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Fe}(\text{CO})_2]_2$ , and this mixture was used (as described below) without further purification.

### Synthesis of $[(\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2)\text{Fe}(\text{CO})_2]_2$

The iron dimer mixture produced above,  $[(\eta^5\text{-C}_5\text{H}_{4-x}(\text{SiMe}_3)_x)\text{Fe}(\text{CO})_2]_2$  ( $x = 1, 2$ ; 79.63 g) was dissolved in  $\text{CH}_2\text{Cl}_2$  and an equimolar solution of iodine in dichloromethane was added under nitrogen. The reaction was monitored by noting the disappearance of the bridging carbonyl peak in the IR spectrum [15]. Once all

the dimer had reacted, the excess of iodine was removed by adding the mixture to an aqueous solution of sodium thiosulphate. The resulting  $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$  emulsion was broken by addition of a saturated sodium chloride solution. The organic layer was separated, and the aqueous layer back-extracted with benzene until almost clear. The organic layers were combined, dried ( $\text{MgSO}_4$ ), and the solvent removed *in vacuo* to yield a mixture of  $[(\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2)\text{Fe}(\text{CO})_2\text{I}]$  and  $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Fe}(\text{CO})_2\text{I}]$ , separated by column chromatography (first fraction  $[(\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2)\text{Fe}(\text{CO})_2\text{I}]$ , 1.165 g, 2.671 mmol; and the second fraction  $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Fe}(\text{CO})_2\text{I}]$ , 1.343 g, 3.690 mmol). Similar reaction between  $\text{C}_5\text{H}_4(\text{SiMe}_3)_2$ , prepared by the published method [14], and  $\text{Fe}(\text{CO})_5$  yielded > 95%  $[(\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2)\text{Fe}(\text{CO})_2\text{I}]$ .

#### Synthesis of $[(\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2)\text{Fe}(\text{CO})(\text{L})\text{I}]$ , $\text{L} = {}^i\text{BuNC}$ , $\text{xyNC}$

A solution of the isonitrile and  $[(\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2)\text{Fe}(\text{CO})_2\text{I}]$  (Table 5) in benzene was heated under reflux. The presence of both mono- and di-substituted isonitrile derivatives was detected by TLC (50:50 benzene/hexane). The products were separated by column chromatography (50:50 benzene/hexane as eluent, with gradual increase in the amount of benzene to 100%), yielding the desired complexes in 25–50% yield (Table 5).

#### Synthesis of $[(\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2)\text{Fe}(\text{CO})(\text{L})\text{I}]$ , $\text{L} = \text{P}(\text{OMe})_3$ , $\text{PMe}_2\text{Ph}$ , $\text{P}(\text{O}-o\text{-Tol})_3$ , $\text{PPh}_3$ , $\text{P}(m\text{-Tol})_3$ , $\text{P}(p\text{-Tol})_3$ , and $\text{P}(\text{CH}_2\text{Ph})_3$

The phosphorus donor ligands (0.8–2.5 mmol; Table 5) were added to a benzene solution of  $[(\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2)\text{Fe}(\text{CO})_2\text{I}]$  (*ca.* 0.5 mmol in 100 ml benzene; Table 5), with or without the  $[(\eta^5\text{-C}_5\text{H}_3)\text{Fe}(\text{CO})_2\text{I}]_2$  catalyst. The mixture was heated under reflux for between 2 and 18 h, after which TLC (50:50 benzene/hexane) showed the absence of starting material. The product was purified by column chromatography to yield the desired mono-substituted complexes. In some cases the presence of a salt,  $[(\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2)\text{Fe}(\text{CO})_2(\text{L})\text{I}]$  ( $\text{L} = \text{PMe}_2\text{Ph}$ ,  $\text{PPh}_3$ ,  $\text{P}(\text{CH}_2\text{Ph})_3$ ) was also detected. Details of quantities used and yields obtained are summarised in Table 5.

#### Measurement of cone angles

Cone angles, with values similar to those generated by Tolman using models, were generated on ALCHEMY [16]. For example, the measurement of the  $\text{PPh}_3$  ligand was achieved by arranging the phenyl rings in a propeller arrangement and measuring the cone enveloping the outermost atoms (the *ortho* ring protons in two cases and the *ipso* carbon atom in the third). Averaging these results, with their relative distributions, gave  $\theta = 145^\circ$  (lit.  $145^\circ$  [1]). Using this approach, the cone angle for  $\text{P}(m\text{-tol})_3$  was calculated to be  $148^\circ$  (the value determined with a maximum cone angle of  $194.4^\circ$  to the *meta* methyl protons; the minimum, as for  $\text{PPh}_3$ ,  $65^\circ$ ; and the intermediate, also as for  $\text{PPh}_3$ ,  $185^\circ$ ). This value differs from the value ( $165^\circ$ ) quoted by Giering [17]. The cone angle of  ${}^i\text{BuNC}$  ( $81^\circ$ ) was similarly measured (assuming an  $\text{Fe}-\text{C}$  bond length of  $1.8 \text{ \AA}$ , and a van der Waals radius of H to be  $1.00 \text{ \AA}$  [1]). The cone angle for  $\text{xyNC}$  ( $99^\circ$ ) was measured by noting that the aromatic ring is oriented perpendicularly [18], yielding a maximum cone angle. These values are in good agreement with the literature values ( ${}^i\text{BuNC}$ :  $68\text{--}70^\circ$ ,  $\text{xyNC}$ :  $53\text{--}106^\circ$ , using a  $\text{M}-\text{C}$  distance of  $1.92 \text{ \AA}$ ) [19].

## Conclusion

Using NMR spectroscopy the effective region in space of a Tolman cone has been determined. This is indicated by the good correlations between  $\Delta(C1-C3)$  or  $\Delta(Si1-Si3)$ ,  $\theta$  and  $\nu(CO)$ . Preferred ligand conformations have been determined by NOE spectroscopy, with L residing close to C5. Hindered rotation was also observed, with the group 15 donor ligands moving in a 'windscreen wiper' motion between the two silyl groups.

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