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The one-step synthesis of chiral amino phosphino ferrocenes

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Abstract

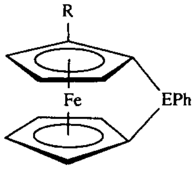
Reaction of the chiral lithium reagent-2-lithio-(α-N,N-dimethyl)aminoethylbenzene with 1,1′-ferrocenediylphenylphosphine gives chiral aminophosphinoferrocenes that contain both chiral carbon and phosphorus centres. Treatment of the ferrocenophane with 2-lithio-N,N-dimethylaminomethylferrocene followed by hydrolysis gives the product ferrocenyl 2-(dimethylaminomethylferrocenyl) phenylphosphine as a pair of diastereomers. The single crystal structures of compound **3a** $PdCl_2$ and compound **4**. $PdCl_2.2CH_2Cl_2$ have been determined. The compounds, 2-(ferrocenylphenylphosphino)-1-(α-N,N'-dimethylaminoethylbenzene)ferrocene, **5** and 1-[2-(α-N,N'-dimethylaminoethylbenzene)phenylphosphino]-1′-diphenylphosphinoferrocene, **6a**, have also been prepared by minor modifications of the methodology developed.

Keywords: Phosphorus; Ferrocene; Iron; Chirality; Palladium; Crystal structure

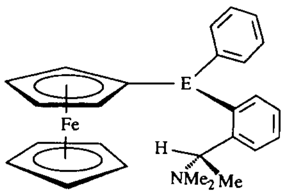
1. Introduction

The chemistry of chiral ferrocenes for use as ligands is again of topical interest; for example, Riant et al. have recently described the stereoselective lithiation of a chiral ferrocenyldioxane derived from ferrocene carboxaldehyde [1], and Matsumoto et al. have reported the synthesis of chiral ferrocenylamines using asymmetric alkylation procedures [2]. This follows the early work on chiral ferrocenes carried out by Kumada and coworkers in organic synthesis [3–12], and Cullen and coworkers on catalyst mechanisms [13–15], which used chiral ferrocenylamines that were first prepared by Marquarding et al. [16] as basic building blocks.

Previously we reported examples of the ring-opening reaction of chiral phosphorus-bridged ferrocenophanes, such as **1c**, which allow the synthesis of a range of new compounds [17,18]. It was of interest to examine the similar ring cleavage using chiral lithium reagents. The reagent chosen was the (S)-2-lithio-α-N,N-dimethylbenzylethylamine, which is derived from the inexpensive commercially available parent amine.



1a. R = H, E = P
1b. R = H, E = As
1c. R = CH(Me)NMe$_2$, E = P



3a. E = P
3b. E = As

2. Results and discussion

The ring opening of **1a** [19–21] at low temperature proceeds with modest enantioselectivity (ca. 62% *e.e.*), but the product diastereomers are easily separated by crystallisation. The major diastereomer is the (S,R)-phenyl(2-(α-N,N-dimethylethylbenzene)phosphino ferrocene derivative, **3a**. The preferential formation of this diastereomer is presumably a result of the preference for attack of the nucleophile to give the transition state shown in **2**. This is in accord with the work

