Synthesis and electrochemistry of complexes containing the ferrocenyl–phosphine ligand PPh(CH₂CH₂-η^5-C₅H₄)₂Fe☆

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Abstract

Treatment of the tethered bis(cyclopentadienyl)-phosphine compound bis(2-cyclopentadienylethyl)phenylphosphine (**1**) produces moderate yields (40–50%) of the ferrocene complex PPh(CH₂CH₂-η^5-C₅H₄)₂Fe (**2**). Reaction of **2** with Me₃NO in tetrahydrofuran gives the phosphine oxide O=PPh(CH₂CH₂-η^5-C₅H₄)₂Fe (**3**) whereas treatment with the metal complexes *trans*-PdCl₂(PhCN)₂, *cis*-PtCl₂(PhCN)₂, Fe₂(CO)₉, and Mo(CO)₅(THF) give the corresponding di- or tri-metallic complexes *trans*-PdCl₂[PPh(CH₂CH₂-η^5-C₅H₄)₂Fe]₂ (**4**), *cis*-PtCl₂[PPh(CH₂CH₂-η^5-C₅H₄)₂Fe]₂ (**5**), (OC)₄FePPh(CH₂CH₂-η^5-C₅H₄)₂Fe (**7**), and (OC)₅MoPPh(CH₂CH₂-η^5-C₅H₄)₂Fe (**8**), respectively, in which **2** is acting as a neutral two-electron-donor phosphine ligand. The electrochemistry of complexes **2**, **3**, **4**, **5** and **7** have been investigated and complexes **3**, **4** and **7** have been characterised further by X-ray crystallography. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

The chemistry of functionalised cyclopentadienyl ligands is a rapidly expanding area of research [1]. Apart from an enhanced thermodynamic stability that is imparted through the chelate effect, changes in the coordination bite angle may also be used to alter the frontier orbitals of the metal–ligand fragment and, thus, alter the reactivity [2]. Alternatively, such ligands may be used to build hetero- and homo-bimetallic complexes which may exhibit interesting and useful properties. Cyclopentadienyl and phosphine ligands are two of the most important ligands in organometallic chemistry:

The major reasons for the successful use of these ligands, particularly in the area of homogeneous catalysis, are their ability to stabilise a range of metal oxidation states and because it is relatively easy to alter their steric and electronic properties by changing their substituents.

There is now a large range of Group 15 functionalised cyclopentadienyl ligands, particularly with amine and amide functionalities [3]. The number of phosphine functionalised cyclopentadienyl ligands is relatively small, but there are now examples of ligands containing zero-, one-, two- or three-atom bridges between the cyclopentadienyl and phosphine moieties [4–7]. Most work to date has focused on the zero- and two-atom bridged ligands. The number of functionalised bis-cyclopentadienyl ligands, however, is still quite small. Ligands prepared to date include pyridyl [8–10], amino [9,11], ether [12], furanyl [13], and arsine [14,15] substituted bis-cyclopentadienyl ligands. Most of the chem-

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istry of these functionalised bis-cyclopentadienyl ligands has focused on the lanthanide coordination chemistry, particularly with the hard nitrogen- and oxygen-containing functional groups. Qian has reported recently a lanthanide complex containing an oxygen atom tethered to two indenyl groups via ethylene bridges [16]. The only examples of bis-cyclopentadienyl-phosphine ligands are $RP(C_5H_4^-)_2$ (R = Cl, alkyl, aryl) [15,17,18] and $C_6H_{11}P(CHMe-2-PPh_2C_5H_3^-)_2$ [19]. This paper reports the synthesis of the bis(cyclopentadienyl)-phosphine ligand precursor, bis(2-cyclopentadienylethyl)phenylphosphine (1), its conversion to the ferrocenyl complex $PhP(CH_2CH_2C_5H_4)_2Fe$ (2), and some phosphine coordination chemistry of 2. Some of this work has been reported in this journal as a communication [20]. Examples of the ligand $[PPh(CH_2CH_2C_5H_4)_2]^{2-}$ coordinated to zirconium have been reported earlier [21] in which the phosphine is intramolecularly coordinated to the metal centre to give a septadentate coordination mode (counting each cyclopentadienyl group as a tridentate ligand) for the ligand.

2. Experimental

2.1. General considerations

All manipulations and reactions were carried out under an inert atmosphere by use of standard Schlenk line techniques. Reagent grade solvents were dried and distilled prior to use: diethyl ether and tetrahydrofuran (THF) from Na/benzophenone; dichloromethane and petroleum ether (50–70°C fraction) from CaH_2. Spiro[2.4]hepta-4,6-diene [22] and phenylphosphine [23] were prepared by published procedures, and bis(benzonitrile)palladium(II) chloride by crystallisation of $PdCl_2$ from benzonitrile. All other reagents were purchased from Aldrich Chemical. ^1H-, $^{13}C\{^1H\}$- and $^{31}P\{^1H\}$-NMR data were collected on a Varian XL-300 spectrometer operating at 300, 75 and 121 MHz, respectively. Unless otherwise stated, spectra were measured at ambient temperature with residue solvent peaks as internal standard for ^1H- and $^{13}C\{^1H\}$-NMR. $^{31}P\{^1H\}$-NMR chemical shifts were reported relative to external 85% H_3PO_4, positive shifts representing deshielding. NMR data for all compounds, except compound 1, are collected together in Table 1. The ^1H- and ^{13}C-NMR assignments for 1 are given in Table 2. EI and FAB mass spectra were collected on a Kratos MS80RFA mass spectrometer. IR spectra were obtained on a Shimadzu FTIR-8201PC spectrophotometer. Elemental analyses were done by Campbell Microanalysis Ser-

vices, Otago University, Dunedin. Cyclic voltammograms of 10^{-3} M solutions of 3, 4, 5 and 7 were recorded using a PAR 173 potentiostat coupled to a home-built waveform generator and a PAR 17S Universal Programmer and a Graphtech WX1200 X–Y recorder. The three-electrode cell was comprised of a platinum-disk working electrode (1 mm diameter), a platinum-wire auxiliary and a Ag/Ag^+ (0.01 M $AgNO_3$, 0.1 M $[Bu_4N]PF_6$–CH_3CN) reference electrode. Cyclic voltammograms of 10^{-3} M solutions of 2 were recorded using a Princeton applied research potentiostat 273 equipped with a BBC/Servogor (XY 733) plotter as the recording instrument. The three-electrode cell was comprised of a platinum-wire auxiliary electrode (0.3 mm diameter), a glassy-carbon disk working electrode (3 mm diameter) and an SCE reference electrode (0.01 M $AgNO_3$, 0.1 M $[Bu_4N]PF_6$–CH_3CN). All potentials are reported versus the couple ferrocene$^+$/ferrocene (Fc^+/Fc) after referencing to in situ ferrocene or cobaltocenium. Before use, electrodes were polished with 1 μm diamond paste and cleaned ultrasonically for 15 s in acetone followed by triply distilled water. All electrochemical measurements were made at 22 ± 2°C and a dinitrogen atmosphere was maintained in the cell.

2.2. Preparation of $PPh(CH_2CH_2C_5H_5)_2$ (1)

A solution of phenylphosphine (2.00 g, 18.2 mmol) and spiro[2.4]hepta-4,6-diene (4.15 g, 45.0 mmol) in THF (60 ml) was cooled to −78°C. n-BuLi (13.0 ml, 1.4 M in hexane, 18.2 mmol) was then added and the solution allowed to warm to ambient temperature. After stirring for 2 h, the mixture was again cooled to −78°C and n-BuLi (15.6 ml, 1.4 M in hexane, 21.8 mmol) added. The solution was then allowed to warm to ambient temperature and stirred overnight. Excess dinitrogen-saturated water was added. The organic layer was collected and the aqueous layer was extracted with 3×50 ml portions of diethyl ether which were added to the organic fraction. The organic fraction was dried over Na_2SO_4 and filtered. Removal of the volatiles in vacuo gave an orange oil which, after chromatography down a 5×5 cm silica column with 1:1 petroleum ether + CH_2Cl_2 produced a colourless oil of 1 (5.05 g, 94% yield). ^{31}P-NMR $(CDCl_3)$: δ −22.25, −22.40, −22.55 (1:2:1 ratio). MS (EI), m/z (rel. intensity): 294 (44) $[M]^+$, 215 (24) $[M-CH_2C_5H_5]^+$, 202 (100) $[PhPH(CH_2CH_2C_5H_5)]^+$, 174 (61) $[Ph(C_5H_5)PH]^+$, 173 (43) $[Ph(C_5H_5)P]^+$, 109 (53) $[PhPH]^+$, 93 (34) $[CH_2CH_2C_5H_5]^+$, 91 (73) $[C_7H_7]^+$, 79 (35) $[CH_2C_5H_5]^+$, 77 (58) $[C_6H_5]^+$. Anal. calc. for $C_{20}H_{23}P$: C, 81.60; H, 7.88; P, 10.52. Found: C, 81.15; H, 8.23; P, 10.17.

