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Novel [3]ferrocenophanes: Syntheses, redox properties and molecular structures of $[Fe{(\eta^5-C_5H_4)CMe_2}_2PR]$ (R = Ph, Cy)

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Abstract

6,6-Dimethylfulvene reacts with Li₂PR to give Li₂[{(C₅H₄)CMe₂}₂PR] [R = Ph (1), Cy (2)]. The ferrocenophanes [Fe{($n^{5}-C_{5}H_{4}$)CMe₂}₂PR] [R = Ph (3), Cy (4)] are obtained in good yield from the lithium reagents 1 and 2 and FeCl₂. Compounds 3 and 4 were characterised spectroscopically (¹H, ¹³C, ³¹P, IR, MS), and by crystal structure determination. Electrochemical investigation shows that 3 undergoes a one-electron oxidation in CH₂Cl₂ solution, which is chemically reversible on the short timescale of cyclic voltammetry, but in the longer time frame of macroelectrolysis the monocation [3]⁺ forms a new species that we tentatively assign as [Fe{($n^{5}-C_{5}H_{4}$)CMe₂}₂P(O)Ph].

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1. Introduction

Ferrocene derivatives usually show high stability and are generally non-toxic. Thus, their industrial applications include additives for heating oil to reduce formation of soot, iron-containing fertilizer, UV absorbers and protective coatings for rockets and satellites [1]. While numerous ferrocenophanes have been reported, the number of structurally characterised compounds in which the cyclopentadienyl ligands are linked by a P-functionalised bridge is limited to [1]ferrocenophanes [2–11], the [2]ferrocenophane [Fe{(C₅Me₄)(C₅H₄)}CH₂PPh] [12], and some adducts of the [5]ferrocenophane [Fe{(η^5 -C₅H₄)CH₂CH₂}₂PPh] and the corresponding phosphine oxide [Fe{(η^5 -C₅H₄)CH₂CH₂}₂P(O)Ph] [13]. To our knowledge no crystal structures of [3]ferrocenophanes with a C–P–C bridge have been reported to date. During our work on P-functionalised cyclopentadienes [14-39] we observed the formation of $Li_2[\{(C_5H_4)CMe_2\}_2PR]$ [R = Ph (1), Cy (2)] as a byproduct in the preparation of $Li[(C_5H_4)CMe_2PHR]$ [R = Ph, Cy], and we have now developed a high yield synthesis of the former product. Here we report the first [3]ferrocenophanes of these ligands, namely, [Fe{ $(\eta^5-C_5H_4)CMe_2$ }_2PR] [R = Ph (3), Cy (4)].

2. Results and discussion

2.1. Synthesis of $Li_2[\{(C_5H_4)CMe_2\}_2PR] \ [R = Ph \ (1), Cy \ (2)] and [Fe\{(C_5H_4)CMe_2\}_2PR] \ [R = Ph \ (3), Cy \ (4)]$

The reaction of Li₂PR with two equivalents of 6,6dimethylfulvene gave Li₂[$(C_5H_4)CMe_2$]₂PR] [R = Ph (1), Cy (2)] as extremely air-sensitive colourless powders (Eq. (1)).

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The compounds Li[(C_5H_4)CMe₂PHR] (R = Ph, Cy) are always obtained as by-products in ca. 40% yield. We assume that Li₂PR attacks the methyl groups of 6,6-dimethylfulvene to give LiPHR, which then reacts with dimethylfulvene to give the observed by-products. The amount of Li[(C_5H_4)CMe₂PHR] was determined by ³¹P NMR spectroscopy and a corresponding amount of ⁿBuLi was added followed by 6,6-dimethylfulvene to give **1** in high yield and purity (97%) and **2** as a mixture with the monolithio salt (ca. 70% purity).

Attempts to further purify **2** failed. Therefore, preparation of the [3]ferrocenophane was carried out with the mixture of **2** and Li[(C_5H_4)CMe₂PHR], and [3]ferrocenophane **4** was purified by recrystallisation from toluene, while **3** was obtained from pure **1** and FeCl₂ in THF (Eq. (2)). The [3]ferrocenophanes are obtained as orange-yellow powders.



