

Multiply substituted cyclopentadienyl metal complexes: I. Solid-state and solution conformational studies on $(\eta^5\text{-C}_5\text{Me}_4\text{R})\text{Fe}(\text{CO})(\text{L})\text{I}$ ($\text{R} = \text{H}, \text{}^t\text{Bu}$)

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Abstract

A series of $(\eta^5\text{-C}_5\text{Me}_4\text{R})\text{Fe}(\text{CO})(\text{L})\text{I}$ complexes ($\text{R} = \text{H}$, $\text{L} = \text{P}(\text{OMe})_3$, PMe_3 , $\text{P}(\text{O}^i\text{Pr})_3$, PPh_3 , $\text{P}(\text{O}-o\text{-tol})_3$, PBz_3 ; $\text{R} = \text{}^t\text{Bu}$, $\text{L} = \text{P}(\text{OMe})_3$, $\text{P}(\text{OPh})_3$, PPh_3) have been synthesized and characterized by spectroscopic techniques (IR, ^1H and ^{13}C NMR). NOE spectroscopy was used to ascertain that the L group resided, on average, away from the bulky ring substituents. Thus, for $\text{R} = \text{}^t\text{Bu}$, L was displaced away from the ${}^t\text{Bu}$ group, while, for $\text{R} = \text{H}$, L resided close to the H group. Crystal structure determinations were performed on $(\eta^5\text{-C}_5\text{Me}_4\text{H})\text{Fe}(\text{CO})(\text{PPh}_3)\text{I}$ (1) and $(\eta^5\text{-C}_5\text{Me}_4\text{}^t\text{Bu})\text{Fe}(\text{CO})[\text{P}(\text{OPh})_3]\text{I}$ (2). Both structures showed expected bond angle and bond length trends. The arrangement of the ligand set (L, CO, I) below the cyclopentadienyl ring in the solid state was the same as that found in solution. These results again reveal the importance of the steric effects associated with the cyclopentadienyl ring substituents on the properties of cyclopentadienyl–metal complexes in both the solution and solid states.

Keywords: Iron; Cyclopentadienyl; Carbonyl; Crystal structure; Ring substituents; Steric effects; NMR

1. Introduction

Since the first synthesis of ferrocene in 1951 [1], the cyclopentadienyl ring has played an important part in the development of both high- [2] and low-oxidation-state [3] organometallic chemistry. This importance relates to the ease of synthesis of cyclopentadienyl complexes, as well as the variation in both steric and electronic properties that can be associated with the ring with the introduction of ring substituents [4,5].

In earlier studies we have shown that substitution of even one of the C_5H_5 ring protons can lead to discernible changes in the physical and chemical properties of cyclopentadienyl–metal complexes [3,6]. Further substitution to give di-, tri-, tetra- and penta-substituted cyclopentadienyl ligands should lead to even more significant changes in these properties [5,7]. For instance, penta-substituted cyclopentadienyl ligands have been used to great advantage in the synthesis of cyclopentadienyl lanthanide and actinide complexes [8–10]. On a

practical note, substituted cyclopentadienyl metal complexes can have improved solubility [5] and stability [9,10] characteristics compared to the related unsubstituted cyclopentadienyl metal complexes [2].

To elaborate further on our earlier studies, we wished to assess the effect of $\text{C}_5\text{Me}_4\text{R}$ ligands on the properties of $(\eta^5\text{-C}_5\text{Me}_4\text{R})\text{Fe}(\text{CO})(\text{L})\text{I}$ complexes. In particular, by using R groups which were both smaller and larger than the Me group, steric effects could be probed by the ligand set attached to iron. To achieve this end we have chosen to synthesize a range of $(\eta^5\text{-C}_5\text{Me}_4\text{R})\text{Fe}(\text{CO})(\text{L})\text{I}$ complexes with $\text{R} = \text{H}$, ${}^t\text{Bu}$ and $\text{L} = \text{Group-15 donor ligands}$. These new complexes have been characterized both in solution (IR, NMR spectroscopy) and the solid state (X-ray crystallography; $\text{R} = \text{H}$, $\text{L} = \text{PPh}_3$; $\text{R} = \text{}^t\text{Bu}$, $\text{L} = \text{P}(\text{OPh})_3$). The data have been compared with earlier studies reported on $(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Fe}(\text{CO})(\text{L})\text{I}$ ($\text{R} = \text{}^t\text{Bu}$) complexes [6].

It is to be noted that numerous transition-metal complexes containing the $\text{C}_5\text{Me}_4\text{R}$ ligand have been reported in the literature, e.g. $\text{R} = \text{menthyl}$ [11], neomenthyl [11], $\text{C}(\text{H})(\text{Ph})\text{Et}$ [12], bridging group (i.e. of type $(\text{C}_5\text{Me}_4)_2\text{X}$, [9,13,14]) $(\text{CH}_2)_2\text{CH} = \text{CH}_2$ [15], H

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[16], CH_2X [17–20], CH_3 [21,22], etc. The $\text{C}_5\text{Me}_4\text{R}$ ligands have also been synthesized directly, by deprotonation of $(\eta^5\text{-C}_5\text{Me}_5)\text{ML}_x$ complexes and from organic fragments in which the metal acts as a template [23–25]. To our knowledge, this latter method is the only reported method for synthesizing the $\text{C}_5\text{Me}_4\text{Bu}$ ligand [22e].

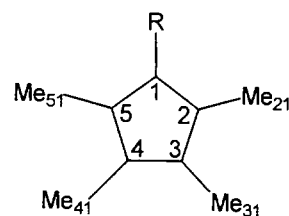


Fig. 1. Numbering scheme used for the $\eta^5\text{-C}_5\text{Me}_4\text{R}$ ligands.

2. Experimental section

2.1. General procedures

All experimental procedures were carried out under a dry nitrogen atmosphere, in dry deoxygenated solvents. The solvents were distilled and dried by standard procedures. A 100-W Hanovia UV irradiation lamp was used for photochemical reactions. Chromatography was carried out on Merck silica gel 60 (particle size, 0.063–0.200 mm). The 2,3,4,5-tetramethylcyclopent-2-enone and $\text{Mo}(\text{CO})_6$ were obtained from Fluka. The $\text{Fe}(\text{CO})_5$, $\text{Fe}_2(\text{CO})_9$ and $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2$ were obtained from Strem Chemicals. The ligands were obtained from various sources. $\text{C}_5\text{Me}_4\text{H}_2$ was prepared according to a literature method [9].

Melting points were determined on a Koffler micro hot-stage apparatus and are uncorrected. Infrared spectra were recorded on a Bruker IFS 88 FT-IR spectrometer, using NaCl solution cells. NMR spectra were recorded on a Bruker AC 200 NMR spectrometer, as C_6D_6 solutions. The numbering system used is indicated in Fig. 1, with protons numbered in relation to the ring-carbon numbering system. Microanalyses were performed by the Division of Energy Technology, CSIR, Pretoria, South Africa.

2.2. Synthesis of $[(\eta^5\text{-C}_5\text{Me}_4\text{H})\text{Fe}(\text{CO})_2]_2$

$\text{Fe}_2(\text{CO})_9$ (24.5 mmol, 8.93 g) was added to a solution of $\text{C}_5\text{Me}_4\text{H}_2$ (24.5 mmol, 3.00 g) in 100 ml benzene, and stirred at room temperature, under a nitrogen atmosphere. Further $\text{Fe}_2(\text{CO})_9$ was added after 17 h (11.0 mmol, 4.00 g) and 24 h (13.5 mmol, 4.93 g). The mixture was stirred for another 24 h, after which it was filtered through celite. The solvent was removed and the product purified by partial dissolution of the material in hexane, and filtration through celite. The residue was extracted with benzene, and recrystallized from benzene to give $[(\eta^5\text{-C}_5\text{Me}_4\text{H})\text{Fe}(\text{CO})_2]_2$. Further product was obtained by recrystallization from the hexane fraction. (Total yield: 2.30 g, 40.3%). $[(\eta^5\text{-C}_5\text{Me}_4\text{H})\text{Fe}(\text{CO})_2]_2$ was obtained as a purple-brown to rust-brown solid. ^1H NMR: δ 1.59 (s, 6H, $\text{H}_{21,51}/\text{H}_{31,41}$), 1.73 (s, 6H, $\text{H}_{21,51}/\text{H}_{31,41}$), 3.75 (s, 1H, H_1). ^{13}C NMR: δ 8.81 (s, $\text{C}_{21,51}/\text{C}_{31,41}$), 10.48 (s, $\text{C}_{21,51}/\text{C}_{31,41}$), 87.60 (s, C_1), 99.24 (s, $\text{C}_{2,5}/\text{C}_{3,4}$), 99.69 (s, $\text{C}_{2,5}/\text{C}_{3,4}$), 245.51 (s, CO). See Table 1 for further analytical and spectroscopic data.