Table 1
^{1}H-, ^{13}C- and ^{31}P-NMR data for compounds **2**, **3**, **4**, **5**, **7** and **8**

	2	**3**	**4**	**5**	**7**	**8**
^{1}H-NMR						
Ph	7.39 (2H)	7.46 (2H)	7.73 (4H)	7.50 (4H)	7.5 (5H)	7.48 (5H)
	7.29 (2H)	7.38 (2H)	7.44 (6H)	7.47 (6H)		
	7.21 (1H)	7.28 (1H)				
Cp	4.06 (2H)	4.14 (2H)	4.12 (4H)	4.11 (4H)	4.13 (2H)	4.11 (2H)
	4.02 (2H)	4.10 (2H)	4.09 (4H)	4.07 (4H)	4.13 (2H)	4.11 (2H)
	4.01 (2H)	4.06 (2H)	4.06 (4H)	4.02 (4H)	4.09 (2H)	4.09 (2H)
	4.01 (2H)	4.01 (2H)	3.97 (4H)	3.83 (4H)	3.94 (2H)	3.95 (2H)
PCH$_2$CH$_2$	2.5–2.3 (4H)	2.58 (2H)	2.9–2.4 (16H)	2.65–2.4 (12H)	2.8–2.5 (8H)	2.7–2.4 (8H)
	2.20 (2H)	2.53 (2H)		2.15–1.95 (4H)		
	2.05 (2H)	2.34 (2H)				
		2.19 (2H)				
^{13}C-NMR						
ipso-Ph $\delta/^1J_{PC}$ (Hz)	140.7/16.4	133.9/94.9	not observed	not observed	134.5/45.9	137.2/32.3
o- and m-Ph δ/J_{PC} (Hz)	130.6/15.7	130.9/8.4	131.6/5.3	131.8/8.4	129.3/7.3	129.0/9.4
	128.0/5.2	128.8/10.4	128.7/4.2	128.8/9.4	128.6/9.4	128.3/8.4
p-Ph $\delta/^4J_{PC}$ (Hz)	127.2/0	131.8/3.0	131.1/0	131.4/0	129.9/2.1	128.7/0
ipso-Cp $\delta/^3J_{PC}$ (Hz)	90.4/2.2	90.0/2.0	91.0/2.0*	90.8/0	89.4/3.0	89.8/3.0
Cp $\delta/^4J_{PC}$ (Hz)	67.9/3.7	67.9	67.7	67.4 (4C)	67.0	66.6
	66.8	67.5	67.2	67.0 (4C)	66.9	66.6
	66.5	67.1	67.1		66.6	66.5
	66.1	66.7	67.0		66.5	66.4
PCH$_2$ $\delta/^1J_{PC}$ (Hz)	22.9/10.5	26.0/65.7	17.6/13.1^a	20.0/m	24.7/25.0 (at 80°C)	22.9/20.3 (at 80°C)
CH$_2$Cp $\delta/^2J_{PC}$ (Hz)	21.4/18.8	18.9/2.0	22.4/0^a	21.6/0	21.9/3.1 (at 80°C)	22.4/0 (at 80°C)
CO $\delta/^2J_{PC}$ (Hz)					213.5/18.8	210.1/21.9 (*trans*)
						205.9/9.2 (*cis*)
^{31}P-NMR (ppm)						
	−16.8	41.6	22.1	4.1	66.7	32.6
				($^1J_{PtP}$ = 3542 Hz)		
				($^2J_{PP}$ = 6 Hz)		

^{a} $^nJ_{PC}$ values for compound **4** are actually $|{}^nJ_{PC} + {}^{n+2}J_{PC}|$ values.

2.3. Preparation of PPh(CH$_2$CH$_2$-η^5-C$_5$H$_4$)$_2$Fe (**2**)

After cooling a solution of **1** (2.40 g, 8.16 mmol) in THF (40 ml) to −78°C, a solution of *n*-BuLi (11.7 ml, 1.4 M in hexane, 16.3 mmol) was added. The solution was then allowed to warm to ambient temperature and was then stirred for 2 h. A slurry of anhydrous FeCl$_2$ (1.08 g, 8.50 mmol) in THF (250 ml) was added and the solution stirred overnight. Filtration through celite to remove insoluble polymeric material followed by removal of the volatiles in vacuo left an orange oil. Chromatography down a 5 × 15 cm silica column with 1:1 petroleum ether + CH$_2$Cl$_2$ eluted an orange product. Recrystallisation from 10:1 petroleum ether + CH$_2$Cl$_2$ yielded orange needles (0.97 g, 34% yield), m.p. 123–125°C. MS (EI), *m/z* (rel. intensity): 348 (100) [M]$^+$, 347 (62) [M−H]$^+$, 346 (19) [M−2H]$^+$, 320 (42) [M−C$_2$H$_4$]$^+$, 270 (15) [M−CH$_2$C$_5$H$_4$]$^+$, 256 (28) [M−CH$_2$CH$_2$C$_5$H$_4$]$^+$. Anal. calc. for C$_{20}$H$_{21}$PFe: C, 68.99; H, 6.08; P, 8.89. Found: C, 68.79; H, 6.17; P, 8.73.

2.4. Preparation of OPPh(CH$_2$CH$_2$-η^5-C$_5$H$_4$)$_2$Fe (**3**)

A solution of **2** (0.20 g, 0.57 mmol) in THF (30 ml) was added to a solution of trimethylamine *N*-oxide (0.13 g, 1.70 mmol) in THF (50 ml). The mixture was heated to reflux and the reaction monitored by ^{31}P-NMR spectroscopy. After completion of the reaction, the volatiles were removed in vacuo. Chromatography down a 2 × 5 cm silica column with CHCl$_3$ eluted a yellow product. Recrystallisation from 1:1 petroleum ether + CH$_2$Cl$_2$ gave dark orange needles (0.15 g, 72% yield). IR (CDCl$_3$): ν_{PO} 1265 cm^{-1}. MS (EI), *m/z* (rel. intensity): 364 (100) [M]$^+$, 348 (10) [M−O]$^+$. Anal. calc. for C$_{20}$H$_{21}$FePO: C, 65.95; H, 5.82. Found: C, 66.22; H, 6.18.

2.5. Preparation of trans-PdCl$_2$[PPh(CH$_2$CH$_2$-η^5-C$_5$H$_4$)$_2$Fe]$_2$ (**4**)

A solution of **2** (0.25 g, 0.72 mmol) in THF (25 ml) was added to a solution of bis(benzonitrile)palla-

dium(II) chloride (0.13 g, 0.35 mmol) in THF (25 ml). After heating to reflux for 12 h, the solution was allowed to cool to ambient temperature whereupon an orange crystalline product precipitated. The solvent was then filtered off and the solid dried in vacuo to give orange crystals of **4** (0.13 g, 43% yield), m.p. 199–205°C. MS (FAB), m/z (rel. intensity): 874 (5) $[M]^+$, 837 (4) $[M-Cl]^+$, 802 (2) $[M-2Cl]^+$, 491 (7) $[ClPdP-(CH_2CH_2C_5H_4)_2Fe]^+$, 454 (9) $[PdPPh(CH_2CH_2-C_5H_4)_2Fe]^+$, 348 (100) $[PPh(CH_2CH_2C_5H_4)_2Fe]^+$. Anal. calc. for $C_{40}H_{42}P_2Cl_2Fe_2Pd\cdot2THF$: C, 56.64; H, 5.74. Found: C, 55.45; H, 5.50. This result is consistent with the loss of 0.4THF prior to analysis.

2.6. Preparation of cis-PtCl_2[PPh(CH_2CH_2-η^5-C_5H_4)_2Fe]_2 (5)

A solution of **2** (0.20 g, 0.57 mmol) in THF (30 ml) was added to a slurry of cis-bis(benzonitrile)platinum(II) chloride (0.14 g, 0.29 mmol) in THF (30 ml). The mixture was heated to reflux for 12 h and cooled at −20 °C for several days. The solvent was decanted off and the precipitate was dried in vacuo to give a gold solid. Recrystallisation from THF gave gold needles (0.17 g, 30% yield). M.p. 214°C (dec.). MS (FAB), m/z (rel. intensity): 962 (5) $[M]^+$, 926 (10) $[M-Cl]^+$, 890 (30) $[M-2Cl]^+$, 540 (28) $[PtPPh(CH_2CH_2C_5H_4)_2Fe]^+$, 348 (100) $[PPh(CH_2CH_2C_5H_4)_2Fe]^+$. Anal. calc. for $C_{40}H_{42}P_2Cl_2Fe_2Pt$: C, 49.91; H, 4.41. Found: C, 49.65; H, 4.45.

2.7. Preparation of (CO)_4FePPh(CH_2CH_2-η^5-C_5H_4)_2Fe (7)

A solution of **2** (0.27 g, 0.78 mmol) in THF (20 ml) was added to a slurry of $Fe_2(CO)_9$ in THF (30 ml). The mixture was stirred overnight and then heated to reflux for 5 h. The volatiles were removed in vacuo and the residue was redissolved in 1:1 petroleum ether + CH_2Cl_2. Chromatography down a 3×12 cm silica column eluted a yellow product. Recrystallisation from petroleum ether yielded orange needles (0.11 g, 27% yield). M.p. 125–127°C. IR (CHCl_3): ν_{CO} 2046 (m), 1969 (w), 1932 (s) cm^{-1}. MS (FAB), m/z (rel. intensity): 516 (18) $[M]^+$, 460 (7) $[M-2CO]^+$, 432 (100) $[M-3CO]^+$, 404 (39) $[M-4CO]^+$, 348 (24) $[M-Fe(CO)_4]^+$. Anal. calc. for $C_{24}H_{21}O_4PFe_2$: C, 55.85; H, 4.11. Found: C, 56.02; H, 4.14.