2.2. Spectroscopic properties of $Li_2[\{(C_5H_4)CMe_2\}_2PR] \ [R = Ph\ (1), Cy\ (2)] \text{ and of } [Fe\{(C_5H_4)CMe_2\}_2PR] \ [R = Ph\ (3), Cy\ (4)]$

Compound 1 was characterised by ¹H, ¹³C, ³¹P and ⁷Li NMR spectroscopy, and 2 only by ³¹P NMR spectroscopy. In the ¹H NMR spectrum, the methyl groups of the CMe₂ group in 1 are inequivalent and exhibit different chemical shifts and coupling constants (0.95 ppm, ³ $J_{P-H} = 15.5$ Hz and 1.79 ppm, ³ $J_{P-H} = 2.6$ Hz). Two multipletts are observed at 5.21 and 5.52 ppm for the expected AA'BB' coupling pattern of the C₅H₄ rings. In

the 13 C NMR spectrum, a large P–C coupling constant is observed for the *ipso* carbon atom and two signals for the *ortho* carbon atoms of the phenyl ring. The latter suggest hindered rotation about the P–C(Ph) bond.

In the ¹H NMR spectra of **3** and **4**, two doublets with different ${}^{3}J_{P-H}$ coupling constants [1.09 ppm, ${}^{3}J_{P-H} =$ 16.8 Hz and 1.65 ppm, ${}^{3}J_{P-H} =$ 2.8 Hz (**3**); 1.39 ppm, ${}^{3}J_{P-H} =$ 15.0 Hz and 1.55 ppm, ${}^{3}J_{P-H} =$ 2.4 Hz (**4**)] are observed for the two inequivalent methyl groups, one of which has a *trans* and the other a *cis* orientation to the lone pair of electrons of the phosphorus atom.

2.3. Molecular structures of $[Fe\{(C_5H_4)CMe_2\}_2PR]$ [R = Ph(3), Cy(4)]

Yellow needles of **3** and **4** were obtained after recrystallisation from *n*-hexane. Compound **3** (Fig. 1) crystallises in the monoclinic space group $P2_1/n$ with four molecules in the unit cell, and compound **4** (Fig. 2) in the monoclinic space group C2/c with eight molecules in the unit cell. Selected bond lengths and angles are given in Table 1. In both [3]ferrocenophanes, the cyclopentadienyl rings are almost synperiplanar and are nearly parallel [deviation 3.9° (**3**) and 4.6° (**4**)]. The small deviation from being parallel is presumably caused by the phosphanylalkyl bridge. The two methyl groups are inequivalent; one has a *trans* and the other a *cis* orientation to the lone pair of electrons of the phosphorus atom. In **3** the phenyl ring and the cyclopentadienyl rings are almost parallel (deviations: 9.6° and 8.0°).



Fig. 1. Molecular structure of $[Fe({(\eta^5-C_5H_4)CMe_2}_2PPh)]$ (3) showing the atom-numbering scheme employed (ORTEP plot, 50% probability, SHELXTL PLUS; XP). Hydrogen atoms are omitted for clarity.



Fig. 2. Molecular structure of $[Fe({(\eta^5-C_5H_4)CMe_2}_2PCy)]$ (4) showing the atom-numbering scheme employed (ORTEP plot, 50% probability, SHELXTL PLUS; XP). Hydrogen atoms are omitted for clarity.

2.4. Electrochemistry

Fig. 3 shows the cyclic voltammetric behaviour of $[Fe{(\eta^5-C_5H_4)CMe_2}_2PPh]$ (3) in CH₂Cl₂ solution.

As expected for a monoferrocene complex, it undergoes an oxidation process ($E^{o_{\prime}} = +0.37$ V, versus SCE) with features of chemical reversibility. In fact, analysis of the cyclic voltammetric responses with scan rate increasing from 0.02 to 2.0 V s⁻¹ shows that: (i) the current function $i_{pa} \cdot v^{-1/2}$ decreases by about 10% for each 10-fold increase of the scan rate; (ii) the current ratio i_{pc} i_{pa} remains constantly equal to 1; and (iii) the peak-topeak separation progressively increases from 76 to 182 mV. These parameters are diagnostic for an electrochemically quasireversible one-electron process which is chemically reversible on the short timescale of cyclic voltammetry [40]. In reality, as deducible from Fig. 3(b)-(d), in the longer timeframe of controlled potential coulometry ($E_w = +0.7 \text{ V}$) the process is accompanied by the formation of a new species which in turn undergoes oxidation at higher potential ($E^{o'} = +0.80$ V). On stepwise oxidation, the original yellow solution ($\lambda_{max} = 440$ nm) tends to become blue after consumption of 0.7 electrons per molecule ($\lambda_{max} = 690$ nm) (Fig. 4); then, after consumption of about 1 electron per molecule, the solution remains blue but the band shows overlap of two close absorptions (λ_{max} = 660 and 690 nm); finally, after consumption of 1.1 electrons per molecule the solution again takes on a yellow colour but absorbs at different wavelengths from the original solution ($\lambda_{max} = 360$ nm). On further exhaustive oxidation in correspondence of the second anodic process ($E_w = +1.0$ V), about two electrons per molecule are consumed. The final solution turns blue again and the spectrum only shows an absorption at $\lambda_{\text{max}} = 690$ nm.