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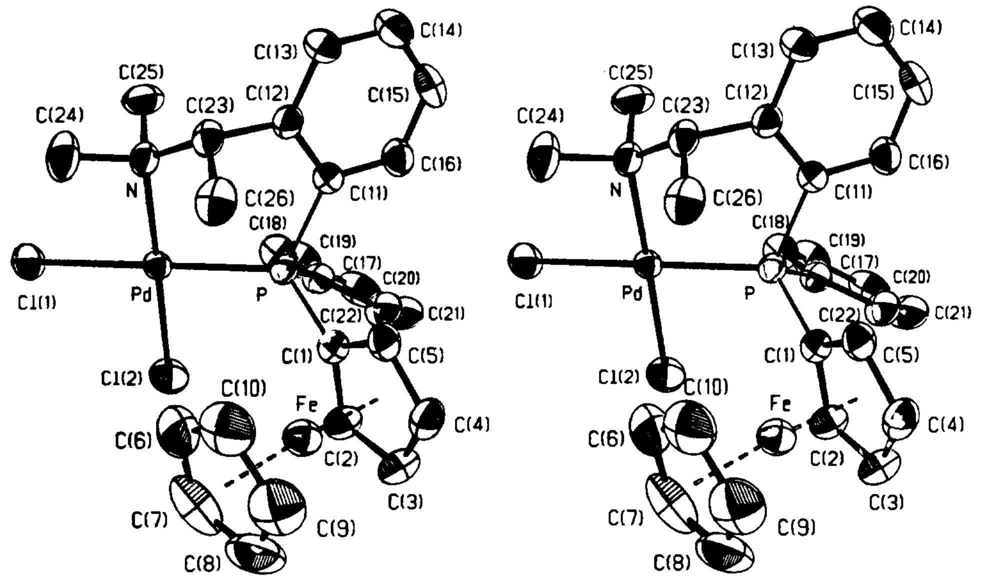
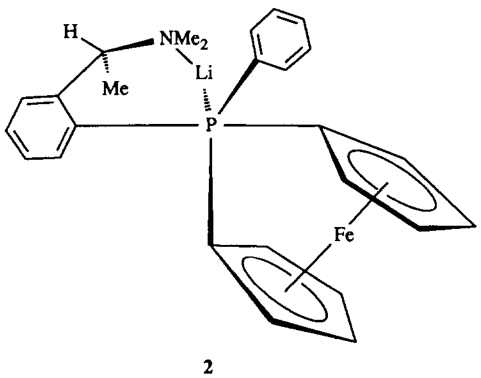


Fig. 1.

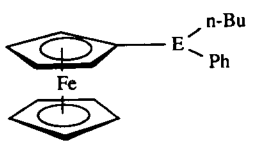
documented by Kyba and Hudson [22] on the reaction of alkyllithium reagents with phosphines leading to inversion at the phosphorus centre. The ferrocenophane is unlikely to occupy both equatorial sites of the trigonal bipyramidal intermediate because of the bite angle restriction, and the P–Fc bond is cleaved in preference to the P–Ph bond. Some interaction between the amino group and the lithium could be envisaged, leading to a six-membered ring. Models of the alternative transition state geometry suggest that the possibility of interactions between the phenyl group and the *N*-dimethyl groups is lessened if the lithium and phenyl groups are interchanged.



2

The by-product $(\eta^5\text{-}C_5H_4PPh(n\text{-}Bu)Fe(\eta^5\text{-}C_5H_5)$, **4**, can be isolated by chromatography. A similar reaction using the arsine-bridged compound, **1b**, results in the isolation of SR-**3b** following crystallisation, in addition to $(\eta^5\text{-}C_5H_4AsPh(n\text{-}Bu))Fe(\eta^5\text{-}C_5H_5)$, the expected by-product.

It would be expected that the use of a more hindered chiral lithium reagent would lead to higher enantioselectivities. Equally, the use of a bulky racemate should lead to high diastereoselectivities. To test the latter hypothesis, in preliminary studies the bulky 2-lithio-*N*,*N*-dimethylmethylferrocene reagent was used in the ring cleavage reaction to give, after hydrolysis, the product **5**. Examination of the crude product by ^1H NMR spectroscopy showed that only one pair of diastereomers are formed, bearing out the hypothesis.



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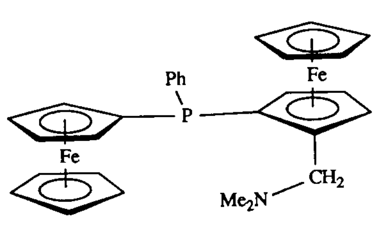

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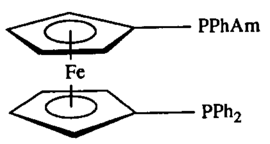