2.8. Preparation of (CO)_5MoPPh(CH_2CH_2-η^5-C_5H_4)_2Fe (8)

A solution of **2** (0.25 g, 0.72 mmol) in THF (20 ml) was added to a slurry of $Mo(CO)_6$ in THF (30 ml). The mixture was heated to reflux for 20 h. The volatiles were removed in vacuo and the residue redissolved in 2:1 petroleum ether + CH_2Cl_2. Chromatography down a 2×20 cm silica column eluted an orange product. Recrystallisation from 2:1 petroleum ether + CH_2Cl_2 yielded orange needles (0.16 g, 38% yield). M.p. 159–162°C. IR (CHCl_3): ν_{CO} 2070 (mw), 1987 (w), 1942 (vs) cm^{-1}. MS (FAB), m/z (rel. intensity): 586 (53) $[M]^+$, 530 (25) $[M-2CO]^+$, 446 (36) $[M-5CO]^+$, 348 (100) $[M-Mo(CO)_5]^+$. Anal. calc. for $C_{25}H_{21}FeMoO_5P$: C, 51.40; H, 3.63. Found: C, 50.77; H, 4.42.

3. X-ray crystallography

3.1. X-ray structure of OPPh(CH_2CH_2-η^5-C_5H_4)_2Fe (3)

Single crystals of **3** were obtained by cooling a petroleum ether + CH_2Cl_2 solution to −20°C. A dark orange rod was mounted on a glass capillary. The unit cell parameters were obtained by least-squares refinement of the setting angles of 18 reflections with $3.57° \leq \theta \leq 12.46°$ from a Siemens P4 diffractometer. Data were refined on F^2 using the full-matrix least-squares method [24] after being corrected for absorption by using the ψ-scan method. The intensities of three standard reflections, measured every 97 reflections throughout the data collection, showed only 14.21% decay. The structure was solved by the heavy atom Patterson method [25]. Hydrogen atoms were fixed in idealised positions with isotropic thermal parameters 1.2 times that of the attached atom. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Neutral scattering factors and anomalous dispersion corrections for non-hydrogen atoms were taken from Ibers and Hamilton [26]. Crystal data, data

Table 2
^{1}H- and ^{13}C-NMR assignments for compound **1**

^{13}C (ppm)	J_{PC} (Hz)	^{1}H (ppm)	Assignment
149.8	$^3J_{PC} = 12.2$		Ipso-Cp
147.3	$^3J_{PC} = 11.0$		Ipso-Cp
138.3	$^1J_{PC} = 10.0$		Ipso-Ph
134.4		6.40	Cp ring A
133.9		6.39	Cp ring A
132.4	$^2J_{PC} = 18.3$	7.55	Ortho-Ph
132.3		6.39	Cp ring B
130.7		6.23	Cp ring B
128.8	$^4J_{PC} = 3.0$	7.34	Para-Ph
128.4	$^3J_{PC} = 7.0$	7.36	Meta-Ph
126.4		6.15	Cp ring B
125.8		6.00	Cp ring A
43.1		2.85	Ring B CH_2
41.2		2.93	Ring A CH_2
28.2	$^1J_{PC} = 12.4$	1.94	PCH_2 ring B
27.3	$^1J_{PC} = 11.7$	1.96	PCH_2 ring A
27.0	$^2J_{PC} = 16.0$	2.47	$CpCH_2CH_2$ ring B
26.2	$^2J_{PC} = 15.7$	2.42	$CpCH_2CH_2$ ring A

Table 3
Crystal data, data collection and refinement parameters for OPPh(CH$_2$CH$_2$C$_5$H$_4$)$_2$Fe (**3**), *trans*-PdCl$_2$[PPh(CH$_2$CH$_2$C$_5$H$_4$)$_2$Fe]$_2$·2THF (**4**·2THF) and Fe(CO)$_4$[PPh(CH$_2$CH$_2$C$_5$H$_4$)$_2$Fe] (**7**)

Parameter	**3**	**4**	**7**
Crystal data			
Empirical formula	C$_{20}$H$_{21}$FeOP	C$_{48}$H$_{58}$Cl$_2$Fe$_2$O$_2$P$_2$Pd	C$_{24}$H$_{21}$Fe$_2$O$_4$P
Formula weight	364.19	1017.88	516.08
Crystal dimensions (mm)	0.70 × 0.15 × 0.15	0.75 × 0.40 × 0.20	0.65 × 0.23 × 0.20
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$P2_1/c$	$Pna2_1$
Z	4	2	8
a (Å)	6.015(5)	16.908(2)	24.060(3)
b (Å)	18.219(8)	7.8432(11)	8.490(2)
c (Å)	14.594(7)	16.686(2)	21.093(6)
α (°)	90	90	90
β (°)	99.11(6)	96.303(9)	90
γ (°)	90	90	90
V (Å^3)	1579(2)	2199.4(5)	4309(2)
$F(000)$	760	1048	2112
$D_{calc.}$ (Mg m^{-3})	1.532	1.537	1.591
μ (Mo–K$_\alpha$) (mm^{-1})	1.058	1.288	1.450
Transmission	0.1657–0.3123	0.3360–0.4225	0.240–0.258
Data collection			
Radiation type	Mo–K$_\alpha$ ($\lambda = 0.71073$ Å)	Mo–K$_\alpha$ ($\lambda = 0.71073$ Å)	Mo–K$_\alpha$ ($\lambda = 0.71073$ Å)
Monochromator	Graphite	Graphite	Graphite
T (K)	158(2)	158(2)	169(2)
θ scan range (°)	2.24–22.50	2.42–25.00	2.54–22.50
Range of h, k, l	$-6 \leq h \leq 0$	$-19 \leq h \leq 20$	$-25 \leq h \leq 0$
	$0 \leq k \leq 19$	$-9 \leq k \leq 0$	$-1 \leq k \leq 9$
	$-15 \leq l \leq 15$	$-19 \leq l \leq 0$	$0 \leq l \leq 22$
Reflections collected	2219	3957	2910
Independent reflections	2067 ($R_{int} = 0.0495$)	3876 ($R_{int} = 0.0153$)	2903 ($R_{int} = 0.2518$)
Solution and refinement data/restraints/parameters	2067/0/208	3876/0/259	2903/1/559
Goodness-of-fit on F^2	0.759	0.936	0.846
Final R indices [$I > 2\sigma > (I)$]	$R_1 = 0.0600$,	$R_1 = 0.0278$,	$R_1 = 0.0395$,
	$wR_2 = 0.1308$	$wR_2 = 0.0660$	$wR_2 = 0.1004$
R indices (all data)	$R_1 = 0.1139$,	$R_1 = 0.0363$,	$R_1 = 0.0576$,
	$wR_2 = 0.1425$	$wR_2 = 0.0679$	$wR_2 = 0.1163$
Residual electron density (e Å^{-3})	0.859 to -0.365	0.530 to -0.336	0.473 to -0.348

collection and refinement parameters are given in Table 3, atomic coordinates and isotropic displacement parameters are given in Table 4, bond distances are given in Table 5 and selected bond angles are given in Table 6. Fig. 1 shows an isotropic displacement plot with the atomic labelling scheme.

3.2. X-ray structure of *trans*-PdCl$_2$[PPh(CH$_2$CH$_2$-η^5-C$_5$H$_4$)$_2$Fe]$_2$ (**4**)

Single crystals of **4**·2THF were obtained by cooling a saturated THF solution to -20°C. An orange plate was mounted on a glass capillary. The unit cell parameters were obtained by least-squares refinement of the setting angles of 20 reflections with $4.84° \leq \theta \leq 12.51°$ from a Siemens P4 diffractometer. Data were refined on F^2 using the full-matrix least-squares method [24] after

being corrected for absorption by using the ψ-scan method. The intensities of three standard reflections, measured every 97 reflections throughout the data collection, showed only 4.64% decay. The structure was solved by direct methods [25]. Hydrogen atoms were fixed in idealised positions with isotropic thermal parameters 1.2 times that of the attached atom. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Neutral scattering factors and anomalous dispersion corrections for non-hydrogen atoms were taken from Ibers and Hamilton [26]. Crystal data, data collection and refinement parameters are given in Table 3, atomic coordinates and isotropic displacement parameters are given in Table 7, bond distances are given in Table 5 and selected bond angles are given in Table 6. Fig. 2 shows an isotropic displacement plot with the atomic labelling scheme.

3.3. X-ray structure of $(OC)_4FePPh(CH_2CH_2-\eta^5-C_5H_4)_2Fe$ (7)

Single crystals of **7** were obtained by cooling a saturated petroleum ether solution to $-20°C$. An orange needle was mounted on a glass capillary. The unit cell parameters were obtained by least-squares refinement of the setting angles of 22 reflections with $5.19° \leq \theta \leq 10.97°$ from a Siemens P4 diffractometer. Data were refined on F^2 using the full-matrix least-squares method [24] after being corrected for absorption by using the ψ-scan method. The intensities of three standard reflections, measured every 97 reflections throughout the data collection, showed no variation within experimental error. The structure was solved by direct methods [25]. Hydrogen atoms were fixed in idealised positions with isotropic thermal parameters 1.2 times that of the attached atom. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Neutral scattering factors and anomalous dispersion corrections for non-hydrogen atoms were taken from Ibers and Hamilton [26]. Crystal data, data collection and refinement parameters are given in Table 3, atomic coordinates and isotropic displacement parameters are given in Table 8, bond distances are given in Table 5 and selected bond angles are given in Table 6. Fig. 3 shows a thermal ellipsoid plot with the atomic labelling scheme.