Table 1		
Selected distances	Å) and bond angles (°) for 3 ar	nd 4

3	
Fe(1)-C(2)	2.034(2)
Fe(1) = C(10)	2.035(2)
Fe(1) - C(7)	2 035(2)
$F_{\alpha}(1) = C(1)$	2.035(2)
Fe(1) - C(6)	2.034(2)
Fe(1)-C(4)	2.037(2)
Fe(1)-C(5)	2.039(2)
Fe(1) - C(9)	2.040(2)
$F_{0}(1) C(2)$	2.010(2)
$\Gamma(1) = C(0)$	2.042(3)
Fe(1)-C(1)	2.045(2)
Fe(1)-C(3)	2.045(2)
P(1) - C(17)	1.844(2)
P(1) = C(11)	1 899(2)
P(1) = C(14)	1.000(2)
P(1) = C(14)	1.900(2)
C(1)-C(5)	1.430(3)
C(1)-C(2)	1.435(3)
CÚ)-CÚD	1 516(3)
C(2) C(2)	1 421(2)
C(2)=C(3)	1.421(3)
C(4) - C(5)	1.431(4)
C(14)–C(15)	1.534(3)
C(14)-C(16)	1.544(3)
$C(\Theta - C(1))$	1 428(3)
C(0) = C(10)	1.427(2)
C(6) - C(7)	1.437(3)
C(6)-C(14)	1.516(3)
C(7)–C(8)	1.422(3)
C(8) - C(9)	1 402(4)
C(0) C(10)	1.405(4)
C(9) = C(10)	1.425(4)
C(11)-C(12)	1.524(3)
C(11)–C(13)	1.549(3)
C(17)-C(22)	1.389(3)
C(17) - C(18)	1 402(3)
C(10) = C(10)	1.402(5)
C(18) - C(19)	1.382(3)
C(19)–C(20)	1.369(4)
C(20)-C(21)	1.380(4)
C(21) = C(22)	1 387(4)
0(21) 0(22)	1.507(1)
C(1)-C(11)-C(13)	108.2(2)
C(12)-C(11)-C(13)	107.2(2)
C(6) - C(14) - C(15)	110 3(2)
C(6) C(14) C(16)	108.6(2)
C(0) - C(14) - C(10)	106.6(2)
C(10) - C(6) - C(7)	106.5(2)
C(8) - C(7) - C(6)	108.8(2)
C(9)-C(8)-C(7)	107.7(2)
C(19) - C(18) - C(17)	121 3(2)
C(5) C(1) C(2)	106 6(2)
C(3) = C(1) = C(2)	100.0(2)
C(4) - C(3) - C(2)	107.9(2)
C(3)-C(4)-C(5)	108.8(2)
C(1)-C(5)-C(4)	107.9(2)
C(15) - C(14) - C(16)	107 7(2)
C(10) = C(14) = C(16)	107.7(2)
C(10) - C(6) - C(14)	126.3(2)
C(7)-C(6)-C(14)	127.2(2)
C(22)-C(17)-C(18)	117.2(2)
C(19) = C(20) = C(21)	119 3(3)
C(6) C(10) C(0)	108 2(2)
C(0) - C(10) - C(9)	108.2(5)
C(2) - C(1) - C(11)	126.9(2)
C(1)-C(11)-C(12)	110.9(2)
C(8)-C(9)-C(10)	108 9(2)
C(11) - P(1) - C(14)	100.16(0)
C(11) = I(1) = C(14)	105.10(9)
C(12) - C(11) - P(1)	119.2(2)
C(13)-C(11)-P(1)	104.5(2)
C(15)-C(14)-P(1)	118.5(2)
C(22) = C(17) = P(1)	115 2(2)
C(17) D(1) C(11)	113.2(2)
U(1/) - r(1) - U(11)	106.26(9)