2.3. Synthesis of $(\eta^5\text{-C}_5\text{Me}_4\text{H})\text{Fe}(\text{CO})_2\text{I}$

$[(\eta^5\text{-C}_5\text{Me}_4\text{H})\text{Fe}(\text{CO})_2]_2$ (4.29 mmol, 2.00 g) was dissolved in 100 ml chloroform, in a 500 ml round-bot-

Table 1
Analytical and spectroscopic data for $(\eta^5\text{-C}_5\text{Me}_4\text{R})$ complexes of iron

Complex	M.P. (°C)	IR ^a $\bar{\nu}(\text{CO})$ (cm^{-1})	Analysis ^b	
			C (%)	H (%)
$[(\eta^5\text{-C}_5\text{Me}_4\text{H})\text{Fe}(\text{CO})_2]_2$	163 (dec)	1929, 1753	56.59 (56.69)	5.58 (5.62)
$(\eta^5\text{-C}_5\text{Me}_4\text{H})\text{Fe}(\text{CO})_2\text{I}$	68.5–69	2023, 1976	36.45 (36.70)	3.51 (3.64)
$(\eta^5\text{-C}_5\text{Me}_4\text{H})\text{Fe}(\text{CO})(\text{L})\text{I}$				
L = PPh_3	148–151	1932	56.06 (56.59)	4.61 (4.75)
L = $\text{P}(\text{OMe})_3$	124–126	1942	34.06 (34.24)	4.81 (4.86)
L = PBz_3	112–115	1929	–	–
L = $\text{P}(\text{O}-o\text{-Tol})_3$	109–111	1957	54.17 (54.41)	4.92 (5.01)
L = $\text{P}(\text{O}-i\text{Pr})_3$	76–78	1933	42.51 (42.25)	6.43 (6.34)
L = PMe_3	125.5–127	1926	–	–
$[(\eta^5\text{-C}_5\text{Me}_4^t\text{Bu})\text{Fe}(\text{CO})_2]_2$	180 (dec)	1923, 1747	–	–
$(\eta^5\text{-C}_5\text{Me}_4^t\text{Bu})\text{Fe}(\text{CO})_2\text{I}$	163–164	2017, 1971	43.07 (43.30)	5.05 (5.09)
$(\eta^5\text{-C}_5\text{Me}_4^t\text{Bu})\text{Fe}(\text{CO})(\text{L})\text{I}$				
L = PPh_3	145–148	1921	–	–
L = $\text{P}(\text{OMe})_3$	100.5–102.5	1934	–	–
L = $\text{P}(\text{OPh})_3$	112.5–115	1954	54.51 (55.04)	5.01 (5.20)

^a Recorded in CH_2Cl_2 . ^b Calculated values in parentheses.

Table 2

Experimental details for the reaction: $(\eta^5\text{-C}_5\text{Me}_4\text{H})\text{Fe}(\text{CO})_2\text{I} + \text{L} \rightarrow (\eta^5\text{-C}_5\text{Me}_4\text{H})\text{Fe}(\text{CO})(\text{L})\text{I} + \text{CO}$

	L = PPh ₃	P(OMe) ₃	PBz ₃	P(O- <i>o</i> -Tol) ₃	P(O- ^{<i>i</i>} Pr) ₃	PMe ₃
Catalyst ^a	1	2	1	1	1	1
Reaction time (h)	18	2	17	1	1	4
Yield (%)	67	71	22	76	86	12
Chromatography eluent	Hexane/benzene	Hexane/benzene	Hexane/CH ₂ Cl ₂	Hexane/benzene	Hexane/benzene	Hexane/benzene
Recrystallisation solvent	Hexane/CH ₂ Cl ₂	Hexane	Hexane/CH ₂ Cl ₂	Hexane	Hexane	Hexane

^a 1 = $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$, 2 = $[(\eta^5\text{-C}_5\text{Me}_4\text{H})\text{Fe}(\text{CO})_2]_2$

tom flask. I₂ (4.29 mmol, 1.09 g) was dissolved in 100 ml chloroform, and approximately 75 ml of the iodine solution was added to the solution, which was stirred at room temperature under a nitrogen atmosphere. The reaction was monitored by IR spectroscopy. On completion of the reaction, the solution was washed with a saturated sodium thiosulphate solution (to remove excess I₂) and water, and dried with anhydrous MgSO₄, and the solvent was removed to yield a black oil (3.22 g). The product was purified by column chromatography (silica gel, hexane, and 3:1 hexane:dichloromethane mixtures as eluents) and obtained as a brown-black solid (2.36 g, 76% yield). ¹H NMR: δ 1.45 (s, 6H, H_{21,51}/H_{31,41}), 1.49 (s, 6H, H_{21,51}/H_{31,41}), 3.60 (s, 1H, H₁). ¹³C NMR: δ 10.12 (s, C_{21,51}/C_{31,41}), 11.72 (s, C_{21,51}/C_{31,41}), 80.91 (s, C₁), 96.26 (s, C_{2,5}/C_{3,4}), 98.47

(s, C_{2,5}/C_{3,4}), 216.03 (s, CO). See Table 1 for further analytical and spectroscopic data.

2.4. Synthesis of $(\eta^5\text{-C}_5\text{Me}_4\text{H})\text{Fe}(\text{CO})(\text{L})\text{I}$

The compounds $(\eta^5\text{-C}_5\text{Me}_4\text{H})\text{Fe}(\text{CO})(\text{L})\text{I}$, (L = P(OMe)₃, PPh₃, PBz₃, PMe₃, P(O-^{*i*}Pr)₃ and P(O-*o*-Tol)₃) were all synthesized by approximately the same procedure, outlined below. $(\eta^5\text{-C}_5\text{Me}_4\text{H})\text{Fe}(\text{CO})_2\text{I}$ (0.5 mmol, 0.18 g), L (0.55 mmol) and approximately 15 mg catalyst ($[(\eta^5\text{-C}_5\text{Me}_4\text{H})\text{Fe}(\text{CO})_2]_2$ or $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$) were heated together under reflux in benzene (20 ml), for 1 to 24 h. The reactions were followed by thin-layer chromatography. The reaction solvent was removed on a rotary evaporator and the product purified by column chromatography (silica gel)

Table 3

¹H NMR data for $(\eta^5\text{-C}_5\text{Me}_4\text{R})\text{Fe}(\text{CO})(\text{L})\text{I}$ (R = H, ^{*t*}Bu) complexes of iron^a

L	δH_1^b	δH_{21}^b	δH_{31}^b	δH_{41}^b	δH_{51}^b
<i>R</i> = H					
P(OMe) ₃ ^c	4.00 (3.4)	1.50	1.64 (1.5)	1.87 (1.8)	1.92
PMe ₃ ^d	3.35 (6.7)	1.19 (1.0)	1.66	1.99 (1.0)	1.89
P(O- ^{<i>i</i>} Pr) ₃ ^e	4.19 (3.6)	1.51 (1.1)	1.67 (1.3)	1.89 (2.2)	2.05
PPh ₃ ^f	2.97 (4.3)	1.20	1.72 (1.1)	2.10	1.51
P(O- <i>o</i> -Tol) ₃ ^g	3.78 (5.3)	1.18	1.62 (2.7)	2.06 (1.8)	1.78
PBz ₃ ^h	2.70 (3.3)	1.07	1.55 (0.8)	1.95	1.61
<i>R</i> = ^{<i>t</i>} Bu					
P(OMe) ₃ ⁱ	1.43	1.66	1.60 (1.1)	1.88 (0.5)	2.26 (1.9)
P(OPh) ₃ ^j	1.40	1.68	1.71 (1.2)	1.86 (0.4)	2.25 (2.2)
PPh ₃ ^k	1.56	1.56	0.82	1.21	2.47

^a Recorded in C₆D₆. δ , in ppm, relative to SiMe₄.^b $J_{\text{H-P}}$, in Hz, given in parentheses.^c P(OMe)₃: 3.47 (d, 9H, $J_{\text{P-H}} = 10.8$ Hz, P(OCH₃)₃)^d PMe₃: 1.16 (d, 9H, $J_{\text{P-H}} = 9.4$ Hz, P(CH₃)₃)^e P(O-^{*i*}Pr)₃: 1.21 (d, 9H, $J_{\text{H-H}} = 6.1$ Hz, P(OCH(CH₃)(CH₃))₃), 1.23 (d, 9H, $J_{\text{H-H}} = 6.1$ Hz, P(OCH(CH₃)(CH₃))₃), 4.84 (d of septets, 3H, $J_{\text{P-H}} = 8.6$ Hz, $J_{\text{H-H}} = 6.1$) P(OCH(CH₃)(CH₃))₃^f PPh₃: 6.99 (m, 9H, H_{m,p} of Ph), 7.83 (m, 6H, H_o of Ph)^g P(O-*o*-Tol)₃: 2.37 (s, 9H, P(O-*o*-CH₃C₆H₄)), 6.78 (m, 9H, H_{m,p} of Ph), 7.58 (d, 3H, $J_{\text{P-H}} = 8.1$ Hz, H_o of Ph)^h PBz₃: 3.39 (dd, 3H, $J_{\text{P-H}} = 9.8$ Hz, $J_{\text{H-H}} = 14.7$ Hz, P(CH₂H_bC₆H₅)₃), 3.60 (dd, 3H, $J_{\text{P-H}} = 6.4$ Hz, $J_{\text{H-H}} = 14.6$ Hz, P(CH₂H_bC₆H₅)₃), 7.05 (m, 15H, P(CH₂H_bC₆H₅)₃)ⁱ P(OMe)₃: 3.46 (d, 9H, $J_{\text{P-H}} = 10.5$ Hz, P(OCH₃)₃)^j P(OPh)₃: 6.79 (m, 3H, H_p of Ph), 6.95 (m, 6H, H_m of Ph), 7.36 (m, 6H, H_o of Ph).^k PPh₃: 6.99 (m, 9H, H_{m,p} of Ph), 7.85 (m, 6H, H_o of Ph)

and recrystallization. For more details, see Table 2; also see Table 1 for the analytical and spectroscopic data, Table 3 for the ^1H NMR data and Table 4 for the ^{13}C NMR data of these new compounds.