Table 4

Atomic coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for OPPh(CH_2CH_2C_5H_4)_2Fe (3)

	x	y	z	U_{eq}
Fe	9231(2)	7651(1)	804(1)	28(1)
P	5404(4)	5961(1)	−1163(2)	29(1)
O	3038(11)	5966(4)	−1026(4)	48(2)
C11	5814(16)	5358(5)	−2124(6)	27(2)
C12	4015(17)	5266(5)	−2820(6)	39(3)
C13	4219(18)	4811(5)	−3560(7)	43(3)
C14	6195(18)	4453(5)	−3595(7)	37(3)
C15	8014(19)	4553(5)	−2906(7)	44(3)
C16	7853(16)	5010(5)	−2162(6)	31(2)
C31	6354(15)	6855(5)	−1482(6)	33(2)
C32	5351(13)	7508(5)	−999(6)	31(2)
C33	7034(17)	7948(5)	−351(6)	33(2)
C34	6547(16)	8308(5)	444(6)	30(2)
C35	8396(16)	8730(5)	809(6)	35(3)
C36	10097(14)	8618(5)	278(6)	30(2)
C37	9263(15)	8129(5)	−445(6)	29(2)
C21	7348(16)	5647(5)	−203(6)	34(2)
C22	7120(15)	5990(5)	749(5)	26(2)
C23	8828(16)	6559(5)	1097(6)	29(2)
C24	8682(16)	7013(5)	1883(6)	33(2)
C25	10707(15)	7396(5)	2109(6)	36(2)
C26	12128(16)	7204(5)	1472(6)	32(2)
C27	10985(14)	6697(5)	875(6)	29(2)

Table 5
Bond lengths (Å) for compounds **3**, **4** and **7**

Bond lengths (Å)	3	4	7	7′
Fe1–CNT(2)	1.65(1)	1.662(3)	1.65(1)	1.64(1)
Fe1–CNT(3)	1.65(1)	1.657(3)	1.63(1)	1.66(1)
Fe1–C23	2.058(8)	2.082(3)	2.041(11)	2.082(11)
Fe1–C24	2.025(9)	2.062(3)	2.043(12)	2.036(11)
Fe1–C25	2.024(9)	2.044(3)	2.055(12)	2.009(12)
Fe1–C26	2.027(9)	2.040(3)	2.053(13)	2.031(11)
Fe1–C27	2.028(9)	2.058(3)	2.030(12)	2.070(11)
Fe1–C33	2.043(9)	2.074(3)	2.018(11)	2.061(9)
Fe1–C34	2.012(10)	2.059(3)	2.019(12)	2.041(11)
Fe1–C35	2.029(9)	2.043(3)	2.021(11)	2.017(11)
Fe1–C36	2.024(9)	2.041(3)	2.039(11)	2.070(10)
Fe1–C37	2.023(8)	2.044(3)	2.044(11)	2.038(9)
P–C11	1.829(9)	1.819(3)	1.833(12)	1.830(11)
P–C21	1.771(9)	1.824(3)	1.833(11)	1.832(11)
P–C31	1.811(9)	1.820(3)	1.824(11)	1.816(11)
C11–C16	1.390(12)	1.385(4)	1.39(2)	1.388(14)
C11–C12	1.372(11)	1.396(4)	1.39(2)	1.39(2)
C12–C13	1.383(12)	1.397(4)	1.38(2)	1.39(2)
C13–C14	1.364(13)	1.369(5)	1.37(2)	1.37(2)
C14–C15	1.376(13)	1.380(5)	1.35(2)	1.41(2)
C15–C16	1.384(12)	1.397(4)	1.39(2)	1.38(2)
C21–C22	1.549(11)	1.551(4)	1.50(2)	1.54(2)
C22–C23	1.490(12)	1.498(4)	1.52(2)	1.51(2)
C23–C24	1.428(12)	1.434(4)	1.44(2)	1.43(2)
C23–C27	1.409(12)	1.427(4)	1.43(2)	1.41(2)
C24–C25	1.397(12)	1.417(4)	1.42(2)	1.40(2)
C25–C26	1.403(12)	1.423(4)	1.41(2)	1.41(2)
C26–C27	1.377(12)	1.424(4)	1.38(2)	1.42(2)
C31–C32	1.553(11)	1.543(4)	1.533(14)	1.532(14)
C32–C33	1.503(12)	1.505(4)	1.53(2)	1.501(14)
C33–C34	1.404(12)	1.434(4)	1.39(2)	1.43(2)
C33–C37	1.409(12)	1.424(4)	1.42(2)	1.42(2)
C34–C35	1.387(12)	1.417(4)	1.41(2)	1.40(2)
C35–C36	1.393(12)	1.419(5)	1.44(2)	1.43(2)
C36–C37	1.411(11)	1.424(4)	1.43(2)	1.40(2)
P–E[a]	1.468(7)	2.3208(7)	2.254(3)	2.226(3)
Pd–Cl		2.2993(7)		
Fe2–C1			1.782(13)	1.813(13)
Fe2–C2			1.812(14)	1.780(13)
Fe2–C3			1.776(12)	1.785(12)
Fe2–C4			1.793(13)	1.793(14)
C1–O1			1.150(14)	1.124(14)
C2–O2			1.135(14)	1.134(14)
C3–O3			1.144(14)	1.163(13)
C4–O4			1.153(14)	1.15(2)

[a] E = O for **3**, Pd for **4** and Fe2 for **7**.

4. Results and discussion

4.1. Synthesis and characterisation of bis(2-cyclopentadienylethyl)phenylphosphine (1)

The most useful synthetic route to prepare a tethered cyclopentadienyl-phosphine ligand depends upon the spacer between the two groups [27]. Whereas reaction of cyclopentadienide with a chlorophosphine will give the zero-atom bridged ligand, the methylene-bridged

Table 6
Selected bond angles (°) for compounds **3**, **4** and **7**

Bond angle (°)	3	4	7	7′
C31–P–C21	107.3(4)	102.59(13)	107.3(6)	103.3(5)
C31–P–C11	104.8(4)	107.11(12)	105.7(5)	103.7(5)
C21–P–C11	105.1(4)	105.24(13)	103.7(5)	103.6(5)
C12–C11–P	117.1(7)	119.8(2)	118.5(9)	121.9(8)
C16–C11–P	122.1(7)	121.1(2)	122.1(10)	119.9(8)
C22–C21–P	115.9(6)	114.1(2)	121.0(8)	115.5(8)
C32–C31–P	114.3(6)	110.2(2)	119.4(8)	114.2(7)
C22–C23–Fe1	134.3(6)	134.6(2)	130.8(8)	137.5(8)
C32–C33–Fe1	131.4(6)	131.1(2)	125.9(7)	131.1(7)
C21–C22–C23	115.6(7)	115.1(2)	116.7(10)	117.5(9)
C24–C23–C22	123.4(8)	124.6(3)	127.8(11)	126.8(10)
C27–C23–C22	131.0(8)	127.8(3)	125.8(11)	125.2(11)
C33–C32–C31	115.0(7)	114.3(2)	113.9(9)	114.2(8)
C34–C33–C32	124.2(9)	125.7(3)	126.7(10)	126.6(9)
C37–C33–C32	128.4(8)	126.8(3)	124.1(9)	125.7(9)
C31–P–E[a]	112.4(4)	113.82(9)	113.4(4)	113.5(4)
C21–P–E[a]	115.3(4)	117.53(9)	111.3(4)	116.1(4)
C11–P–E[a]	111.1(4)	109.70(9)	114.8(4)	115.0(4)
Cl–Pd–P		92.01(3)		
ClA–Pd–P		87.99(3)		
P–Fe2–C1			179.7(4)	171.9(4)
P–Fe2–C2			87.7(4)	88.4(4)
P–Fe2–C3			88.0(4)	92.3(4)
P–Fe2–C4			87.7(4)	84.0(4)

[a] E = O for **3**, Pd for **4** and Fe2 for **7**.