Table 1 (continued)	
3	
C(21)-C(22)-C(17)	121.1(2)
C(3)-C(2)-C(1) C(20)-C(19)-C(18)	108.8(2)
C(5) = C(1) = C(11)	120.0(2) 126.4(2)
C(1) - C(11) - P(1)	106.3(1)
C(6)–C(14)–P(1)	106.5(1)
C(16)-C(14)-P(1)	104.8(2)
C(18)–C(17)–P(1)	127.5(2)
C(17)-P(1)-C(14)	103.44(9)
4	
Fe(1)–C(4)	2.031(2)
Fe(1)-C(2)	2.031(2)
Fe(1)-C(7)	2.033(2)
Fe(1) = C(10) Fe(1) = C(3)	2.035(2)
Fe(1) = C(5)	2.038(2)
Fe(1) - C(8)	2.046(2)
Fe(1)–C(9)	2.046(2)
Fe(1)-C(1)	2.051(2)
P(1)–C(17)	1.887(2)
P(1)-C(14)	1.905(2)
P(1) = C(11)	1.90/(2)
C(14) = C(15)	1.518(5)
C(14)-C(16)	1.548(3)
C(17)-C(18)	1.535(3)
C(6)–C(10)	1.441(3)
C(3)–C(4)	1.393(4)
C(1)–C(2)	1.433(3)
C(1)-C(5)	1.434(3)
C(7) = C(8)	1.420(3)
C(9) = C(10)	1.404(4)
C(2)-C(3)	1.422(3)
C(18)–C(19)	1.527(3)
C(11)–C(12)	1.547(3)
C(20)–C(21)	1.514(4)
C(22)-C(21)	1.528(3)
C(17) = C(22) C(5) = C(4)	1.334(3)
C(1) = C(1)	1.515(3)
C(11)–C(13)	1.530(3)
C(1) - C(11) - C(13)	111.3(2)
C(1)-C(11)-C(12)	107.2(2)
C(13)–C(11)–C(12)	107.5(2)
C(1)-C(11)-P(1)	108.5(1)
C(13)-C(11)-P(1)	116.9(1)
C(12)-C(11)-P(1)	104.9(1)
C(7) = C(6) = C(10)	106.5(2)
C(10) - C(6) - C(14)	120.8(2)
C(21)-C(22)-C(17)	112.2(2)
C(6)–C(14)–C(15)	109.5(2)
C(6)-C(14)-C(16)	107.4(2)
C(15)-C(14)-C(16)	108.8(2)
C(19)–C(18)–C(17)	111.6(2)
C(18)-C(17)-C(22)	109.6(2)
C(1/)-P(1)-C(11) C(6) C(14) P(1)	102.95(8)
C(0) - C(14) - r(1) C(15) - C(14) - P(1)	100.1(1)
C(16)-C(14)-P(1)	105.4(1)
C(19)-C(20)-C(21)	110.8(2)
C(4)-C(3)-C(2)	108.1(2)

C(2) $C(1)$ $C(5)$	
(2) - (1) - (3)	106.0(2)
C(8)–C(9)–C(10)	108.4(2)
C(2)-C(1)-C(11)	126.1(2)
C(5)–C(1)–C(11)	127.9(2)
C(8)–C(7)–C(6)	108.6(2)
C(9)–C(8)–C(7)	108.3(2)
C(9)–C(10)–C(6)	108.2(2)
C(3)-C(2)-C(1)	108.8(2)
C(3)–C(4)–C(5)	108.6(2)
C(4)-C(5)-C(1)	108.5(2)
C(20)–C(21)–C(22)	111.9(2)
C(20)-C(19)-C(18)	111.3(2)
C(14)–P(1)–C(11)	108.89(8)
C(17)–P(1)–C(14)	108.50(8)
C(18)–C(17)–P(1)	121.3(1)
C(22)-C(17)-P(1)	109.6(1)



Fig. 3. Cyclic voltammetric responses recorded at a platinum electrode for a CH₂Cl₂ solution of [Fe{ $(\eta^5-C_5H_4)CMe_2$ }PPh] (3) $(1.9 \times 10^{-3} \text{ mol dm}^{-3})$ before and after controlled potential coulometry. [NBu₄][PF₆] (0.2 mol dm⁻³) supporting electrolyte. (a) Original solution; (b) after consumption of 0.7 electrons per molecule; (c) after consumption of 0.9/1.0 electrons per molecule; (d) after consumption of 1.1 electrons per molecule. (\bullet) Starting potential. Scan rate: 0.2 V s⁻¹.