2.5. Synthesis of *tert*-butyl-tetramethylcyclopentadiene ($\text{C}_5\text{Me}_4\text{BuH}$)

2,3,4,5-Cyclopent-2-ene (25.0 mmol, 3.46 g) and 20 ml dry diethyl ether were placed in a flame-dried 100 ml round-bottom flask, with a stirrer bar. The solution was cooled to -78°C , with stirring, and $^t\text{BuLi}$ (27.5 mmol, 1.7 M, 16.2 ml) was added dropwise via a syringe. The reaction mixture was stirred at -78°C for 1 h, quenched by the addition of water (approximately 1 ml), and allowed to warm up to room temperature slowly (1 h). A few drops of concentrated H_2SO_4 were added, the reaction mixture stirred for a further 15 min, washed with concentrated sodium bicarbonate solution, and then twice by water. The organic layer was then dried with anhydrous MgSO_4 , and the solvent was removed (crude yield, 3.91 g). The product was purified by column chromatography (silica gel, eluent hexane). The clear to light-yellow product eluted rapidly, as two bands, corresponding presumably to different isomers of the substituted cyclopentadiene (2.95 g, 66% yield). $\text{C}_5\text{Me}_4\text{BuH}$ (isomeric mixture). ^1H NMR: δ 0.86–0.88

(singlets, $\text{C}_5\text{Me}_4\text{BuH}$), 0.94–1.57 (singlets, $\text{C}_5\text{Me}_4\text{BuH}$), 1.9–2.6 (multiplets, $\text{C}_5\text{Me}_4\text{BuH}$).

2.6. Synthesis of $[(\eta^5\text{-C}_5\text{Me}_4\text{Bu})\text{Fe}(\text{CO})_2]_2$

The dimer was obtained from the reaction between the cyclopentadienyl ligand and $\text{Fe}(\text{CO})_5$. *Tert*-butyl-tetramethyl-cyclopentadiene (10 mmol, 1.78 g) and $\text{Fe}(\text{CO})_5$ (30 mmol, 5.88 g) were heated together under reflux in octane (70 ml) for three days. The reaction mixture was cooled to room temperature, and filtered under a nitrogen atmosphere through a very thin layer of celite (about 1 cm thick and about 5 cm diameter), with benzene and dichloromethane as solvents. Red-purple crystals separated after partial removal of the solvent (0.44 g, 15% yield). $[(\eta^5\text{-C}_5\text{Me}_4\text{Bu})\text{Fe}(\text{CO})_2]_2$. ^1H NMR: δ 1.50 (s, 6H, $\text{H}_{21,51}/\text{H}_{31,41}$), 1.56 (s, 9H, ^tBu), 1.83 (s, 6H, $\text{H}_{21,51}/\text{H}_{31,41}$). See Table 1 for further analytical and spectroscopic data.

2.7. Synthesis of $(\eta^5\text{-C}_5\text{Me}_4\text{Bu})\text{Fe}(\text{CO})_2\text{I}$

The dimer, $[(\eta^5\text{-C}_5\text{Me}_4\text{Bu})\text{Fe}(\text{CO})_2]_2$ (0.78 mmol, 0.45 g), was dissolved in 30 ml chloroform. I_2 (0.78 mmol, 0.20 g), in chloroform (40 ml), was added in small portions, over a period of 3.5 h. During this time, the mixture was stirred at room temperature under a

Table 4
 ^{13}C NMR data for $(\eta^5\text{-C}_5\text{Me}_4\text{H})\text{Fe}(\text{CO})(\text{L})\text{I}^a$

L	δ C ₂₁	δ C ₃₁	δ C ₄₁	δ C ₅₁	δ C ₁	δ C ₂ –C ₅ ^b	δ CO ^b
<i>R = H</i>							
$\text{P}(\text{OMe})_3$ ^c	11.21	9.96	11.41	12.33	82.80	85.11, 95.83(3.6) 93.85, 98.27(4.7)	221.95(44.2)
PMe_3 ^d	11.30	10.18	12.41	12.71	84.25	77.92, 94.38(2.5) 91.24, 98.82(4.5)	221.81(32.5)
$\text{P}(\text{O-}^i\text{Pr})_3$ ^e	11.10	10.05	11.44	12.71	84.58	82.24, 96.26(3.4) 94.54, 97.01(5.6)	222.56(45.5)
PPh_3 ^f	11.08	10.53	12.68	11.80	80.21	86.70, 91.25(3.4) 95.32, 100.10(1.6)	223.86(29.8)
$\text{P}(\text{O-}o\text{-Tol})_3$ ^g	10.80	9.79	12.71	11.98	79.34	86.41, 93.48(6.1) 94.22, 103.54(4.6)	221.32(41.6)
<i>R = ^tBu</i>							
$\text{P}(\text{OMe})_3$ ^h	13.36	10.24	11.28	15.48	ⁱ	86.55, 93.30	ⁱ
$\text{P}(\text{OPh})_3$ ^j	13.52	10.53	11.41	15.62	87.25	95.12, 95.87 ⁱ , 99.38(4.5)	221.23

^a Recorded in C_6D_6 . δ , in ppm, is relative to C_6D_6 (central peak at 128.03 ppm)

^b $J_{\text{C-P}}$, in Hz, are given in parentheses.

^c $\text{P}(\text{OMe})_3$: 53.40 (d, $J_{\text{C-P}} = 5.9$ Hz, $\text{P}(\text{OCH}_3)_3$)

^d PMe_3 : 20.54 (d, $J_{\text{C-P}} = 29.9$ Hz, $\text{P}(\text{CH}_3)_3$)

^e $\text{P}(\text{O-}^i\text{Pr})_3$: 24.22(d, $J_{\text{C-P}} = 2.9$ Hz, $\text{P}(\text{OCH}(\text{CH}_3)(\text{CH}_3))_3$), 24.26 (d, $J_{\text{C-P}} = 1.8$ Hz, $\text{P}(\text{OCH}(\text{CH}_3)(\text{CH}_3))_3$), 70.52 (d, $J_{\text{C-P}} = 6.8$ Hz, $\text{P}(\text{OCH}(\text{CH}_3)\text{CH}_3)_3$)

^f PPh_3 : 128.14 (s, C_m of Ph), 129.88 (s, C_p of Ph), 134.70 (d, $J_{\text{C-P}} = 9.5$ Hz, C_o of Ph), 136.77 (d, $J_{\text{C-P}} = 40.0$ Hz, C_i of Ph).

^g $\text{P}(\text{O-}o\text{-Tol})_3$: 17.61 (s, $\text{P}(\text{O-}o\text{-CH}_3\text{C}_6\text{H}_4)_3$), 120.61 (d, $J_{\text{C-P}} = 3.7$ C_oH of Ph), 124.50, 126.80, 131.74 (singlets, $\text{C}_{m,p}$ of Ph), 129.76 (d, $J_{\text{C-P}} = 5.4$ Hz, C_oMe of Ph), 151.52 (d, $J_{\text{C-P}} = 12.7$ Hz, C_i of Ph)

^h $\text{P}(\text{OMe})_3$: 53.45 (d, $J_{\text{C-P}} = 6.6$ Hz, $\text{P}(\text{OCH}_3)_3$); δ $\text{C}(\text{CH}_3)_3 = 32.28$, δ $\text{C}(\text{CH}_3)_3 = 33.70$

ⁱ not observed

^j $\text{P}(\text{OPh})_3$: 121.71–129.63; δ $\text{C}(\text{CH}_3)_3 = 32.23$, δ $\text{C}(\text{CH}_3)_3 = 33.74$. (m, $\text{P}(\text{OPh})_3$: $\text{C}_{o,m,p}$), 152.74 (d, $J_{\text{C-P}} = 13.5$ Hz, $\text{P}(\text{OPh})_3$: C_{ipso}).