ligand is best prepared by reaction of an appropriate phosphide with a pentafulvene. The trimethylene-bridged ligands are best prepared by reaction of cyclopentadienide with a 3-chloropropylphosphine. Analogous routes are generally unsuitable for ethylene-bridged ligands due to a range of undesirable side reactions. One notable exception is the one-pot synthesis of 2-(tetramethylcyclopentadienyl)-1-(diphenylphosphino)ethane by Szymoniak and coworkers by treatment of tetramethylcyclopentadiene with 2-chloroethyl tosylate followed by lithium diphenylphosphide [28]. More generally, the ethylene-bridged ligands are best prepared by the ring-opening reaction of a spiro[2.4]hepta-4,6-diene with a phosphide. Thus, the route taken to prepare bis(2-cyclopentadienylethyl)-phenylphosphine (**1**) involves the treatment of two
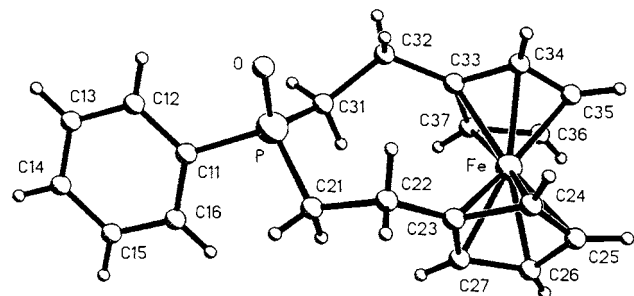
Table 7
Atomic coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for *trans*-PdCl$_2$[PPh(CH$_2$CH$_2$C$_5$H$_4$)$_2$Fe]$_2$·2THF (**4**·2THF)

	x	y	z	U_{eq}
Pd	5000	0	5000	14(1)
Fe	1560(1)	3338(1)	5055(1)	21(1)
P	3864(1)	1039(1)	4252(1)	16(1)
Cl	5529(1)	2691(1)	5179(1)	25(1)
C11	3940(2)	730(4)	3183(2)	21(1)
C12	4239(2)	2036(5)	2734(20)	32(1)
C13	4356(2)	1768(5)	1928(2)	40(1)
C14	4177(2)	223(5)	1572(2)	42(1)
C15	3877(2)	−1076(5)	2008(2)	41(1)
C16	3762(2)	−828(4)	2816(2)	32(1)
C21	3632(2)	3293(3)	4358(2)	20(1)
C22	2906(2)	3914(4)	3782(2)	25(1)
C23	2197(2)	4435(4)	4188(2)	22(1)
C24	1386(2)	4129(4)	3870(2)	26(1)
C25	878(2)	5025(4)	4346(2)	31(1)
C26	1368(2)	5902(4)	4961(2)	34(1)
C27	2177(2)	5537(4)	4866(2)	29(1)
C31	2950(2)	1(4)	4476(2)	21(1)
C32	2839(2)	226(4)	5376(2)	22(1)
C33	2078(2)	1104(4)	5525(2)	24(1)
C34	1991(2)	2316(4)	6153(2)	30(1)
C35	1172(2)	2718(4)	6135(2)	37(1)
C36	747(2)	1778(4)	5501(2)	33(1)
C37	1306(2)	797(4)	5118(2)	27(1)
O	9590(2)	1636(5)	7869(2)	83(1)
C41	9139(3)	1195(7)	7160(3)	73(1)
C42	8316(2)	1745(6)	7230(3)	63(1)
C43	8376(3)	2997(6)	7909(3)	65(1)
C44	9253(3)	3209(6)	8097(2)	72(2)

equivalents of spiro[2.4]hepta-4,6-diene with phenylphosphine and two equivalents of *n*-BuLi, followed by aqueous hydrolysis (Scheme 1). After chromatography, **1** is obtained in high yield as a colourless or slightly yellow oil.

Compound **1** has been characterised by ^{1}H-, ^{13}C{^{1}H}-, ^{31}P{^{1}H}-NMR, ^{1}H/^{13}C-HETCOR-, and ^{1}H-COSY-NMR spectroscopy, as well as by mass spectrometry and microanalysis. ^{1}H- and ^{13}C{^{1}H}-NMR

Fig. 1. Isotropic displacement plot with the atomic numbering scheme for OPPh(CH$_2$CH$_2$C$_5$H$_4$)$_2$Fe (**3**).
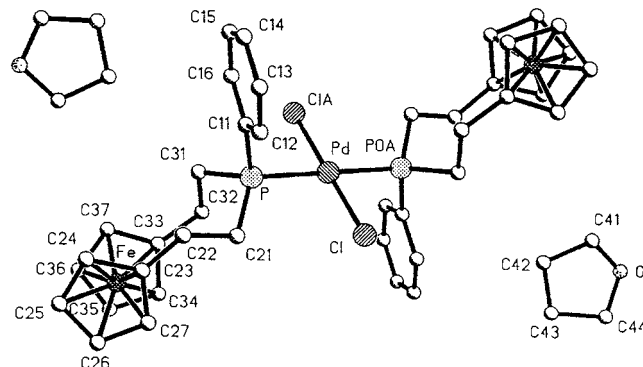
Fig. 2. Isotropic displacement plot with the atomic numbering scheme for *trans*-PdCl$_2$[PPh(CH$_2$CH$_2$C$_5$H$_4$)$_2$Fe]$_2$ (**4**).

Table 8
Atomic coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for $Fe(CO)_4[PPh(CH_2CH_2C_5H_4)_2Fe]$ (**7**)

	x	y	z	U_{eq}
Molecule 1				
Fe1	5007(1)	12900(2)	4372(1)	20(1)
Fe2	4166(1)	8559(2)	2043(1)	20(1)
P	4863(1)	9487(3)	2652(1)	18(1)
C1	3613(5)	7825(14)	1565(6)	32(3)
C2	3695(5)	9060(12)	26820(7)	30(3)
C3	4329(4)	10056(13)	1485(6)	23(3)
C4	4504(5)	6678(15)	2065(6)	29(3)
O1	3258(4)	7390(11)	1245(5)	47(3)
O2	3394(3)	9403(9)	3073(4)	32(2)
O3	4413(4)	11027(10)	1121(4)	39(2)
O4	4716(4)	5460(10)	2076(5)	42(2)
C11	5562(5)	8922(13)	2390(6)	25(3)
C12	5788(5)	9681(14)	1868(6)	33(3)
C13	6304(5)	9280(18)	1638(6)	41(3)
C14	6599(5)	8100(16)	1927(7)	41(4)
C15	6379(6)	7348(17)	2435(8)	46(4)
C16	5863(5)	7737(14)	2687(6)	31(3)
C21	4821(4)	8708(14)	3461(5)	23(3)
C22	5213(5)	9264(13)	3968(6)	32(3)
C23	4993(5)	10500(12)	4421(6)	26(3)
C24	4439(5)	11125(14)	4458(6)	29(3)
C25	4409(5)	12131(15)	4995(6)	34(3)
C26	4935(6)	12115(15)	5288(6)	44(4)
C27	5288(5)	11148(13)	4950(6)	33(3)
C31	4873(5)	11630(13)	2711(6)	25(3)
C32	5399(4)	12461(12)	2948(5)	16(2)
C33	5301(4)	13554(13)	3515(5)	20(3)
C34	4817(4)	14378(12)	3654(6)	21(3)
C35	4892(4)	15229(12)	4222(5)	23(3)
C36	5453(5)	14937(12)	4427(6)	29(3)
C37	5705(4)	13883(12)	3985(5)	22(3)
Molecule 2				
Fe1′	2619(1)	3494(2)	3104(1)	19(1)
Fe2′	2096(1)	7828(2)	5378(1)	24(1)
P′	2762(1)	6349(3)	4951(1)	18(1)
C1′	1506(5)	8770(15)	5753(6)	33(3)
C2′	1721(5)	7659(16)	4655(6)	36(3)
C3′	2534(5)	9525(13)	5397(6)	27(3)
C4′	2164(5)	6507(15)	6037(6)	30(3)
O1′	1131(4)	9336(11)	5976(4)	46(2)
O2′	1485(4)	7642(12)	4189(5)	55(3)
O3′	2810(3)	10649(10)	5393(5)	43(2)
O4′	2229(4)	5646(11)	6453(4)	46(2)
C11′	3432(4)	6422(12)	5361(5)	21(2)
C12′	3580(4)	5315(14)	5816(6)	27(3)
C13′	4090(5)	5385(15)	6121(6)	34(3)
C14′	4465(5)	6549(16)	5972(6)	27(3)
C15′	4315(4)	7702(14)	5524(5)	25(3)
C16′	3804(4)	7628(11)	5229(5)	17(2)
C21′	2614(5)	4238(13)	4892(6)	26(3)
C22′	2068(4)	3805(14)	4558(6)	31(3)
C23′	2106(4)	3189(13)	3890(6)	23(3)
C24′	1806(4)	3748(16)	3352(6)	33(3)
C25′	1867(5)	2669(16)	2855(6)	36(3)
C26′	2200(5)	1418(15)	3072(6)	32(3)
C27′	2347(5)	1740(13)	3711(6)	28(3)
C31′	2932(4)	6896(12)	4142(5)	19(2)
C32′	3415(4)	5959(12)	3855(5)	14(2)
C33′	3263(4)	5035(11)	3274(5)	15(2)

Table 8 (continued)

	x	y	z	U_{eq}
C34′	2927(4)	5561(14)	2758(5)	23(3)
C35′	2927(5)	4386(13)	2291(5)	27(3)
C36′	3267(5)	3113(13)	2512(5)	26(3)
C37′	3466(4)	3508(13)	3116(6)	21(2)

spectroscopy (see Table 2) indicate that there are two major cyclopentadiene ring isomers, shown below as ring A and ring B, in approximately equal amounts. No peaks corresponding to the third possible ring isomer, C, have been observed. There are six multiplets in the vinyl proton region (three from ring A and three from ring B) which are associated with six carbon resonances in the ^{13}C-NMR spectrum. Two singlets in the methylene region (2.93 and 2.85 ppm) and their associated ^{13}C resonances are assigned to the cyclopentadiene methylene groups. Combinations of the two ring isomers should give three isomers of compound **1** in about a 1:2:1 ratio. The methylene region is expected to be complex—with up to four ABCD patterns that could be observed. The HETCOR (8.456 T) spectrum, however, distinguishes only four proton environments each of which is associated with a different carbon atom. This observation is consistent with each set of A/B and C/D resonances being approximately degenerate and the nature of one ring isomer having little or no effect on the chemical shifts observed for the other cyclopentadienylethyl substituent. That there are indeed three isomers for **1** was confirmed by $^{31}P\{^1H\}$-NMR spectroscopy which gives three peaks (-22.55, -22.40 and -22.25 ppm) resulting from the *AA*, *AB* and *BB* isomers (not necessarily in that order). Although the nature of one ring does not significantly affect the ^1H and ^{13}C chemical shifts of either the phenyl atoms or the other cyclopentadienylethyl substituent atoms, it does affect the ^{31}P chemical shift. Paolucci and coworkers, based on ^1H- and $^{13}C\{^1H\}$-NMR spectroscopy, reported that they observed only the mixed *AB* isomer for the related compound 2,6-bis(cyclopentadienylmethyl)pyridine [10]. They may not have been able to detect the presence of the *AA* and *BB* isomers.