In an attempt to account for such electrochemical behaviour, it is useful to note that the formation of uncharacterised products was also observed in the irreversible oxidation of both the [1]ferrocenophane $[Fe(\eta^5-C_5H_4)_2PPhMe]^+$ [41] and the [5]ferrocenophane $[Fe\{(\eta^5-C_5H_4)CH_2CH_2\}_2PPh]$ [13]. In particular, in the latter case, this has been attributed to a dimerisation reaction (with formation of a P–P bond) rather than to formation of the corresponding phosphine oxide $[Fe\{(\eta^5-C_5H_4)CH_2CH_2\}_2P(O)Ph]$ [13], since the oxidation potential of the by-product arising from the primary process $[Fe\{(\eta^5-C_5H_4)CH_2CH_2\}_2PPh]^{0/+}$ looks different from that of a crystallographically characterised sample of $[Fe\{(\eta^5-C_5H_4)CH_2CH_2\}_2P(O)Ph]$. We



Fig. 4. UV/Vis spectral profiles obtained on stepwise oxidation of $[Fe\{(\eta^5-C_5H_4)CMe_2\}_2PPh]$ (3) $(1.9 \times 10^{-3} \text{ mol dm}^{-3})$ in correspondence of the primary anodic process. CH_2Cl_2 solution containing $[NBu_4][PF_6]$ (0.2 mol dm⁻³) as supporting electrolyte. (a) Original solution; (b) after 0.7 electrons/molecule; (c) after 0.9/1.0 electrons/molecule; (d) after 1.1 electrons/molecule.

note, however, that the comparison of the two oxidation processes was done in different solvents. In our case we are inclined to assign the secondary step as due to the process $[Fe{(\eta^5-C_5H_4)CMe_2}_2P(O)Ph]^{0/+}$, since $[Fe{(\eta^5-C_5H_4)CMe_2}_2PPh]$, even in the solid state, proved to be air-sensitive. This assumption is also supported by the observation that a powdered sample that was not maintained under strictly anaerobic conditions (for about one month) also showed this second oxidation step.

Table 2 Crystal data and structure refinement for **3** and **4**

	3	4
Empirical formula	C ₂₂ H ₂₅ FeP	C ₂₂ H ₃₁ FeP
$M_{ m r}$	376.24	382.29
Temperature (K)	220(2)	210(2)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	C2/c
Unit cell dimensions		
a (Å)	15.7183(6)	35.053(5)
b (Å)	8.5450(3)	6.386(5)
<i>c</i> (Å)	15.7434(6)	18.088(5)
β (°)	117.916(1)	111.124(5)
$V(\text{\AA}^3)$	1868.5(1)	3777(3)
Ζ	4	8
$\rho_{\text{calc.}}$ (Mg m ⁻³)	1.337	1.345
<i>F</i> (000)	792	1632
Crystal size (mm)	$0.50 \times 0.30 \times 0.20$	$0.40 \times 0.20 \times 0.10$
Absorption coefficient (mm^{-1})	0.892	0.884
Θ range (°)	1.51-28.28	1.25-28.95
Reflections collected	11 382	14839
Independent reflections	4446	4628
R _{int}	0.0255	0.0332
Parameters	317	341
$R[I > 2\sigma(I)]$	0.0362	0.0314
wR_2 (all data)	0.1124	0.0978
$\Delta/\rho_{\rm min.}$ (e Å ⁻³)	0.475	0.299
$\Delta/\rho_{\rm max.}$ (e Å ⁻³)	-0.743	-0.356

Table 3

Formal electro	de potentials (V,	, vs. SCE) for	the one-electron	oxidation
of different ph	osphaferrocenop	ohanes		

Complex	$E^{o\prime}$	Solvent	Ref.
$[Fe(C_5Me_4)_2PPh]$	+0.37	CH_2Cl_2	[45]
	+0.50	THF	[45]
$[Fe(C_5H_4)_2PPhMe]^+$	+1.11 ^a	CH_2Cl_2	[41]
$[Fe\{(C_5Me_4)(C_5H_4)\}CH_2PPh]$	+0.26	CH_2Cl_2	[12]
$[Fe\{(C_5H_4)CMe_2\}_2PPh]$	+0.37	CH_2Cl_2	b
$[Fe\{(C_5H_4)CH_2CH_2\}_2PPh]$	$+0.04^{a}$	MeCN	[13]
$[Fe(C_5H_5)_2]$	+0.39	CH_2Cl_2	b

^a Peak potential for irreversible processes.

^b This work.