6 Am = $2\text{-}C_6H_4H(Me)NMe_2$

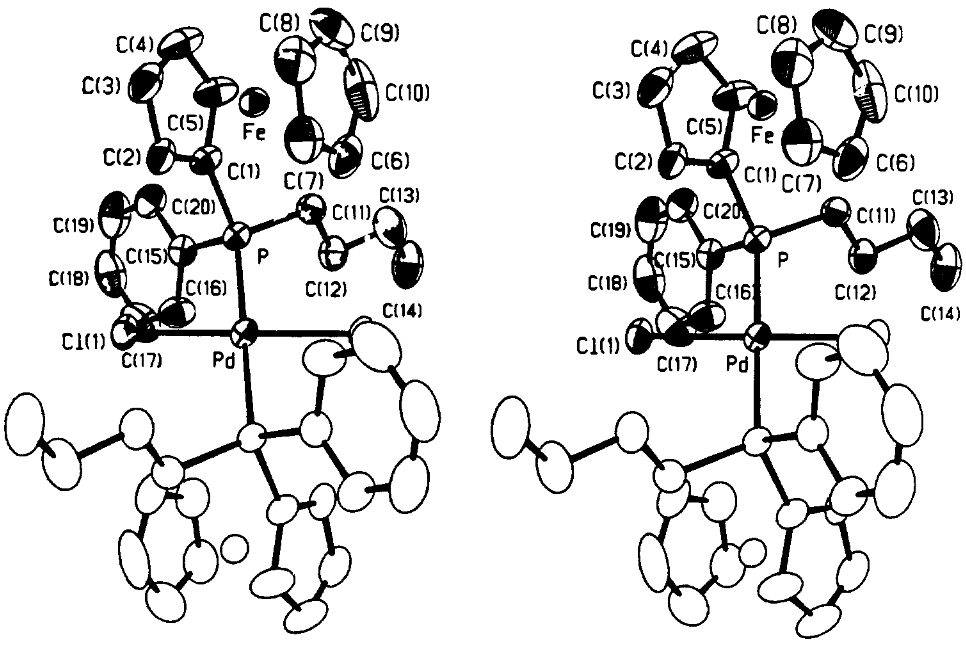

Fig. 2.

Table 1
Crystallographic data [a]

compound	3a.PdCl$_2$	(4a)$_2$.PdCl$_2$.2CH$_2$Cl$_2$
formula	$C_{26}H_{28}Cl_2FeNPPd$	$C_{42}H_{46}Cl_2Fe_2P_2Pd.2CH_2Cl_2$
fw	618.64	1071.64
crystal system	orthorhombic	triclinic
space group	$P2_12_12_1$	$P1$ [b]
a (Å)	10.9672(3)	9.962(2)
b (Å)	13.7846(4)	12.458(2)
c (Å)	16.6895(7)	9.744(2)
α (deg)	-	92.30(1)
β (deg)	-	112.361(8)
γ (deg)	-	79.86(1)
V (Å^3)	2523.1(2)	1100.4(3)
Z	4	1
D_c	1.629	1.617
$F(000)$	1248	544
$\mu(\text{MoK}_\alpha)$ (cm^{-1})	15.70	15.21
crystal dimensions (mm)	0.22 × 0.27 × 0.32	0.28 × 0.40 × 0.61
transmission factors	0.646–0.726	0.562–0.686
scan type	$\omega - 2\theta$	$\omega - 2\theta$
scan range (deg in ω)	$0.65 + 0.35 \tan\theta$	$0.90 + 0.35 \tan\theta$
scan speed (deg/min)	1.1–10.0	1.5–10.0
data collected	$+h, +k, +l$	$+h, \pm k, \pm l$
2θ max (deg)	60	55
crystal decay	negligible	23%
unique reflections	4097	5043
reflections with $I \geq 3\sigma(I)$	3189	4190
number of variables	289	241
R	0.025	0.043
Rw	0.028	0.060
S	1.121	2.539
mean Δ/σ (final cycle)	0.02	0.05
max Δ/σ (final cycle)	0.08	0.19
residual density (e/Å^3)	0.38	1.36 (near Pd)

[a] Temperature 295 K, Enraf-Nonius CAD4-F diffractometer, Mo K_α radiation ($\lambda_{K\alpha 1} = 0.70930$, $\lambda_{K\alpha 2} = 0.71359$ Å), graphite monochromator, takeoff angle 2.7°, aperture $(2.0 + \tan\theta) \times 4.0$ mm at a distance of 173 mm from the crystal, scan range extended by 25% on both sides for background measurement, $\sigma^2(I) = C + 2B + [0.04(C - B)]^2$ (C = scan count, B = normalized background count), function minimized: $\Sigma w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2(F)$, $R = \Sigma \| F_o| - |F_c\| / \Sigma |F_o|$, $R_w = (\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2)^{1/2}$, $S = (\Sigma(|F_o| - |F_c|)^2/(m - n))^{1/2}$. Values given for R, R_w, and S are based on those reflections with $I \geq 3\sigma(I)$.