(A) (B) (C)
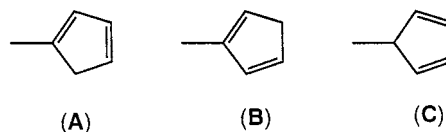
The P–C coupling constants are consistent with those found for $PhPEt_2$ and PhP^nPr_2 [29,30]. The $^1J_{PC}$ coupling constants are smaller than the $^2J_{PC}$ values: for the ethylene bridge, $^1J_{PC} = 12.4$ and 11.7 Hz versus 12.5 Hz for $PhPEt_2$ and 12.8 Hz for $PhPn\text{-}Pr_2$ whereas $^2J_{PC} = 16.0$ and 15.7 Hz versus 14.7 Hz for $PhPEt_2$ and 15.4 Hz for $PhPn\text{-}Pr_2$. For the phenyl ring, the $^1J_{PC}$
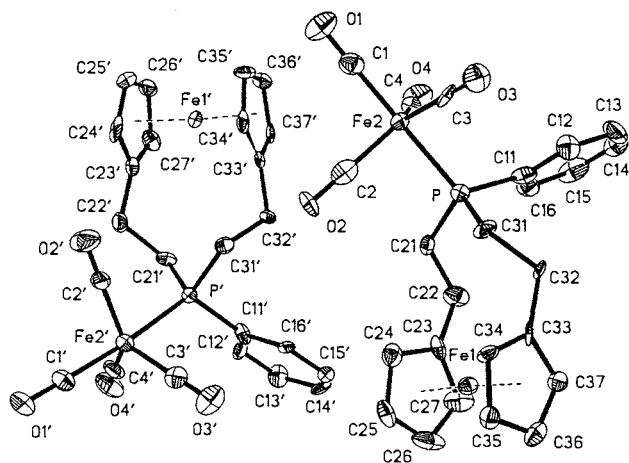
Fig. 3. Thermal ellipsoid plot with the atomic numbering scheme for $Fe(CO)_4[PPh(CH_2CH_2C_5H_4)_2Fe]$ (**7**).

coupling constant of 10.0 Hz appears to be small compared with 17.9 Hz for $PhPEt_2$, however, the $^2J_{PC}$ (18.3 vs. 18.6 Hz) and $^3J_{PC}$ (7.0 vs. 6.7 Hz) coupling constants are similar.

4.2. Synthesis and characterisation of $PPh(CH_2CH_2-\eta^5-C_5H_4)_2Fe$ (2)

Deprotonation of **1** with two equivalents of n-BuLi followed by treatment with $FeCl_2$ gives the ferrocene complex $PPh(CH_2CH_2-\eta^5-C_5H_4)_2Fe$ (**2**) in moderate yields of 40–50%. A significant amount of dark brown gelatinous material, which is presumably polymeric, is produced also. We have been unable to isolate any other compounds. The ^1H-NMR spectrum is consistent with an average C_s symmetry with the mirror plane through the phenyl group and the Fe and P atoms: There is one ABCD pattern for the cyclopentadienyl protons and one ABCD pattern for the methylene protons. The $^{13}C\{^1H\}$-NMR spectrum is also consistent with a C_s structure. $^{31}P\{^1H\}$-NMR spectroscopy shows one peak at -16.8 ppm. This is small upfield shift of 3.6 ppm from the protonated ligand **1** and indicates that the P atom is not coordinated to an Fe atom.
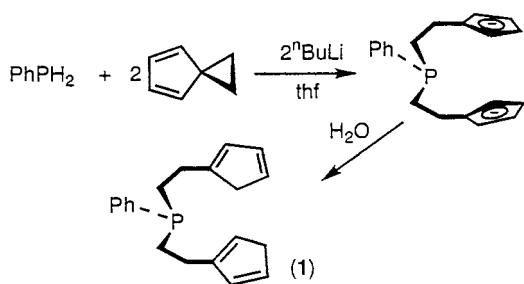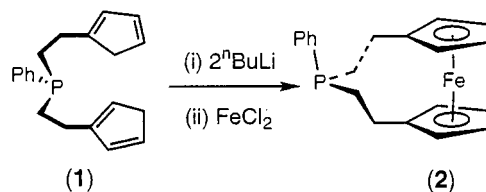
4.3. Synthesis and characterisation of $OPPh(CH_2CH_2-\eta^5-C_5H_4)_2Fe$ (3)

Treatment of **2** with trimethylamine-N-oxide in THF gives the phosphine oxide complex $O=PPh(CH_2CH_2-\eta^5-C_5H_4)_2Fe$ (**3**) (Scheme 2). Air oxidation of solutions of **2** also give this product, however, the reaction is not as clean. As with **2**, NMR spectroscopy indicates C_s symmetry with the mirror plane through the phenyl group and the Fe, P and O atoms: the four ring protons exhibit an ABCD pattern and there are five ring carbon atoms in the ^{13}C-NMR spectrum. The ^{31}P resonance has shifted 58.4 ppm downfield from that found in **2** to 41.6 ppm. This chemical shift difference is typical for the formation of phosphine oxides.

An X-ray crystallographic analysis of **3** was carried out to determine the ligand conformation. This analysis showed one unique molecule of **3** per asymmetric unit. The molecule consists of a fully eclipsed ferrocene unit (the C33–CNT(3)–CNT(2)–C23 dihedral angle is 9.7°) with the two cyclopentadienyl rings linked to a phosphorus atom by ethylene bridges (Fig. 1). The phosphorus atom is approximately tetrahedral and has a phenyl substituent and oxygen atom attached to it in addition to the ethylene bridges to the ferrocenyl unit.

The CNT(2)–Fe–CNT(3) angle of 177.5° indicates that there may be a small amount of ring strain. This is
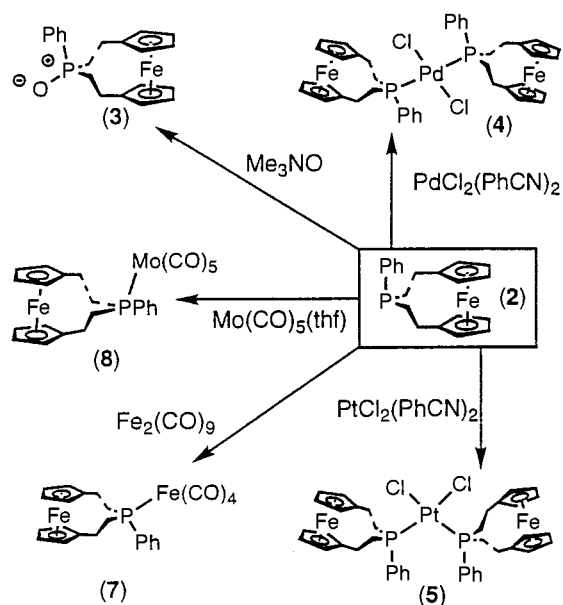
Scheme 1.

Scheme 2.

also indicated by the angles between the Cp–CH$_2$ vector and the cyclopentadienyl ring plane which averages 6.5°. The conformer adopted has an approximate mirror plane through the Fe, O, P and C11 atoms (O–P–Fe–CNT(3) = 77.6° and C11–P–Fe–CNT(2) = 85.1°). The phenyl ring is twisted out of this plane. This conformation results in the less bulky oxygen atom being oriented towards the ferrocenyl unit (Fe–P–O = 108.2°) while the bulkier phenyl group is oriented away from the ferrocenyl unit (Fe–P–C11 = 140.4°).

4.4. Synthesis and characterisation of the trinuclear complexes trans-PdCl$_2$[PPh(CH$_2$CH$_2$-η^5-C$_5$H$_4$)$_2$Fe]$_2$ (4) and cis-PtCl$_2$[PPh(CH$_2$CH$_2$-η^5-C$_5$H$_4$)$_2$Fe]$_2$ (5)

Trinuclear heterobimetallic complexes were prepared by treating *trans*-PdCl$_2$(PhCN)$_2$ and *cis*-PtCl$_2$(PhCN)$_2$ with two equivalents of **2** to give *trans*-PdCl$_2$[PPh(CH$_2$CH$_2$-η^5-C$_5$H$_4$)$_2$Fe]$_2$ (**4**) and *cis*-PtCl$_2$[PPh(CH$_2$CH$_2$-η^5-C$_5$H$_4$)$_2$Fe]$_2$ (**5**), respectively (Scheme 2). As with **2**, both of these complexes exhibit ABCD patterns for the cyclopentadienyl and methylene protons in the ^{1}H-NMR spectrum. The ^{31}P chemical shift of 22.1 ppm for **4** is 38.9 ppm upfield of that observed for **2** whereas a chemical shift of 4.1 ppm is observed for **5**—an upfield shift of 20.9 ppm from that of **2**. These upfield shifts are consistent with coordination of the phosphine to the metal centre. Similar upfield shift changes are observed for analogous Pd–PPhMe$_2$ (42.3 ppm) [31] and Pt–PEt$_3$ (29.1 ppm) [32] systems. A one bond ^{195}Pt–^{31}P coupling constant of 3542 Hz for complex **5** is consistent with a *cis* geometry for this complex [33].