nitrogen atmosphere, and the reaction was monitored by IR spectroscopy. The appearance of the carbonyl stretching peaks for the iodo derivative ($\bar{\nu}(\text{CO}) (\text{CH}_2\text{Cl}_2) = 2017, 1971 \text{ cm}^{-1}$), and the disappearance of the carbonyl peaks of the dimer ($\bar{\nu}(\text{CO}) (\text{CH}_2\text{Cl}_2) = 1923, 1747 \text{ cm}^{-1}$) indicated the progress of the reaction. When all the dimer had reacted, the mixture was washed twice with concentrated sodium thiosulphate, and then twice with water. The chloroform layer was dried with anhydrous MgSO_4 , and the solvent was evaporated off (crude yield 0.64 g). The product was purified by column chromatography (silica, hexane (100%) to hexane:dichloromethane mixtures (up to a ratio of 3:2), as eluents). The product recrystallized from the solvent as the solvent was partially removed on the rotary evaporator and the fine red-brown crystals were filtered off (0.56 g, 86% yield). $(\eta^5\text{-C}_5\text{Me}_4\text{Bu})\text{Fe}(\text{CO})_2\text{I}$. $^1\text{H NMR}$: δ 1.12 (s, 9H, ^tBu), 1.61, 1.73 (s, 6H, $\text{H}_{21,51}/\text{H}_{31,41}$). $^{13}\text{C NMR}$: δ 10.79 (s, $\text{C}_{21,51}/\text{C}_{31,41}$), 13.73 (s, $\text{C}_{21,51}/\text{C}_{31,41}$), 32.16 (s, $\text{C}(\text{CH}_3)_3$), 33.26 (s, $\text{C}(\text{CH}_3)_3$), 97.52 (s, $\text{C}_1/\text{C}_{2,5}/\text{C}_{3,4}$), 98.67 (s, $\text{C}_1/\text{C}_{2,5}/\text{C}_{3,4}$), 101.10 (s, $\text{C}_1/\text{C}_{2,5}/\text{C}_{3,4}$), 216.83 (s, CO). See Table 1 for further analytical and spectroscopic data.

2.8. Synthesis of $(\eta^5\text{-C}_5\text{Me}_4\text{Bu})\text{Fe}(\text{CO})(\text{L})\text{I}$

2.8.1. Catalytic procedure

$(\eta^5\text{-C}_5\text{Me}_4\text{Bu})\text{Fe}(\text{CO})_2\text{I}$ (0.50 mmol, 0.21 g), L (0.55 mmol) and about 10 mg catalyst, $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$, were heated under reflux in 25 ml benzene. The reactions were followed by thin-layer chromatography.

2.8.1.1. $L = \text{P}(\text{OMe})_3$. All the starting material, $(\eta^5\text{-C}_5\text{Me}_4\text{Bu})\text{Fe}(\text{CO})_2\text{I}$, was used up after 18 h, and the product, $(\eta^5\text{-C}_5\text{Me}_4\text{Bu})\text{Fe}(\text{CO})\{\text{P}(\text{OMe})_3\}\text{I}$, was obtained as a dark brown solid (0.10 g, 39% yield) after purification by column chromatography (silica gel, hexane/benzene mixtures as eluent).

2.8.1.2. $L = \text{PPh}_3$. The desired product, $(\eta^5\text{-C}_5\text{Me}_4\text{Bu})\text{Fe}(\text{CO})\{\text{PPh}_3\}\text{I}$, could not be obtained in significant yield, even after two days reaction time. However, the ‘‘catalyst’’ formed a product, $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})\{\text{PPh}_3\}\text{I}$.

2.8.1.3. $L = \text{P}(\text{O}Ph)_3$. The desired product was formed in very low yield, after a two-day reaction. The reaction mixture was purified by column chromatography (silica gel, hexane/dichloromethane mixtures as eluent), which separated excess $\text{P}(\text{O}Ph)_3$, unreacted starting material, $(\eta^5\text{-C}_5\text{Me}_4\text{Bu})\text{Fe}(\text{CO})_2\text{I}$ (0.03 g), product, $(\eta^5\text{-C}_5\text{Me}_4\text{Bu})\text{Fe}(\text{CO})\{\text{P}(\text{O}Ph)_3\}\text{I}$ (0.03 g), and ‘‘catalytic product’’, $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})\{\text{P}(\text{O}Ph)_3\}\text{I}$ (0.05 g).

2.8.2. Photochemical reaction

$(\eta^5\text{-C}_5\text{Me}_4\text{Bu})\text{Fe}(\text{CO})_2\text{I}$ (0.200 mmol, 0.0832 g) and L (0.240 mmol), dissolved in THF (40 ml), were irradiated with UV light. The reactions were followed by thin-layer chromatography, which indicated completion of reaction after 2.3 h ($L = \text{PPh}_3$) and 1.8 h ($L = \text{P}(\text{O}Ph)_3$). The products were purified by column chromatography (silica gel, hexane: $\text{CH}_2\text{Cl}_2 = 9:1$ to 6:4 as eluent). $(\eta^5\text{-C}_5\text{Me}_4\text{Bu})\text{Fe}(\text{CO})\{\text{PPh}_3\}\text{I}$ was obtained as a light brown solid by recrystallization from toluene at 0°C . $(\eta^5\text{-C}_5\text{Me}_4\text{Bu})\text{Fe}(\text{CO})\{\text{P}(\text{O}Ph)_3\}\text{I}$ was obtained as a green solid by recrystallization from CH_2Cl_2 /hexane at room temperature. See Table 1 for the analytical and spectroscopic data, Table 3 for the $^1\text{H NMR}$ data and Table 4 for the $^{13}\text{C NMR}$ data of these $(\eta^5\text{-C}_5\text{Me}_4\text{Bu})\text{Fe}(\text{CO})(\text{L})\text{I}$ compounds.

2.9. Crystal structure determination

Single crystals of $(\eta^5\text{-C}_5\text{Me}_4\text{H})\text{Fe}(\text{CO})(\text{I})(\text{PPh}_3)$ (**1**) and $(\eta^5\text{-C}_5\text{Me}_4\text{Bu})\text{Fe}(\text{CO})(\text{I})\{\text{P}(\text{O}Ph)_3\}$ (**2**) were obtained by recrystallization from CH_2Cl_2 /hexane at 0°C and were mounted on glass fibres. Crystallographic analyses were based on room-temperature X-ray diffraction data collected with an Enraf–Nonius CAD4 four-circle single-crystal diffractometer, using graphite-monochromated Mo K α radiation. Cell constants were measured and refined from 25 accurately measured reflections in the range $15^\circ \leq \theta \leq 20^\circ$. Standard reflections were measured every hour of exposure time. Each data set was corrected for crystal decay and Lorentz-polarization effects. Data reduction was done using the

Table 5
Crystallographic data for **1** and **2**

Chem. formula	$\text{FeC}_{28}\text{H}_{28}\text{OPI}$	$\text{FeC}_{32}\text{H}_{36}\text{O}_4\text{PI}$
F.W.	594.254	698.361
Cryst. systems	Monoclinic	Monoclinic
Space group	C 2/c	P2 ₁ /c
<i>a</i> (Å)	23.863(3)	20.695(2)
<i>b</i> (Å)	15.353(2)	8.7436(6)
<i>c</i> (Å)	17.560(2)	17.632(3)
<i>V</i> (Å ³)	5100.8(13)	3132.71(63)
α (deg)	–	–
β (deg)	127.547(10)	100.93(1)
γ (deg)	–	–
<i>Z</i>	8	4
<i>d</i> _{calc} (g cm ⁻³)	1.547	1.480
<i>T</i> (°C)	23 ± 2	23 ± 2
2 α range (deg)	6–54	6–60
No. of data colltd.	5768	5222
No. of data observed	3171	2476
No. of variables	264	250
<i>R</i> ^a	0.047	0.071
<i>R</i> _w ^b	0.039	0.059

$$^a R = \sum ||F_o| - |F_c|| \quad ^b R_w = \sum (||F_o| - |F_c|| w^{1/2}) / \sum (|F_o| w^{1/2})$$

XTAL suite of programs [26]. Analytical absorption corrections using the NRCVAX suite of programs [27] were applied to both data sets. Unit-cell parameters and details of the data collections are given in Table 5.

The structures of **1** and **2** were solved by Patterson methods, and subsequent Fourier synthesis revealed the remaining non-hydrogen atoms. Refinement was carried out using full-matrix least-squares calculations in which the hydrogen atoms (except the H1 cyclopentadienyl ring atom) were included at calculated positions. All the non-hydrogen atoms were refined anisotropically for structure **1**. For structure **2** the phenyl carbon atoms were not refined anisotropically, although the remaining non-hydrogen atoms were. The phenyl rings were refined as rigid bodies for both **1** and **2**. The *R* values converged to 0.047 and 0.071 for structures **1** and **2** respectively. All calculations were performed using the SHELX set of programs [28].

Final positional parameters are found in Tables 6 and 7, and selected bond lengths and angles for **1** and **2** are given in Table 8. Figs. 2 and 3, obtained using ORTEP [29], show the structures of **1** and **2**.