[b] Reduced cell (Donnay convention).

If a model related to that used to describe lithium attack of the chiral amine is used to describe the transition state, strong interference can be seen between the η-C_5H_5 group and the attacking lithiating agent with the PPh group if they lie on the same side of the molecule. There is no such interaction if the other enantiomer of the lithium reagent is applied to this model, and so the formation of one diastereomeric pair can be explained.

The absolute stereochemistry of the ligand **3a** was proved by formation of the palladium dichloride complex, which was structurally characterised. In addition the structure of the palladium complex of the by-product, **4**, itself a useful catalyst, was also determined. Stereoviews of these molecules are shown in Figs. 1 and 2. Bond lengths and angles are listed in Tables 1–4.

Compound **3a** (FAPP) is an isomer of the most widely used ferrocenylaminophosphine PPFA. Although there is no plane of chirality because of 1,2-hetero distribution of the ferrocenyl ring in this ligand, it is expected that this ligand and its derivatives will be a useful addition to the range of chiral ligands available given the nature of this facile synthetic procedure.

Replacement of the lithium on the otherwise unsubstituted cyclopentadienyl ring in **3a** by reaction with a range of electrophiles can lead to a variety of products. For example, the reaction with $ClPPh_2$ gives the bis phosphine derivative **6a** in high yield. The latter product is isomeric with the well known ligand BPPFA.

In summary, a one step route to new ligands which contain both chiral phosphorus and carbon centres has been developed.

3. Experimental detail

3.1. Preparation of (S,R)-3a and (S,R)-3b

This procedure has been carried out starting from 1–10 g of 1,1′-ferrocenediylphenylphosphine.

A mixture of *n*-butyllithium (1.1 molar equivalent from a 1.5 M solution in hexanes) and S-*α*-*N*,*N*-dimethylaminoethylbenzene (1.0 molar equivalent) in diethyl ether (20 molar equivalent) was stirred for 24 h at 20°C, then was cooled to ca. 30°C. A solution of ferrocenediylphenylphosphine (for **3a**) or ferrocenediylphenylarsine (for **3b**) (0.5 molar equivalent) in the minimum quantity of diethyl ether required for complete solution was added slowly, the mixture allowed to warm to room temperature, and then treated with degassed water (ca. 10 molar equivalents). The golden-yellow organic layer was separated, and the aqueous layer was extracted with diethyl ether until the extracting solution was colourless. The combined ether solutions were dried over $MgSO_4$, then reduced in volume to give an oily solid, which was dissolved in the minimum quantity of diethyl ether and chromatographed on a neutral alumina support (activity grade 1). Elution with progressively polar fractions of hexane and diethyl ether gave (i) residual **1**, (ii) *n*-butylphenylphosphinoferrocene as a pale-yellow band (hexane/ether 20:80), and finally (iii) (S,R) and (S,S)-**3a** or **3b**. The ratio of diastereomers can be determined by integration of the ^1H NMR spectrum, and was observed to be 4.3:1 for **3a**. Crystallisation from hexanes/diethyl ether affords pure (S,R)-**3a** in 50–65% yield based on the ferrocenophane. When the reaction

Table 2
Bond lengths (Å) with estimated standard deviations in parentheses [a]