To assist in the characterisation of **4**, and to investigate the conformation adopted by the ligand, an X-ray crystal structure determination was carried out. The crystal structure shows that one independent molecule of **4** lies with the palladium atom on a crystallographic inversion center while one independent molecule of THF does not. This gives two molecules of THF for each molecule of **4**. Fig. 2 shows an isotropic plot of one molecule of **4** with the adopted numbering scheme.

Molecule **4** consists of a square-planar *trans*-dichlorodiphosphine-palladium centre and, as is usually observed with such complexes [34], the Pd–P bond distances (2.3208(7) Å) are longer than the Pd–Cl bond distances (2.2993(7) Å). Each phosphine has one phenyl substituent and one ferrocenyl substituent which is linked to the phosphorus atom by two ethylene bridges—one from each cyclopentadienyl group. The tetrahedral geometry of the phosphorus atom is distorted by ring strain such that the angle between the two methylene carbon atoms is reduced to 102.59(13)°. By comparison, the angles between the phenyl and the methylene carbon atoms are 105.24(13) and 107.11(12)°. Further evidence of ring-strain is provided

by consideration of the angle between the cyclopentadienyl planes (which are tilted away from the heterocyclic ring) of 6.1°, the CNT(2)–Fe–CNT(3) angle of 175.7°, and the angles between each cyclopentadienyl plane and its associated Cp–CH$_2$ bond vector which are 7.6° (ring C23–C26) and 4.4° (ring C33–C36). Consequently, the angle between the two Cp–CH$_2$ bond vectors is 19.6° (the C22–C23–C33–C32 dihedral angle of 6.8° contributes only 1.5° to this value). This is in contrast to the apparently ring-strain-free ferrocene complex Me$_2$Si(OSiMe$_2$C$_5$H$_4$)$_2$Fe (**6**) that was reported by Manners and coworkers [18]. In **6**, the angle between the cyclopentadienyl rings is less than 2° while the average angle between each cyclopentadienyl plane and its *ipso*-Cp–Si bond vector is only 1.6°. It is most likely that any ring-strain in **6** is relieved by the wide angles at the oxygen atoms (average Si–O–Si = 159.7°). By comparison, all of the ring angles at the sp^3 hybridised atoms in **4** are less than 116°. Both **4** and **6** exhibit an eclipsed geometry for the cyclopentadienyl rings (the cyclopentadienyl rings are 5.1° from a perfectly eclipsed geometry in **4** and 0.9° from a perfectly eclipsed geometry in **6**). The C–Si bonds in **6**, however, are rotated 72.9° from the fully eclipsed geometry.

The conformer adopted for the ring backbone of **4** is one that places the PdCl$_2$P and phenyl groups in approximately equivalent environments (Pd–P–Fe–CNT(3) = 49.0° and C11–P–Fe–CNT(2) = 53.0° while Fe–P–Pd = 130.9° and Fe–P–C11 = 119.3°) and as far away from the ferrocene unit as possible when allowing for reasonable bond angles and bond distances for the ring atoms. The nature of this conformer can be rationalised by considering the similar steric properties of the phenyl and PdCl$_2$P groups which both have flat structures. As a result of this steric similarity, there is a pseudo C_2 axis through the P and Fe atoms. The conformer adopted by **6**, however, is dominated by steric interactions between the SiMe$_2$ groups attached to the cyclopentadienyl rings.

4.5. Synthesis and characterisation of the dinuclear complexes (OC)$_4$FePPh(CH$_2$CH$_2$-η^5-C$_5$H$_4$)$_2$Fe (7) and (OC)$_5$MoPPh(CH$_2$CH$_2$-η^5-C$_5$H$_4$)$_2$Fe (8)

Dinuclear complexes were prepared by treating either Fe$_2$(CO)$_9$ or Mo(CO)$_5$(THF) with one equivalent of **1** to give (CO)$_4$FePPh(CH$_2$CH$_2$-η^5-C$_5$H$_4$)$_2$Fe (**7**) or (CO)$_5$MoPPh(CH$_2$CH$_2$-η^5-C$_5$H$_4$)$_2$Fe (**8**), respectively (Scheme 2). The infrared spectra of **7** and **8** both show the expected three ν_{CO} stretches (2A$_1$ and E) for Fe(CO)$_4$L and Mo(CO)$_5$L complexes with approximate C_{3v} and C_{4v} symmetry, respectively. Again, the ^{1}H-NMR spectra exhibit a single ABCD pattern for the cyclopentadienyl ring protons while the ^{13}C-NMR spectra show five environments for the cyclopentadienyl ring carbon atoms. The methylene carbons of both
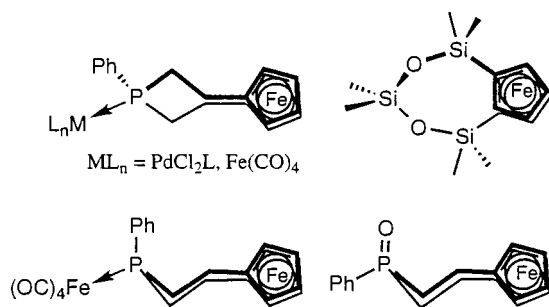
Fig. 4. Illustration of the conformational differences between complexes 3, 4, 6 and 7.

complexes show a number of resonances at room temperature due to the slow interconversion of conformers. At elevated temperatures, only two resonances are observed as conformational interconversion becomes rapid. The carbonyl ligands for 7 appear as one doublet ($^2J_{PC} = 18.8$ Hz), as is expected for an Fe(CO)$_4$L complex undergoing rapid Berry pseudorotation. Complex 8, on the other hand, shows two carbonyl environments. Large downfield shifts relative to 2 for the ^{31}P-NMR resonances (66.7 ppm for 7, $\Delta = 83.5$ ppm, and 32.6 ppm for 8, $\Delta = 49.4$ ppm) are consistent with coordination of phosphorus to these metal carbonyls.

An X-ray crystal structure analysis of 7 revealed the presence of two independent molecules in the asymmetric unit with differing backbone conformations. Fig. 3 shows a thermal ellipsoid plot of the two molecules and Fig. 4 illustrates the essential differences between the conformers adopted by 3, 4, 6 and the two molecules of 7. The unprimed molecule has a conformation similar to that found for the solid-state structure of 3: the Fe1, Fe2, P and C11 atoms are approximately coplanar with an approximate mirror plane through them. In this case, however, the phenyl group is oriented towards the ferrocene unit (Fe1–P–C11 = 109.6°) and the bulkier Fe(CO)$_4$ group is directed away from the ferrocene unit (Fe1–P–Fe2 = 135.4°). Like compounds 3 and 4, evidence of ring-strain is provided by the angle between the cyclopentadienyl planes (which are tilted away from the heterocyclic ring) of 7.1°, the CNT(2)–Fe–CNT(3) angle of 176.1°, and the angles between each cyclopentadienyl plane and its associated Cp–CH$_2$ bond vector which are 10.1° (ring C23–C26) and 4.1° (ring C33–C36). Consequently, the angle between the two Cp–CH$_2$ bond vectors is 21.3°. The primed molecule exhibits a conformation similar to that of 4: there is a pseudo C_2 axis through the Fe1′ and P′ atoms and the Fe(CO)$_4$ and phenyl groups are in approximately equivalent environments (C11′–P′–Fe1′–CNT(3)′ = 50.2° and Fe2′–P′–Fe1′–CNT(2)′ = 54.8°). There appears to be less strain in this conformation: The angle between the cyclopentadienyl planes (which are tilted away from the heterocyclic ring) is only 3.2° and the angles be-

tween each cyclopentadienyl plane and its associated Cp–CH$_2$ bond vector are only 4.9° (ring C23–C26) and 0.1° (ring C33–C36). Consequently, the angle between the two Cp–CH$_2$ bond vectors is significantly less at 14.9° (vs. 19.1, 19.6 and 21.3° for molecules 3, 4, and the unprimed molecule of 7, respectively). The CNT(2)–Fe–CNT(3) angle of 175.7° is similar to that of the other structures.

4.6. ^{13}C-NMR spectra of complexes 2, 3, 4, 5, 7 and 8

The ^{13}C spectrum of 2 is similar to that of 1, but with a number of resonances shifted upfield. The ipso-cyclopentadienyl ring carbon appears at 90.4 ppm with the other ring resonances at 66.1–67.9 ppm. These are typical of ferrocene complexes. The ethylene-bridge carbons are shifted upfield by ca. 5 ppm with a small decrease in the $^1J_{PC}$ coupling constant and a small increase in the $^2J_{PC}$ coupling constant. Similarly, the phenyl resonances exhibit minor variations with the exception of $^1J_{PC}$ which has increased from 10.0 to 16.4 Hz. This is much more like PhPEt$_2$ (17.9 Hz).