Details of crystallographic parameters, a table of

Table 6
Fractional coordinates and isotropic displacement parameters of the non-hydrogen atoms of structure **1**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
I	0.67146(2)	0.51621(3)	0.40714(3)	*0.0629(3)
FE	0.68556(4)	0.48866(5)	0.27111(5)	*0.0383(4)
P	0.80402(7)	0.49549(9)	0.3730(1)	*0.0354(7)
O	0.6762(3)	0.3077(3)	0.2897(3)	*0.073(4)
C(1)	0.6655(3)	0.5090(5)	0.1412(4)	*0.063(4)
C(2)	0.6706(3)	0.5919(4)	0.1777(4)	*0.056(4)
C(3)	0.6182(3)	0.5979(4)	0.1882(4)	*0.057(4)
C(4)	0.5805(3)	0.5171(5)	0.1580(4)	*0.064(4)
C(5)	0.6087(3)	0.4637(4)	0.1257(5)	*0.067(4)
C(6)	0.7168(4)	0.6655(5)	0.1884(6)	*0.099(6)
C(7)	0.6005(4)	0.6783(5)	0.2186(6)	*0.113(7)
C(8)	0.5152(3)	0.4959(7)	0.1517(6)	*0.131(7)
C(9)	0.5798(5)	0.3753(6)	0.0768(6)	*0.133(7)
C(10)	0.6840(3)	0.3738(5)	0.2878(4)	*0.054(4)
C(11)	0.8466(2)	0.5866(2)	0.4588(3)	*0.037(3)
C(12)	0.9184(2)	0.5844(2)	0.5363(3)	*0.047(4)
C(13)	0.9497(2)	0.6551(2)	0.5990(3)	*0.055(4)
C(14)	0.9092(2)	0.7279(2)	0.5844(3)	*0.061(5)
C(15)	0.8374(2)	0.7301(2)	0.5069(3)	*0.064(5)
C(16)	0.8061(2)	0.6594(2)	0.4441(3)	*0.053(4)
C(17)	0.8506(2)	0.4015(3)	0.4529(3)	*0.044(4)
C(18)	0.9094(2)	0.3653(3)	0.4654(3)	*0.058(4)
C(19)	0.9430(2)	0.2930(3)	0.5249(3)	*0.081(5)
C(20)	0.9179(2)	0.2568(3)	0.5718(3)	*0.089(6)
C(21)	0.8592(2)	0.2931(3)	0.5592(3)	*0.087(6)
C(22)	0.8255(2)	0.3654(3)	0.4998(3)	*0.063(4)
C(23)	0.8447(2)	0.5013(2)	0.3115(3)	*0.041(3)
C(24)	0.8287(2)	0.4352(2)	0.2466(3)	*0.053(4)
C(25)	0.8565(2)	0.4379(2)	0.1960(3)	*0.069(5)
C(26)	0.9002(2)	0.5066(2)	0.2104(3)	*0.077(5)
C(27)	0.9162(2)	0.5727(2)	0.2754(3)	*0.074(5)
C(28)	0.8884(2)	0.5701(2)	0.3259(3)	*0.053(4)

Table 7
Fractional coordinate and isotropic displacement parameters of the non-hydrogen atoms of structure **3**

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
FE	0.1752(1)	0.20317(9)	0.1540(2)	*0.0381(6)
I	0.21625(5)	0.08862(5)	0.29064(9)	*0.0632(4)
P	0.2717(2)	0.2857(2)	0.1493(3)	*0.0367(9)
O(1)	0.2697(5)	0.4287(4)	0.0895(7)	*0.050(2)
O(2)	0.3248(4)	0.3393(4)	0.2223(7)	*0.045(2)
O(3)	0.3195(5)	0.1729(4)	0.1168(7)	*0.057(2)
C(1)	0.0756(7)	0.1372(6)	0.111(1)	*0.036(2)
C(2)	0.1137(7)	0.0006(6)	0.125(1)	*0.039(2)
C(3)	0.1657(7)	0.0079(7)	0.082(1)	*0.051(2)
C(4)	0.1589(7)	0.1417(7)	0.037(1)	*0.059(2)
C(5)	0.1056(7)	0.2224(6)	0.053(1)	*0.047(2)
C(6)	0.0124(9)	0.1633(7)	0.137(1)	*0.074(2)
C(7)	-0.0216(8)	0.3159(7)	0.117(1)	*0.084(2)
C(8)	0.0209(7)	0.1546(7)	0.227(1)	*0.071(2)
C(9)	-0.0401(9)	0.0420(7)	0.101(1)	*0.089(2)
C(10)	0.1037(7)	-0.1400(6)	0.171(1)	*0.057(2)
C(11)	0.2178(7)	-0.1203(6)	0.076(1)	*0.065(2)
C(12)	0.1934(6)	0.1785(6)	-0.028(1)	*0.059(2)
C(13)	0.0833(7)	0.3727(7)	0.011(1)	*0.074(2)
C(14)	0.1498(9)	0.3780(6)	0.193(1)	*0.072(2)
O(4)	0.1320(7)	0.4813(5)	0.2140(8)	*0.092(2)
C(2b)	0.3535(4)	0.3892(3)	0.3556(6)	0.057(2)
C(3b)	0.3516(4)	0.4827(3)	0.4193(6)	0.091(3)
C(4b)	0.3152(4)	0.6180(3)	0.4102(6)	0.102(3)
C(5b)	0.2807(4)	0.6598(3)	0.3373(6)	0.089(3)
C(6b)	0.2826(4)	0.5664(3)	0.2736(6)	0.083(3)
C(1b)	0.3189(4)	0.4311(3)	0.2828(6)	0.049(2)
C(2a)	0.3367(4)	0.4487(3)	-0.0075(6)	0.057(2)
C(3a)	0.3904(4)	0.5113(3)	-0.0340(6)	0.074(3)
C(4a)	0.4318(4)	0.6147(3)	0.0121(6)	0.072(2)
C(5a)	0.4195(4)	0.6555(3)	0.0845(6)	0.075(3)
C(6a)	0.3659(4)	0.5930(3)	0.1109(6)	0.065(2)
C(1a)	0.3244(4)	0.4896(3)	0.0649(6)	0.039(2)
C(2c)	0.4349(3)	0.1453(3)	0.1264(6)	0.059(2)
C(3c)	0.4944(3)	0.0784(3)	0.1608(6)	0.084(3)
C(4c)	0.4966(3)	-0.0232(3)	0.2222(6)	0.077(3)
C(5c)	0.4391(3)	-0.0578(3)	0.2492(6)	0.085(3)
C(6c)	0.3796(3)	0.0091(3)	0.2148(6)	0.067(2)
C(1c)	0.3775(3)	0.1107(3)	0.1534(6)	0.051(2)

anisotropic thermal factors, and a complete list of bond distances and angles for each structure have been deposited at the Cambridge Crystallographic Data Centre.

3. Results and discussion

3.1. Synthesis

The reduction of 2,3,4,5-tetramethylcyclopent-2-enone by LiAlH₄, followed by acid-catalysed dehydration, yielded tetramethylcyclopentadiene [9]. This ligand was reacted with Fe₂(CO)₉ and produced [(η⁵-C₅Me₄H)Fe(CO)₂]₂ as purple-brown crystals. The cleavage of this dimer with iodine gave a high yield of dark-brown crystals of (η⁵-C₅Me₄H)Fe(CO)₂I. Reaction of (η⁵-C₅Me₄H)Fe(CO)₂I, with L (L = P(OMe)₃,

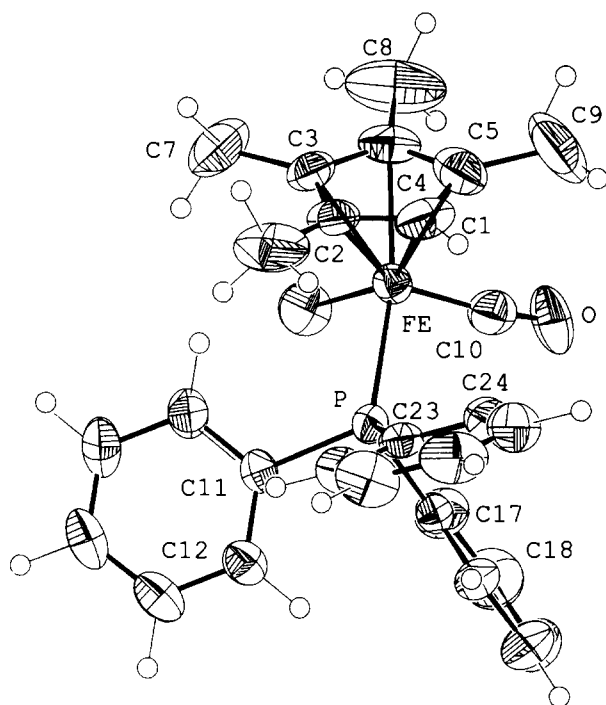


Fig. 2. ORTEP plot of 1 (side view).

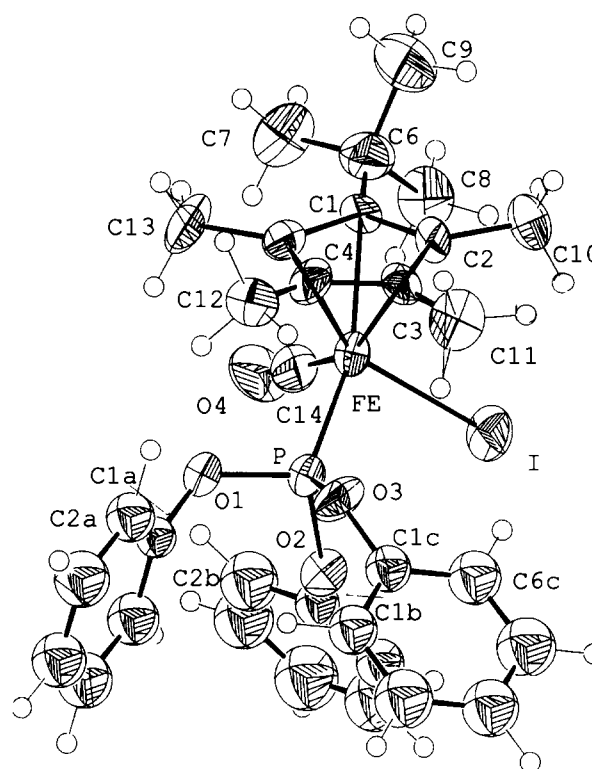


Fig. 3. ORTEP plot of 2 (side view).