Bond	Length (Å)	Bond	Length (Å)
3a·$PdCl_2$			
Pb–Cl(1)	2.3872(10)	C(1)–C(5)	1.435(5)
Pd–Cl(2)	2.2955(10)	C(2)–C(3)	1.420(6)
Pd–P	2.2345(9)	C(3)–C(4)	1.401(6)
Pd–N	2.108(3)	C(4)–C(5)	1.425(6)
Fe–C(1)	2.053(4)	C(6)–C(7)	1.377(8)
Fe–C(2)	2.032(4)	C(6)–C(10)	1.393(8)
Fe–C(3)	2.019(4)	C(7)–C(8)	1.403(9)
Fe–C(4)	2.040(4)	C(8)–C(9)	1.429(9)
Fe–C(5)	2.052(4)	C(9)–C(10)	1.391(8)
Fe–C(6)	2.056(5)	C(11)–C(12)	1.404(5)
Fe–C(7)	2.038(5)	C(11)–C(16)	1.400(5)
Fe–C(8)	2.033(5)	C(12)–C(13)	1.391(5)
Fe–C(9)	2.057(5)	C(12)–C(23)	1.513(5)
Fe–C(10)	2.039(5)	C(13)–C(14)	1.374(6)
Fe–Cp(1)	1.642(2)	C(14)–C(15)	1.371(7)
Fe–Cp(2)	1.663(2)	C(15)–C(16)	1.379(6)
P–C(1)	1.804(4)	C(17)–C(18)	1.383(6)
P–C(11)	1.833(3)	C(17)–C(22)	1.392(5)
P–C(17)	1.827(3)	C(18)–C(19)	1.400(6)
N–C(23)	1.513(5)	C(19)–C(20)	1.348(7)
N–C(24)	1.514(5)	C(20)–C(21)	1.376(7)
N–C(25)	1.485(5)	C(21)–C(22)	1.389(6)
C(1)–C(2)	1.431(5)	C(23)–C(26)	1.498(6)
4a$_2$·$PdCl_2$·$2CH_2Cl_2$			
Pd–P	2.3386(8)	C(1)–C(2)	1.442(5)
Pd–Cl(1)	2.3036(8)	C(1)–C(5)	1.419(5)
Fe–C(1)	2.032(3)	C(2)–C(3)	1.420(6)
Fe–C(2)	2.038(4)	C(3)–C(4)	1.395(7)
Fe–C(3)	2.049(4)	C(4)–C(5)	1.424(6)
Fe–C(4)	2.042(4)	C(6)–C(7)	1.389(7)
Fe–C(5)	2.036(4)	C(6)–C(10)	1.420(8)
Fe–C(6)	2.046(4)	C(7)–C(8)	1.386(7)
Fe–C(7)	2.033(4)	C(8)–C(9)	1.416(8)
Fe–C(8)	2.039(4)	C(9)–C(10)	1.417(8)
Fe–C(9)	2.040(4)	C(11)–C(12)	1.512(5)
Fe–C(10)	2.025(5)	C(12)–C(13)	1.524(6)
Fe–Cp(1)	1.643(2)	C(13)–C(14)	1.504(7)
Fe–Cp(2)	1.649(2)	C(15)–C(16)	1.386(5)
P–C(1)	1.798(3)	C(15)–C(20)	1.395(5)
P–C(11)	1.833(4)	C(16)–C(17)	1.388(6)
P–C(15)	1.817(3)	C(17)–C(18)	1.387(8)
Cl(2)–C(21)	1.714(8)	C(18)–C(19)	1.362(8)
Cl(3)–C(21)	1.681(9)	C(19)–C(20)	1.391(6)

[a] Cp(1) and Cp(2) refer to the centriods of the C(1–5) and C(6–10) cyclopentadienyl rings, respectively.

was carried out on a 10 mmol scale, with 2.92 g of the ferrocenophane, a 65% yield of product was obtained. Alternatively the diastereomers may be separated on a preparative plate (suitable for only small scales).

(S,R-**3a**): ^{1}H NMR (CDCl$_3$) δ, 0.74 (d, 3H), 2.28 (s, 6H), 3.91 (dq, 1H), 3.73 (m, 1H), 4.07 (s, 5H), 4.32 (m, 1H), 4.33 (m, 1H), 4.41 (m, 1H), 6.95 (m, 1H), 7.09 (m, 1H), 7.23–7.37 (m, 4H), 7.43–7.52 (m, 3H). Mass Spectrum, parent ion at m/z 441. Anal. Calc. for $C_{26}H_{28}FeNP$, C, 70.76; H, 6.39; N, 3.17. Found: C, 70.42; H, 6.49; N, 3.17%.

(S,R-**3b**): ^{1}H NMR (CDCl$_3$) δ, 1.03 (d, 3H), 2.02 (d, 6H), 3.50 (q, 1H), 3.71 (m, 1H), 4.07 (s, 5H), 4.26 (m, 1H), 4.28 (m, 1H), 4.37 (m, 1H), 7.08 (dd, 1H), 7.13 (dd, 1H), 7.20 (td, 1H), 7.25–7.33 (m, 4H), 7.43–7.48 (dd's, 2H). Mass Spectral, parent ion at m/z 485. Anal. Calc. for $C_{26}H_{28}AsFeN$, C, 64.35; H, 5.82; N, 2.89. Found: C, 64.75; H, 5.91; N, 2.71%.