Coordination of 2 to oxygen or a metal complex gives the largest chemical shift change to the ipso-phenyl carbon and the methylene-carbon atoms. The ipso-carbon atoms all move upfield from 140.7 ppm to between 133.9 and 137.2 ppm. For the methylene-carbon atoms, the β-carbon atoms all exhibit upfield shifts whereas the α-carbon atoms are shifted downfield for complexes 3, 7 and 8, but upfield for the palladium and platinum complexes 4 and 5. The behaviour shown by complexes 3, 7 and 8 is the same as that of PhPEt$_2$ when coordinated to a Ni(CO)$_3$ fragment [30].

The one-bond P–C coupling constants increase by variable amounts upon coordination of 2. The largest increase is observed for the phosphine oxide 3 (16.4 to 94.9 Hz for the ipso-phenyl carbon and 10.5 to 65.7 Hz for the α-methylene carbon atoms). There is a strong correlation between the coupling constants of the ipso-carbon atom and the α-methylene carbon atoms ($R^2 = 0.97$). The two-bond P–C coupling constants, however, all decrease upon coordination of 2: from 15.7 Hz to less than 10 Hz for the ortho-phenyl carbon atoms and from 10.5 Hz to less than 4 Hz for the β-methylene carbon atoms.

4.7. Electrochemistry of complexes 2, 3, 4, 5 and 7

The electrochemistry of complexes 2, 3, 4, 5 and 7 was investigated by cyclic voltammetry. The results are summarised in Table 9. Fig. 5 shows a typical cyclic voltammogrametric response in acetonitrile for complex 2: an irreversible oxidation occurs at $E_p = -0.34$ V versus Fc$^+$/Fc followed by a reversible oxidation at $E_{1/2} = 0.10$ V versus Fc$^+$/Fc. This is similar to that observed by Butler and coworkers for the ferrocene

Table 9
Electrochemical data for compounds **2**, **3**, **4**, **5** and **7** (V vs. Fc^+/Fc)

Compound (solvent)	Scan rate (mV s^{-1})	E_p	$E_{1/2}$	E_p
2 (CH_3CN)	200	−0.34	0.10	
3 (CH_2Cl_2)	200		−0.01	
4 (CH_2Cl_2)	100		−0.005	
5 (CH_2Cl_2)	100		0.08	
7 (CH_3CN)	100	0.02	0.05	
7 (CH_2Cl_2)	50		0.05	0.35[a]

[a] Associated with a reduction peak at $E_p = -0.36$ V.

complex $Fe(C_5H_4PPhBu)(C_5H_4\text{-}2,2'\text{-bipyridyl})$ [35] and by Kagan and coworkers for $Fe(C_5H_5)(C_5H_3(CHO)\text{-}PPh_2)$ [36]. For the latter complex, the irreversible oxidation was ascribed to oxidation of the phosphorus atom to a phosphonium radical cation (after electron transfer to an Fe(III) centre) with subsequent oxidation to the phosphine oxide by traces of water. Similarly, Podlaha and coworkers observed two oxidations for $Fe(C_5H_4PPh_2)(C_5H_4COOR)$ (R = H, Me) for which they proposed, for the first oxidation, a mechanism similar to that given by Kagan and coworkers. For the second oxidation process, they observed almost identical potentials to those of the isolated phosphine oxide complexes, and thus attributed the second process to oxidation of the Fe(II) centre of the phosphine oxide complex [37]. For $Fe(C_5H_4PPh_2)_2$ (dppf), which exhibits a single oxidation process, Pilloni proposed the cation radical–substrate coupling mechanism in which, after oxidation at the iron centre and intramolecular transfer of an electron from phosphorus to iron, there is a rapid dimerisation or reaction with substrate to give a P–P bonded dinuclear dication or cation, respectively [38]. This P–P bonded species then undergoes irreversible reaction with water to give phosphine oxide and phosphonium species. We tentatively propose here a similar process for the electrochemistry of complex **2** (Scheme
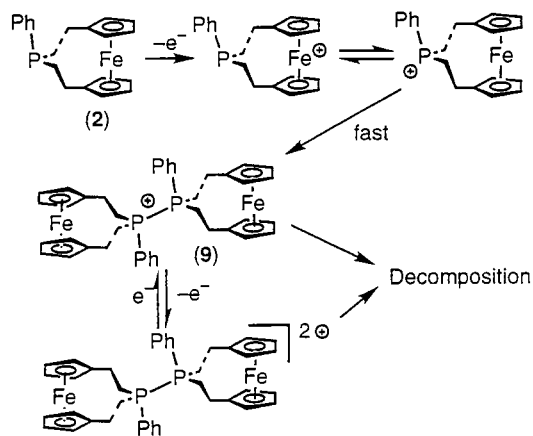
Scheme 3.

3): oxidation at the iron centre is followed by transfer of an electron to iron from phosphorus which is driven by a fast reaction with starting substrate to give the P–P bonded cation **9**, the second oxidation is proposed to occur at an iron centre of **9**. The CV of the phosphine oxide **3** shows a simple reversible oxidation at $E_{1/2} = -0.01$ V (compared with 0.10 V for the second oxidation process of **2**) which indicates that the second oxidation process of **2** cannot be due to a phosphine oxide complex. Attempts to isolate **9** have so far been unsuccessful.

The cyclic voltammograms of the tetracarbonyl iron adduct **7** in acetonitrile and dichloromethane are quite different. In acetonitrile, an irreversible oxidation at $E_p = 0.02$ V appears very close to a reversible oxidation at $E_{1/2} = 0.05$ V (Fig. 6). In addition, there is a broad reduction peak at $E_p = -0.65$ V. In dichloromethane, the reversible process still appears at $E_{1/2} = 0.05$ V (Fig. 7(a)), but now the irreversible process occurs at $E_p = 0.35$ V and is associated with adsorption at the electrode, hence the large reduction peak for the reversible process (Fig. 7(b)), as well as a small reduction peak at $E_p = -0.36$ V. The reversible process is attributed to oxidation of the ferrocene centre and the irreversible process is assigned to oxidation of the tetracarbonyl-
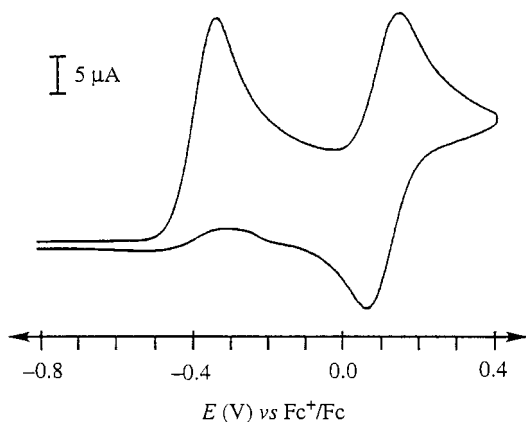

Fig. 5. Cyclic voltammogram of $PPh(CH_2CH_2C_5H_4)_2Fe$ (**2**) in acetonitrile (200 mV s^{-1}).
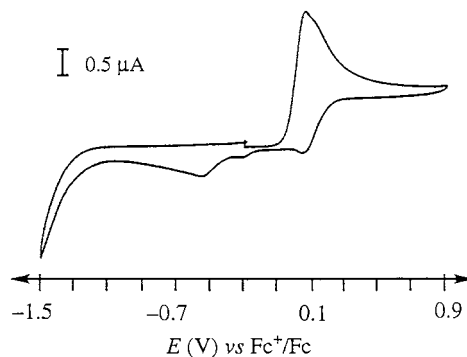
Fig. 6. Cyclic voltammogram of $Fe(CO)_4[PPh(CH_2CH_2C_5H_4)_2Fe]$ (**7**) in acetonitrile (100 mV s^{-1}).

phosphine–iron fragment. Apparently, the more polar and coordinating acetonitrile solvent is able to keep the product of this oxidation in solution and is probably taking part in the oxidation process by coordination to the oxidised iron centre via formation of an [Fe(CO)$_4$(CH$_3$CN)(PR$_3$)]$^+$ intermediate, hence the lower oxidation potential. Bond and coworkers observed irreversible oxidations at 1.2 V versus Ag/AgCl for monophosphino–tetracarbonyl-iron complexes in acetone [39].

The cyclic voltammograms of the trinuclear complexes **4** and **5** were recorded to determine if there is any electronic communication between the ferrocene centres—there are two cross-linked chains, each of seven non-conjugated atoms, between the ferrocene centres. A single two-electron reversible redox process ($E_{1/2} = -0.005$ V for **4** and 0.08 V for **5**, versus Fc$^+$/Fc) was observed for both complexes indicating that there is no significant communication.

5. Conclusions

We have described the synthesis of a novel multidentate ligand containing two cyclopentadienyl sub-

stituents and one phosphine group. The ferrocene complex contains an uncoordinated phosphine group which is then able to coordinate to other metal centres such as Fe(CO)$_4$ and PdCl$_2$. The crystal structures of **3**, **4** and **7** reported here, as well as the zirconocene complexes [21] reported previously, indicate that the ligand is highly flexible and is able to adopt a range of conformations.

6. Supplementary information available

Tables of crystal data, structure refinement details, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates are available from the authors or from the Cambridge Crystallographic Data Centre, Lensfield Road, Cambridge, CB2 1EW, UK.

Acknowledgements

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