$P(O^iPr)_3$ in the presence of $[(\eta^5-C_5Me_4H)Fe(CO)_2]_2$ as catalyst gave the required product (Table 2). The larger phosphite, $P(O-o-Tol)_3$, and the phosphines PMe_3 , PPh_3 and PBz_3 required the more active catalyst, $[(\eta^5-C_5H_5)Fe(CO)_2]_2$, to produce the required substituted complex. No reaction between $(\eta^5-C_5Me_4H)Fe(CO)I$ and L was observed in the absence of catalyst under similar reaction conditions. Presumably electronic and steric arguments account for these observations.

When $[(\eta^5-C_5H_5)Fe(CO)_2]_2$ was used as the catalyst, both $(\eta^5-C_5H_5)Fe(CO)(L)I$ and the dimer $[(\eta^5-C_5Me_4H)Fe(CO)_2]_2$ were formed as side-products, as

detected by NMR spectroscopy. The formation of these products from the catalyst, $[(\eta^5-C_5H_5)Fe(CO)_2]_2$, during thermal reaction between $(\eta^5-C_5Me_4H)Fe(CO)_2I$ and L, can be readily rationalized by a radical mechanism:

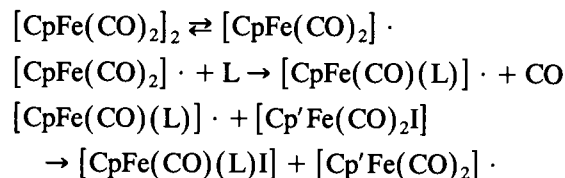


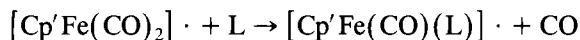
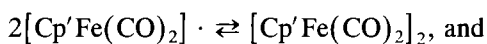
Table 8
Comparison between bond lengths and bond angles for 1, 2 and 3

	1	2	3
Cp ^a : C–C (Å)	1.37(1)–1.43(1) ^b	1.38(2)–1.50(2) ^c	1.385(8)–1.425(8)
Cp ^a : C–Me (Å)	1.50(1)–1.53(1)	1.49(2)–1.57(2)	–
Cp ^a : C– ⁱ Bu (Å)	–	1.50(2)	1.522(7)
Fe–Cen (Å)	1.737	1.741	1.731
Fe–CO (Å)	1.792(7)	1.794(13)	1.769(6)
C–O (Å)	1.036(9)	1.069(16)	1.095(6)
Fe–I (Å)	2.641(1)	2.599(19)	2.618(1)
Fe–P (Å)	2.245(2)	2.14(4)	2.234(1)
Fe–C–O (deg)	172.5(5)	176.9(12)	178.3(5)
Cen–Fe–CO (deg)	121.2	122.1	127.2
Cen–Fe–I (deg)	121.6	122.1	120.0
Cen–Fe–P (deg)	128.3	125.9	123.1

^a Cp = cyclopentadienyl

^b C1–C2, 1.391(11); C2–C3, 1.374(13); C3–C4, 1.430(10); C4–C5, 1.383(11); C5–C1, 1.396(12).

^c C1–C2, 1.427(15); C2–C3, 1.430(20); C3–C4, 1.409(15); C4–C5, 1.382(18); C5–C1, 1.504(17)



etc., where $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ and $\text{Cp}' = \eta^5\text{-C}_5\text{H}_4\text{Me}$.

Successful synthesis of the *free tert*-butyltetramethylcyclopentadiene ligand was achieved in this study by the reduction of 2,3,4,5-tetramethylcyclopent-2-enone with $^1\text{BuLi}$ at low temperature (-78°C), followed by hydration to the tertiary alcohol. Water was eliminated from this alcohol by acid-catalysed dehydration, to give the desired product. *Tert*-butyltetramethylcyclopentadiene was obtained as a light-yellow liquid after purification by column chromatography. Vacuum distillation led to decomposition of this material, with the formation of a very-high-boiling, darker residue over time.

$[(\eta^5\text{-C}_5\text{Me}_4\text{Bu})\text{Fe}(\text{CO})_2]_2$ was obtained by the thermal reaction between $\text{Fe}(\text{CO})_5$ and *tert*-butyltetramethylcyclopentadiene in octane. In contrast with the analogous tetramethylcyclopentadienyl dimer, $[(\eta^5\text{-C}_5\text{Me}_4\text{-}^1\text{Bu})\text{Fe}(\text{CO})_2]_2$ appeared to decompose very easily, especially in solution. Attempts to produce the dimer using $\text{Fe}_2(\text{CO})_9$ at room temperature gave low yields of $[(\eta^5\text{-C}_5\text{Me}_4\text{Bu})\text{Fe}(\text{CO})_2]_2$ together with large quantities of $\text{Fe}_3(\text{CO})_{12}$ which proved difficult to remove from the dimer. The iodo derivative, $(\eta^5\text{-C}_5\text{Me}_4\text{Bu})\text{Fe}(\text{CO})_2\text{I}$, was obtained from the dimer by standard procedures, as fluffy red-brown crystals, in high yield.

The ligand-substitution reaction, $(\eta^5\text{-C}_5\text{-Me}_4\text{Bu})\text{Fe}(\text{CO})_2\text{I} + \text{L} \rightarrow (\eta^5\text{-C}_5\text{Me}_4\text{Bu})\text{Fe}(\text{CO})(\text{L})\text{I}$ ($\text{L} = \text{PPh}_3, \text{P}(\text{OMe})_3$ and $\text{P}(\text{OPh})_3$), was attempted by the catalytic procedures described above for $(\eta^5\text{-C}_5\text{-C}_5\text{Me}_4\text{H})\text{Fe}(\text{CO})_2\text{I}$. This method only gave the required product for $\text{L} = \text{P}(\text{OMe})_3$, and then only when the catalyst $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ was used. The use of this catalyst in reactions with $\text{L} = \text{PPh}_3$ and $\text{P}(\text{OPh})_3$ led mainly to the formation of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{L})\text{I}$. However, the desired products of the carbonyl substitutions reactions, $(\eta^5\text{-C}_5\text{Me}_4\text{Bu})\text{Fe}(\text{CO})(\text{L})\text{I}$, were obtained successfully and cleanly when the reagents $(\eta^5\text{-C}_5\text{Me}_4\text{-}^1\text{Bu})\text{Fe}(\text{CO})_2\text{I}$ and L ($\text{L} = \text{PPh}_3, \text{P}(\text{OMe})_3$ and $\text{P}(\text{OPh})_3$) were reacted photochemically.

All the above complexes containing the $\text{C}_5\text{Me}_4\text{H}$ and $\text{C}_5\text{Me}_4\text{Bu}$ rings were characterized by melting points, micro-analyses and IR and NMR spectroscopy. As expected, the carbonyl stretching frequencies in the infrared spectra of the complexes containing $\text{C}_5\text{Me}_4\text{R}$ rings occurred at higher wavenumbers for $\text{C}_5\text{Me}_4\text{H}$ than for $\text{C}_5\text{Me}_4\text{Bu}$. X-Ray crystallographic studies on $[(\eta^5\text{-C}_5\text{Me}_4\text{H})\text{Fe}(\text{CO})(\text{PPh}_3)]\text{I}$ and $(\eta^5\text{-C}_5\text{Me}_4\text{Bu})\text{Fe}(\text{CO})(\text{P}(\text{OPh})_3)]\text{I}$ also confirmed the structures of the new complexes (see below).

NOE spectroscopy was also used to assign ring atoms (C and H) to specific resonances to enable conformational properties to be deduced.