On this basis, a tentative explanation of the electrochemical data would be that the primarily generated ferrocenium ion [3]⁺ reacts with traces of air (or water from the nominally anhydrous solvent) to give [Fe{(η^5 -C₅H₄)CMe₂}₂P(O)Ph]⁺, which, because of the inappropriate potential, is reduced to the corresponding ferrocene [Fe{(η^5 -C₅H₄)CMe₂}₂P(O)Ph]; on application of the proper potential, the latter is again oxidised to the corresponding monocation.

Table 3 compiles the redox potentials for the ferrocene/ferrocenium process in a series of phosphaferrocenophanes.

We note that the oxidation of methylated derivatives such as $[Fe{(C_5H_4)CMe_2}_2PPh]$, $[Fe(C_5Me_4)_2PPh]$ and $[Fe{(C_5Me_4)(C_5H_4)}CH_2PPh]$ occurs at potentials similar to that of unsubstituted ferrocene, and this suggests that the electron-donating ability of the bridging carbon atoms or the cyclopentadienyl methyl groups is attenuated by the electron-withdrawing ability of the PPh group.

3. Experimental

3.1. General

All experiments were carried out under purified dry nitrogen. Solvents were dried and freshly distilled under argon. The NMR spectra were recorded with an AVANCE DRX 400 spectrometer (Bruker), ¹H NMR: internal standard TMS; ¹³C NMR: internal standard TMS; ³¹P NMR: external standard 85% H₃PO₄. The IR spectra were recorded on an FT-IR spectrometer Perkin–Elmer System 2000 in the range 350–4000 cm⁻¹. MS: MAT 8230 (Finnigan) 70 eV. The melting points were determined in sealed capillaries under nitrogen and are uncorrected (BOETIUS). Materials and apparatus for electrochemistry and spectroelectrochemistry have been described elsewhere [42]. Potential values are referred to the saturated calomel electrode (SCE).

 Li_2PR (R = Ph, Cy) were prepared from PH_2R and two equivalents of MeLi. FeCl₂ is commercially available.

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3.2. Synthesis of dilithiumphenylphosphinobis(dimethylmethylcyclopentadienide), $Li_2[\{(C_5H_4)CMe_2\}_2PPh]$ (1)

6,6-Dimethylfulvene (4.33 ml, 36 mmol) was added dropwise to a suspension of Li₂PPh (2.2 g, 18 mmol) in 50 ml of Et₂O and stirred for at least 12 h, during which time the yellow suspension turned colourless. The solid was isolated by filtration, washed 3 times with 30 ml of Et₂O and dried in vacuo. The amount of $Li[(C_5H_4)CMe_2PHPh]$ was determined by ³¹P NMR spectroscopy. The mixture was dissolved in 30 ml of THF and the appropriate amount of ⁿBuLi (corresponding to the amount of $Li[(C_5H_4)CMe_2PHPh])$ was added. The solvent was evaporated, the residue was suspended in Et₂O and the appropriate amount of 6,6-dimethylfulvene was added. After stirring for 12 h the colourless solid was isolated by filtration, washed with Et₂O and n-hexane and dried. Yield: 4.9 g (81.5%) of 1 as a colourless air-sensitive powder. M.p.: 256 °C (decomp.).

¹H NMR (THF-*d*₈): δ 0.95 (d, ³*J*_{P-H} = 15.5, 6H, C*H*₃ in CMe₂), 1.79 (d, ³*J*_{P-H} = 2.6, 6H, C*H*₃ in CMe₂), 5.21 (m, 4H, C*H* in C₅H₄), 5.52 (m, 4H, C*H* in C₅H₄), 7.26 (m, 3H, *o*- and *p*-C*H* in Ph), 7.93 (m, 2H, *m*-C*H* in Ph). ¹³C{¹H} NMR (THF-*d*₈): δ 26.20 (d, ²*J*_{P-C} = 4.1, C-CH₃), 35.50 (d, ²*J*_{P-C} = 26.5, C-CH₃), 37.40 (d, ¹*J*_{P-C} = 39.4, C-CH₃), 102.30 (s, *m*-C in C₅H₄), 104.10 (d, ³*J*_{P-C} = 6.6, *o*-C in C₅H₄), 127.58 (d, ²*J*_{P-C} = 14.1, *ipso*-C in C₅H₄), 127.64 (d, ³*J*_{P-C} = 8.4, *m*-C in Ph), 128.50 (s, *p*-C in Ph), 136.00 (d, ²*J*_{P-C} = 14.1, *o*-C in Ph), 138 (d, br, ²*J*_{P-C} = 14.0, *o*-C in Ph), 143.80 (d, ¹*J*_{P-C} = 41.9, *ipso*-C in Ph). ³¹P NMR (THF-*d*₈): δ 42.9, s. ⁷Li NMR (THF-*d*₈): δ = -7.2, s. IR \tilde{v} (cm⁻¹): 3074 w (*v*(CH) aryl), 2864 m (*v*(CH₃)), 1462–1360 m (δ (CH₃)).