3.2. Preparation of 5

A solution containing n-BuLi (7.5 mmol, 5 ml of 1.5 M in hexane) and α-dimethylaminoethylferrocene (1.0

Table 3
Bond angles (deg) with estimated standard deviations in parentheses [a]

Bonds	Angle (°)	Bonds	Angle (°)
3a · PdCl$_2$			
Cl(1)–Pd–Cl(2)	89.31(4)	C(7)–C(6)–C(10)	107.9(5)
Cl(1)–Pd–P	168.94(3)	C(6)–C(7)–C(8)	108.9(5)
Cl(1)–Pd–N	90.86(8)	C(7)–C(8)–C(9)	107.3(6)
Cl(2)–Pd–P	85.15(4)	C(8)–C(9)–C(10)	106.4(6)
Cl(2)–Pd–N	177.48(9)	C(6)–C(10)–C(9)	109.5(5)
P–Pd–N	95.10(8)	P–C(11)–C(12)	121.3(3)
Cp(1)–Fe–Cp(2)	176.18(13)	P–C(11)–C(16)	119.8(3)
Pd–P–C(1)	119.60(12)	C(12)–C(11)–C(16)	118.5(3)
Pd–P–C(11)	112.99(12)	C(11)–C(12)–C(13)	119.1(4)
Pd–P–C(17)	110.38(13)	C(11)–C(12)–C(23)	123.6(3)
C(1)–P–C(11)	106.3(2)	C(13)–C(12)–C(23)	117.2(3)
C(1)–P–C(17)	103.4(2)	C(12)–C(13)–C(14)	121.4(4)
C(11)–P–C(17)	102.5(2)	C(13)–C(14)–C(15)	119.8(4)
Pd–N–C(23)	116.0(2)	C(14)–C(15)–C(16)	120.2(4)
Pd–N–C(24)	109.3(2)	C(11)–C(16)–C(15)	121.0(4)
Pd–N–C(25)	107.6(2)	P–C(17)–C(18)	118.4(3)
C(23)–N–C(24)	105.8(3)	P–C(17)–C(22)	122.0(3)
C(23)–N–C(25)	110.2(3)	C(18)–C(17)–C(22)	119.6(3)
C(24)–N–C(25)	107.7(3)	C(17)–C(18)–C(19)	119.2(4)
P–C(1)–C(2)	124.3(3)	C(18)–C(19)–C(20)	120.8(5)
P–C(1)–C(5)	126.8(3)	C(19)–C(20)–C(21)	120.7(4)
C(2)–C(1)–C(5)	108.0(3)	C(20)–C(21)–C(22)	119.7(4)
C(1)–C(2)–C(3)	107.2(3)	C(17)–C(22)–C(21)	119.9(4)
C(2)–C(3)–C(4)	109.0(4)	N–C(23)–C(12)	113.0(3)
C(3)–C(4)–C(5)	108.7(4)	N–C(23)–C(26)	113.7(3)
C(1)–C(5)–C(4)	107.0(3)	C(12)–C(23)–C(26)	111.4(3)
4a$_2$ · PdCl$_2$ · 2CH$_2$Cl$_2$			
P–Pd–Cl(1)	88.14(3)	C(6)–C(7)–C(8)	109.4(5)
P–Pd–P′	180	C(7)–C(8)–C(9)	108.7(4)
P–Pd–Cl(1)′	91.86(3)	C(8)–C(9)–C(10)	106.3(5)
Cl(1)–Pd–Cl(1)′	180	C(6)–C(10)–C(9)	108.5(5)
Pd–P–C(1)	113.27(11)	P–C(11)–C(12)	115.4(3)
Pd–P–C(11)	117.96(12)	C(11)–C(12)–C(13)	111.7(3)
Pd–P–C(15)	111.15(12)	C(12)–C(13)–C(14)	114.2(4)
C(1)–P–C(11)	103.8(2)	P–C(15)–C(16)	118.3(3)
C(1)–P–C(15)	106.6(2)	P–C(15)–C(20)	122.3(3)
C(11)–P–C(15)	103.0(2)	C(16)–C(15)–C(20)	119.4(3)
P–C(1)–C(2)	125.2(3)	C(15)–C(16)–C(17)	120.1(4)
P–C(1)–C(5)	127.7(3)	C(16)–C(17)–C(18)	120.0(5)
C(2)–C(1)–C(5)	107.0(3)	C(17)–C(18)–C(19)	120.3(4)
C(1)–C(2)–C(3)	107.6(4)	C(18)–C(19)–C(20)	120.4(4)
C(2)–C(3)–C(4)	108.7(4)	C(15)–C(20)–C(19)	119.9(4)
C(3)–C(4)–C(5)	108.5(4)	Cl(2)–C(21)–Cl(3)	114.6(5)
C(1)–C(5)–C(4)	108.2(4)	Cp(1)–Fe–Cp(2)	178.2(1)
C(7)–C(6)–C(10)	107.1(4)		