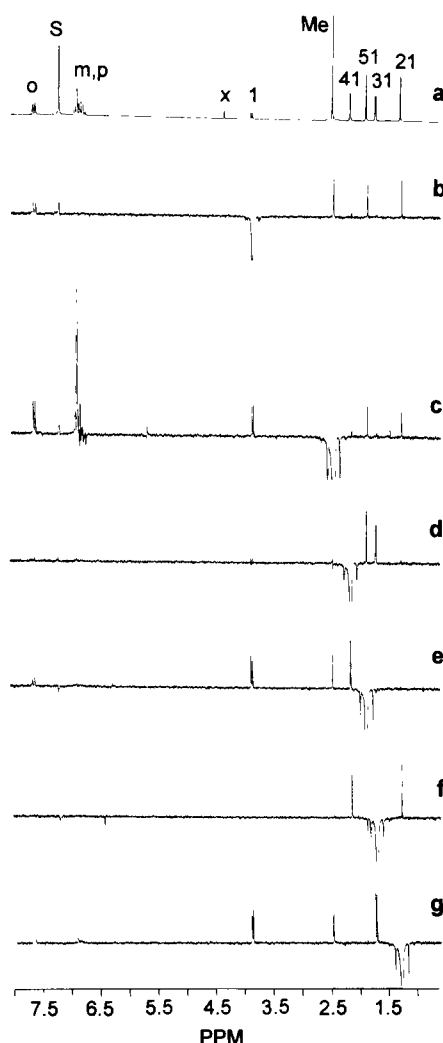


Fig. 4. NOE spectra for $(\eta^5\text{-C}_5\text{Me}_4\text{H})\text{Fe}(\text{CO})(\text{P}(\text{O}-o\text{-Tol})_3)\text{I}$. Curve (a), non-irradiated spectrum: o, m, p, Me are the ortho-, meta-, para-hydrogen and methyl signals of $\text{P}(\text{O}-o\text{-Tol})_3$, x is an impurity peak, S is the solvent (deuterated benzene) peak, 1, 21–51 are the cyclopentadienyl ring protons. Curves (b)–(g), irradiation of (b) H_1 , (c) Me, (d) H_{41} , (e) H_{51} , (f) H_{31} , (g) H_{21} .

3.1.1. $(\eta^5\text{-C}_5\text{Me}_4\text{H})\text{Fe}(\text{CO})(\text{L})\text{I}$

The ^1H NMR spectra of the $(\eta^5\text{-C}_5\text{Me}_4\text{H})\text{Fe}(\text{CO})(\text{L})\text{I}$ complexes (Table 3) show four separate resonances for the four methyl groups ($\text{H}_{21}\text{--H}_{51}$), and an additional absorption for H_1 (See Fig. 1 for cyclopentadienyl ring numbering scheme). A typical ^1H NMR spectrum ($(\eta^5\text{-C}_5\text{Me}_4\text{H})\text{Fe}(\text{CO})(\text{P}(\text{O}-o\text{-Tol})_3)\text{I}$) is shown in Fig. 4, curve (a). The four ring-methyl proton absorptions occur in the 1.0–2.1 ppm region, and are well separated, with up to three methyl groups coupled to phosphorus. Ring-methyl groups were assigned by means of NOE spectroscopy. For example, irradiation of the H_1 resonance led to the growth of two methyl group resonances only, and these can be assigned to the H_{21} and H_{51} protons (Fig. 4, curve (b)). The spectra of the complexes with $\text{L} = \text{P}(\text{OMe})_3, \text{PPh}_3, \text{P}(\text{O}-o\text{-Tol})_3$ and PMe_3

were also assigned by NOE spectroscopy, while, for $L = \text{PBz}_3$ and $\text{P}(\text{O}^i\text{Pr})_3$, assignments were made by comparison with the other spectra.

The chemical shift of H_1 reflects the electronic nature of L . When L is a phosphine, the chemical shift of H_1 occurs in the 2.70–3.35 ppm region, and, when L is a phosphite, H_1 is more deshielded, and its resonance occurs in the 3.78–4.19 ppm region.

Assignment of the four separate methyl-carbon resonances, C_{21} to C_{51} (Table 4), was achieved by the use of CH-correlated spectra. The ring carbons C_1 to C_5 appeared as five different resonance groups in the ^{13}C NMR spectra. The C_1 resonance could be recognized by its higher intensity relative to the other four resonances. However, since all four of the carbons C_2 to C_5 were attached to other carbon atoms (C_{21} to C_{51}), CH-correlated spectra did not distinguish between the four different resonances. Hence definite assignment of C_2 to C_5 was not possible. Generally two of these resonances were coupled to the P atom of ligand, L , and two of them were not. Although it is tempting to use this coupling information to assign the C_2 – C_5 resonances, the ^{13}C NMR data for the $(\eta^5\text{-C}_5\text{H}_4\text{Bu})\text{Fe}(\text{CO})(\text{L})\text{I}$ complexes has revealed that no simple correlation exists between phosphorus and the coupling of the cyclopentadienyl ring carbons [6].

We have shown previously that, for the $(\eta^5\text{-C}_5\text{H}_4\text{Bu})\text{Fe}(\text{CO})(\text{L})\text{I}$ series, a correlation exists between the size of L and the NMR parameter $\Delta(\text{H}_2\text{--H}_5)$. However, for both the ^1H and ^{13}C spectra of the $(\eta^5\text{-C}_5\text{Me}_4\text{H})\text{Fe}(\text{CO})(\text{L})\text{I}$ complexes (Tables 3 and 4), no correlation could be obtained between the separation of the peaks and the steric size of the ligands L . This relates to the small spectral ranges in which their methyl resonances occur (δ 1.07–2.10 ppm for H_{21} – H_{51} and δ 9.79–12.71 ppm for C_{21} – C_{51}). Similar observations were noted for related ruthenium complexes [30]. It is unfortunate that the resonances of C_2 – C_5 could not be unequivocally assigned, since their proximity to L would make them much better at “sensing” the steric size of L . These resonances do indeed occur over a wide spectral range (δ 77.92–103.54 ppm).

3.1.2. $(\eta^5\text{-C}_5\text{Me}_4\text{Bu})\text{Fe}(\text{CO})(\text{L})\text{I}$

Assignments of the ^1H and ^{13}C NMR spectra for $(\eta^5\text{-C}_5\text{Me}_4\text{Bu})\text{Fe}(\text{CO})(\text{L})\text{I}$ were also deduced from NOE and CH-correlated spectra as outlined above. The ^1H NOE spectra for $(\eta^5\text{-C}_5\text{Me}_4\text{Bu})\text{Fe}(\text{CO})\{\text{P}(\text{OMe})_3\}\text{I}$ is discussed below. It is to be noted that in the non-irradiated ^1H NMR spectrum (Fig. 4, curve (a)) all four methyl resonances are distinct, again with coupling between only two of the methyl protons and the P atom of the ligand. The ^tBu group gives rise to a singlet in the same region as, and in some cases overlapping with, the methyl resonances. The methyl groups did not appear in a specific order in the spectra. Although the

H_{21} – H_{51} resonances of the complex with $L = \text{PPh}_3$ occurred over a larger range (δ 0.82–2.47 ppm), compared to the complexes with $L = \text{P}(\text{OPh})_3$ and $\text{P}(\text{OMe})_3$ (δ 1.60–2.26 ppm), the data set is too small to speculate about a correlation between the size of L and the separations between any of the ring resonances.

The chemical-shift positions of the ^tBu peaks of the $(\eta^5\text{-C}_5\text{Me}_4\text{Bu})\text{Fe}(\text{CO})(\text{L})\text{I}$ complexes can be compared to those of the $(\eta^5\text{-C}_5\text{H}_4\text{Bu})\text{Fe}(\text{CO})(\text{L})\text{I}$ complexes [6], for the same or very similar L . It was found that the ^tBu resonance in the ^1H NMR spectra appeared at higher chemical-shift positions for the $\text{C}_5\text{Me}_4\text{Bu}$ complexes. The ^{13}C NMR resonances change in the same direction. This suggests that methyl substitution of the ring leads to *deshielding* of the ^tBu group, which is counter-intuitive. However, a possible explanation for this phenomenon is that the four electron-donating methyl groups on the cyclopentadienyl ring lead to increased π -bonding from the cyclopentadienyl ring to iron. Thus, electron density is withdrawn from the cyclopentadienyl ligand as a *whole*, including the attached ^tBu group.

3.2. Solution conformational studies

3.2.1. $(\eta^5\text{-C}_5\text{Me}_4\text{H})\text{Fe}(\text{CO})(\text{L})\text{I}$

NOE spectroscopy was used to obtain the conformational preferences of these complexes. These were deduced from the relative growths of the H_{21} – H_{51} absorptions when an L absorption was irradiated (Fig. 4, curve (c)), and the relative growths of the L peak when H_{21} to H_{51} were in turn irradiated (Fig. 4, curves (d)–(g)). It was found that L spent most of the time in the proximity of the smallest ring substituent, H_1 (percent enhancement = 8.0), and the Me groups adjacent to H_1 (H_{21} , percent enhancement = 1.0; H_{51} , percent enhancement = 1.4) (percent enhancements for H_{31} and H_{41} are 0.5 and 0.2 respectively). The NOE spectra of the other compounds ($L = \text{PMe}_3$, $\text{P}(\text{OMe})_3$, PPh_3) showed that L was closest to H_1 and only *one* of the ring methyl groups, H_{21} . See Fig. 5(a) for the representation of the preferential conformer. Note that the protons on the methyl groups closest to the L group exhibit no coupling to P, whereas the “*trans*”-methyl protons (H_{31} , H_{41}) couple most strongly to P (Table 3).