3.3. Synthesis of dilithiumcyclohexylphosphinobis-(dimethylmethylcyclopentadienide), $Li_2[\{(C_5H_4)CMe_2\}_2PCy](2)$

Analogously to the synthesis of 1 from Li_2PCy (1 g, 7.8 mmol) in 50 ml Et_2O and 6,6-dimethylfulvene (1.9 ml, 15.6 mmol). The amount of $Li[(C_5H_4)CMe_2PHCy]$ was determined by ³¹P NMR spectroscopy. The mixture was dissolved in 30 ml of THF and the appropriate amount of "BuLi (corresponding to the amount of $Li[(C_5H_4)CMe_2PHCy])$ was added. The solvent was evaporated, the residue suspended in Et₂O and the appropriate amount of 6,6-dimethylfulvene added. After stirring for 12 h the colourless solid was isolated by filtration, washed with Et₂O and *n*-hexane and dried. Yield: 2.5 g of 2 (m.p.: 257 °C (decomp.)) as a colourless air-sensitive powder, which contained ca. 30% of $Li[(C_5H_4)CMe_2PHCy]$. Attempts to further purify 2 failed. Therefore the mixture was employed in the synthesis of 4.

³¹P NMR (THF- d_8): δ 54.0, s.

3.4. Synthesis of [bis(cyclopentadienyldimethylmethyl)phenylphosphino]ferrocenophane, [Fe $\{(C_5H_4)CMe_2\}_2PPh$] (3)

Solid 1 (1.2 g, 3.6 mmol) was added in small portions to a suspension of FeCl₂ (0.46 g, 3.6 mmol) in 50 ml of THF. The solution turned yellow to brown. After stirring overnight the solvent was evaporated and 50 ml of Et₂O was added to the remaining brown oil, giving a brown solid and an orange solution. The solution was filtered over dry Al₂O₃, and the residue washed repeatedly with Et₂O until the washings were colourless. The Et₂O fractions were combined and the solvent evaporated. Fifty millilitres of hexane was added to the residue, filtered and the hexane evaporated leaving 1.0 g (74%) of **3** as an orange powder. Yellow crystals were obtained from a concentrated solution of **3** in *n*-hexane at -20 °C. M.p.: 143 °C.

¹H NMR (CDCl₃): δ 1.09 (d, ³J_{P-H} = 16.8, 6H, CH₃ in CMe₂), 1.65 (d, ${}^{3}J_{P-H} = 2.8$, 6H, CH₃ in CMe₂), 4.05 (s, 2H, CH in C₅H₄), 4.16 (s, 2H, CH in C₅H₄), 4.19 (s, 2H, CH in C₅H₄), 4.41 (s, 2H, CH in C₅H₄), 7.42 (m, 3H, o- and p-CH in Ph), 7.86 (m, 2H, m-CH in Ph). ¹³C{¹H} NMR (CDCl₃): δ 24.3 (d, ²J_{P-C} = 5.0, C-CH₃), 31.7 (d, ${}^{2}J_{P-C} = 33.9$, C-CH₃), 32.1 (d, ${}^{1}J_{P-C}$ = 22.3, C-CH₃), 67.0 (d, ${}^{4}J_{P-C}$ = 2.1, CH in C₅H₄), 67.2 (d, ${}^{4}J_{P-C} = 2.5$, CH in C₅H₄), 68.8 (d, ${}^{3}J_{P-C} = 6.2$, *C*H in C₅H₄), 95.0 (d, ${}^{2}J_{P-C} = 12.4$, *ipso-C* in C₅H₄), 127.8 (d, ${}^{3}J_{P-C} = 8.3$, *m*-*C* in Ph), 129.0 (s, *p*-*C* in Ph), 136.7 (d, ${}^{2}J_{P-C} = 23.9$, *o-C* in Ph), 137.8 (d, ${}^{1}J_{P-C}$ = 34.7, *ipso-C* in Ph). ³¹P NMR (CDCl₃): δ = 50.5, s. IR (KBr), \tilde{v} (cm⁻¹): 3077 m (v(CH) aryl), 2969 s (v(CH₃)), 1431 br, m (δ (CH₃)), 1359 m (v(CC) in C_5H_4). EI-MS: m/z = 376 (100%, M⁺), 268 (69%, M^+ – PPh), and fragmentation products thereof. Anal. Calc. for C₂₂H₂₅PFe (376): C, 70.2; H, 6.7; P, 8.2. Found: C, 70.1; H, 5.1; P, 7.6%.

3.5. Synthesis of [bis(cyclopentadienyldimethylmethyl)cyclohexylphosphino]ferrocenophane, [$Fe\{(C_5H_4)CMe_2\}_2PCy\}$ (4)

The mixture containing **2** (0.50 g, 1.47 mmol) and $\text{Li}[(C_5\text{H}_4)\text{CMe}_2\text{PHCy}]$ (0.15 g, 0.65 mmol), obtained as described above, was added as a solid in small portions to a suspension of FeCl₂ (0.23 g, 1.8 mmol) in 25 ml of THF. The solution turned yellow, then brown and finally almost black. After stirring overnight the solvent was evaporated and 50 ml of Et₂O was added to the remaining black oil giving a brown solid and an orange solution. The solution was filtered over dry Al₂O₃, and the residue washed repeatedly with Et₂O until the washings were colourless. The Et₂O fractions were combined and the solvent evaporated. The residue was recrystallised from 10 ml of *n*-hexane giving 0.27 g (48%) of **4** as yellow crystals. M.p.: 188 °C.

¹H NMR (CDCl₃): δ 1.2–1.9 (br, m, 11H, CH and CH_2 in Cy), 1.39 (d, ${}^{3}J_{P-H} = 15.0$, 6H, CH_3 in CMe₂), 1.55 (d, ${}^{3}J_{P-H} = 2.4$, 6H, CH₃ in CMe₂), 3.99 (s, 2H, CH in C₅H₄), 4.04 (s, 2H, CH in C₅H₄), 4.09 (s, 2H, CH in C_5H_4), 4.27 (s, 2H, CH in C_5H_4). ¹³C{¹H} NMR (CDCl₃): δ 24.92 (d, ²J_{P-C} = 4.2, C- CH_3), 26.49 (s, C4 in Cy), 28.85 (d, ${}^{3}J_{P-C} = 9.3$, C3 in Cy), 32.43 (d, ${}^{2}J_{P-C} = 31.9$, C-CH₃), 32.65 (d, C- CH_3 , ${}^2J_{P-C} = 26.5$), 34.40 (d, $J_{P-C} = 15.2$, C2 in Cy), 38.84 (d, ${}^{1}J_{P-C} = 35.0$, C1 in Cy), 66.37 (d, ${}^{4}J_{P-C}$ = 2.7, CH in C₅H₄), 66.86 (d, ${}^{4}J_{P-C}$ = 2.0, CH in C_5H_4), 68.66 (d, ${}^3J_{P-C} = 8.4$, CH in C_5H_4), 68.75 (s, CH in C_5H_4), 96.2 (d, ${}^2J_{P-C} = 11.3$, *ipso-C* in C_5H_4). ³¹P NMR (CDCl₃): δ 67.8, s. IR (KBr), \tilde{v} (cm⁻¹): 2970 s (v(CH₃)), 1444 br, m (δ (CH₃)), 1359 m $(v(CC) \text{ in } C_5H_4)$. EI-MS: $m/z = 382 (26\%, M^+)$, 267 $(100\%, M^+ - PCy)$, and fragmentation products thereof. Anal. Calc. for C₂₂H₃₁PFe (382): C, 69.1; H, 8.2. Found: C, 68.5; H, 7.3%.

3.6. Data collection and structural refinement of 3 and 4

Data (λ (Mo K α) = 0.71073 Å) were collected with a Siemens CCD (SMART) diffractometer. All observed reflections were used for refinement (SAINT) of the unit cell parameters. Empirical absorption correction was applied with SADABS [43]. The structures were solved by direct methods (SHELXTL PLUS) [44]. Fe, P and C atoms were refined anisotropically; H atoms were located by difference maps and refined isotropically. Table 2 lists crystallographic details.

4. Supplementary material

CCDC 266919 (3) and 266918 (4) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK via www.ccdc.cam.ac.uk/ data_request/cif, e-mail: deposit@ccdc.cam.ac.uk.

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