3.2.2. $(\eta^5\text{-C}_5\text{Me}_4\text{Bu}^t)\text{Fe}(\text{CO})(\text{L})\text{I}$

The NOE spectra showed that the ligand set had definite conformational preferences with respect to orientation about the Fe-ring centroid axis. The spectra suggest that L spends most of its time away from the largest ring substituent, ^tBu . For example, Fig. 5(b) suggests that L is in the vicinity closest to H_{31} and H_{41} (percent enhancements, 2.0 each). The NOE experiments show that L is also close to H_{51} (percent enhancement, 1.0), and that L lies away from H_{21} and ^tBu (percent enhancements, 0.5 each). The NOE spectra of

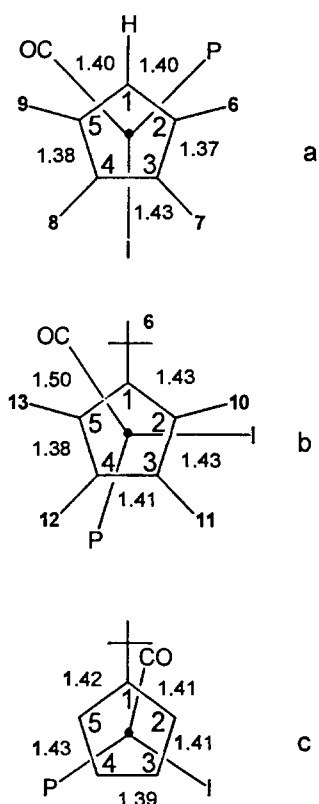


Fig. 5. Ligand conformational arrangement and crystal structural data for (a) **1**, (b) **2**, (c) **3** (C–C bond length data accuracy: see Table 8). The conformers shown correspond to those in Figs. 2–5 and Ref. [6], with the CO, P and L ligands *below* the ring plane.

the other compounds (L = PPh₃ and P(OPh)₃) also indicate conformations where L is closest to H₄₁ and away from H₂₁ and ^tBu. Fig. 5(b) represents this preferential conformer.

3.2.3. Comparison of the (η⁵-C₅H₄^tBu)Fe(CO)(L)I, (η⁵-C₅Me₄H)Fe(CO)(L)I and (η⁵-C₅Me₄Bu)Fe(CO)(L)I complexes

The different electronic natures of the three different series of compounds are indicated by their IR spectra. For the same L groups, ν(CO) decreases as more electron-donating groups are introduced onto the cyclopentadienyl ring, (η⁵-C₅H₄^tBu)Fe(CO)(L)I > (η⁵-C₅Me₄H)Fe(CO)(L)I > (η⁵-C₅Me₄Bu)Fe(CO)(L)I.

NMR spectra reveal that, in solution, all of the new complexes show conformations that reduce steric interactions between L and the ring atoms. The complexes containing the large ^tBu substituents on the cyclopentadienyl ring, (η⁵-C₅H₄^tBu)Fe(CO)(L)I and (η⁵-C₅Me₄Bu)Fe(CO)(L)I, adopt conformations where the L group points away from this substituent. In the (η⁵-C₅Me₄H)Fe(CO)(L)I complexes, the L group is found close to the H group, avoiding the four larger methyl groups on the cyclopentadienyl ring.

3.3. Solid-state structures and conformations

Crystal structure determinations were carried out for (η⁵-C₅Me₄H)Fe(CO)(PPh₃)I (**1**) and (η⁵-C₅Me₄Bu)Fe(CO){P(OPh)₃}I (**2**) to assess their solid-state conformations and to permit comparison with the known crystal structure of (η⁵-C₅H₄^tBu)Fe(CO)(PPh₃)I (**3**) [6]. The use of L = PPh₃ instead of L = P(OPh)₃ in **2** would have been preferable, and would have given a closer series of complexes Cp^ηFe(CO)(PPh₃)I (Cp^η = η⁵-C₅Me₄H, η⁵-C₅Me₄Bu and η⁵-C₅H₄^tBu) for comparison. However, suitable crystals could not be obtained for (η⁵-C₅Me₄Bu)Fe(CO)(PPh₃)I, and the crystal structure of (η⁵-C₅Me₄Bu)Fe(CO){P(OPh)₃}I (**2**) was determined instead. The NMR spectra revealed similar solution conformers for (η⁵-C₅Me₄Bu)Fe(CO)(L)I (L = PPh₃ and P(OPh)₃), and thus the P(OPh)₃ complex should still provide the required information to compare the effects of variation of ring substituents on the solid-state conformers.

Comparisons between complexes **1** and **2** and a related complex (η⁵-C₅H₄^tBu)Fe(CO)(PPh₃)I (**3**) (Fig. 5) show that the magnitudes of various bond lengths and bond angles are comparable (see Table 8). Surprisingly, the electron-donating substituents had little effect on the observed Fe–Cen (Cen = cyclopentadienyl ring centroid) bond lengths, which are almost identical for **1**, **2** and **3**, and range from 1.731 to 1.737 to 1.741 Å. These values are comparable to Fe–Cen distances for other related complexes [31]. Similarly, the differences between C–O, Fe–CO and Fe–I bond lengths for **1**, **2** and **3** are small (C–O: 1.04(1), 1.07(2), 1.095(6) Å; Fe–CO: 1.792(7), 1.794(13), 1.769(6) Å; Fe–I: 2.642(1), 2.599(19), 2.618(1) Å. The Cen–Fe–L bond angles, where L = CO, I, PPh₃ or P(OPh)₃, did not change significantly with L in **1**, **2** and **3** (Cen–Fe–L bond angle range: 121.2, 122.1 and 127.2°).

As expected, the Fe–P bond length in **2** is shorter than that in **1** (Fe–P: **1**, 2.245(2) Å; **2**, 2.139(4) Å). This is related to the stronger metal-to-phosphorus back-bonding in the P(OPh)₃ complex (**2**) compared to the PPh₃ complex (**1**).

The cyclopentadienyl C–C bond lengths show fairly significant deviations for both complexes **1** and **2**, indicating that cyclopentadienyl ring aromaticity has been disturbed (cyclopentadienyl C–C bond lengths: **1**, 1.37(1)–1.43(1); **2**, 1.38(2)–1.50(2)) (see Fig. 5).

In a recent publication [32] on Cp^{*}Co(CO)₂ complexes (Cp^{*} = η⁵-C₅H₅, η⁵-C₅Me₅, η⁵-C₅Bz₅), it was shown that the cyclopentadienyl C–C bonds which are eclipsed by carbonyl ligands (as viewed along the cyclopentadienyl centroid–metal axis) are longer, whereas the shortest bonds are those which are non-eclipsed [32]. Similarly, for **1**, **2** and **3**, the shortest cyclopentadienyl C–C bond lengths all pertain to bonds that are not eclipsed by any ligand and/or are adjacent to a bond

eclipsed by the phosphine or phosphite ligand (see Fig. 5).

The above discussion shows that there are no significant structural differences between **1**, **2** and **3** as reflected by bond length and angle data. Also, the bond length data (e.g. Fe–Cen distance) do not reflect any significant electronic differences between these complexes (see Table 8).

However, the different steric effects for these three complexes are reflected by the different arrangements of the ligand set relative to the cyclopentadienyl ring. In each case, the bulky PPh₃ or P(OPh)₃ ligand was positioned away from the largest cyclopentadienyl ring substituent(s). Hence in **1** the PPh₃ ligand is found close to the smallest cyclopentadienyl ring substituent, H. In **2** the P(OPh)₃ ligand is far from the largest cyclopentadienyl ring substituent ^tBu. A similar result was obtained for **3**, in which the PPh₃ ligand was positioned away from the large ^tBu substituent. This appears to be a very general phenomenon. Indeed a recent crystal structure determination of (C₅Me₄H)₂TiCl₂ also indicates that the smallest ring substituent occupies the least sterically hindered space [33]. The CO and I ligands did not adopt preferential positions.

Another possible indicator of the steric effects experienced by the cyclopentadienyl rings is the angle by which the cyclopentadienyl ring substituents (Me, ^tBu) deviate from the ring mean plane. In both **1** and **2** these angles are large [31] and in the direction away from the metal-ligand set (deviation angles: 3.2–9.7°).

In summary: the solution conformations are similar to those observed in the solid state.

4. Conclusions

As discussed above, NMR spectroscopy showed that (η^5 -C₅Me₄R)Fe(CO)(L)I (R = H, ^tBu) complexes displayed definite conformational preferences with regard to the position of the ligand set (CO, L and I) attached to iron, relative to the cyclopentadienyl ring substituents as viewed down the Fe-ring centroid axis. The conformational preferences were such that the relatively large phosphine and phosphite ligands on iron were positioned away from the largest substituents on the cyclopentadienyl ring. Thus for R = H, the L group was found close to R, while for R = ^tBu, the L group was found away from R. This can be rationalized in terms of steric interaction between L and the cyclopentadienyl ring substituents. The accommodation of the other ligands (CO and I) can be expected to lead to finer adjustments to the conformations. The molecular structures of (η^5 -C₅Me₄H)Fe(CO)(PPh₃)I and (η^5 -C₅Me₄-^tBu)Fe(CO){P(OPh)₃}I were determined by X-ray crystallography. The conformations of these complexes in

the solid state (with respect to the position of L) corresponded to those obtained in solution, showing that the preferred conformations are those where the L group is positioned in such a way as to avoid interaction with the larger cyclopentadienyl ring substituents.

Acknowledgements

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