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[a] Primed atoms have coordinates related to those in Table 2 by the symmetry operation: $1-x$, $1-y$, $1-z$.

g, 6.7 mmol) in diethyl ether (50 ml) was stirred overnight, then cooled to −30°C. Ferrocenediylphenylphosphine (1.0 g, 3.4 mmol) in the minimum volume of diethyl ether required for complete solution, was slowly added and the mixture allowed to warm slowly to room temperature, then stirred for a further 1 h. Hydrolysis (H_2O, 25 ml) followed by ether extraction (3 × 20 ml) yielded a clear orange solution. Column chromatography on neutral alumina (activity upgrade II) with diethyl ether as eluant afforded **5**. Concentration and crystallization from hexane gave **5** as orange-yellow crystals, yield 73%.

5: ^1H NMR. δ 1.75 (3, 6), 3.37 (q, 2), 3.86 (m, 2), 3.97 (s, 5), 4.18 (t, 1), 4.31 (d, 1), 4.35 (m, 1), 4.42 (m, 1), 4.59 (m, 1), 7.28–7.33 (m, 3), 7.54–7.63 (2). Anal. Calc. for $C_{29}H_{30}Fe_2NP$: C, 65.08; H, 5.65; N, 2.62. Found: C, 65.37; H, 5.53; N, 2.55%. 400 MHz ferrocenyl region: 3.86 (2m's, H_C, H_D), 4.18 (t, H_B), 4.31 (dddd, H_G), 4.35 (bdd, H_A), 4.42 (ddd, H_F), 4.59 (ddd, H_E). Mass spectrum, parent ion at m/z 535.

Compound **6a** was prepared by quenching the ring-cleavage reaction intermediate with an equimolar quantity of chlorodiphenylphosphine.

(S,R-**6a**): ^1H NMR ($CDCl_3$) δ, 0.68 (9d, 3H), 2.25 (s, 6H), 3.81 (q, 1H), 3.62 (m, 1H), 3.77 (m, 1H), 4.23 (m, 2H), 4.30 (m, 1H), 4.37 (m's, 3H), 6.93 (dd, 1H), 7.12 (t, 1H), 6.84–7.40 (m's, 12H), 7.41–7.51 (m, 5H). Mass Spectrum, parent ion at m/z 625. Anal. Calc. for $C_{33}H_{37}FeNP_2$, C, 72.97; H, 5.80; N, 2.24. Found: C, 71.84; H, 5.80; N, 1.79%.

3.3. Preparation of metal complexes

A slight molar excess of the ligand (S,R-**3a**) or **5** or a two-fold excess of the ligand **4**, was added to a solution of (COD)$PdCl_2$ in CH_2Cl_2 (0.2 g per 5 ml), causing a change of colour. After 8 h stirring the solution was filtered through a small Celite plug, and an equal volume of hexane was added as a top layer. Slow diffusion (3–5 d) resulted in formation of crystalline products in essentially quantitative yield.

(S,S-**3a**)$PdCl_2$: ^1H NMR ($CDCl_3$) 2.06 (d, 3H), 2.86 (s, 3H), 3.03 (s, 3H), 4.34 (q, 1H), 4.10 (m, 1H), 4.33 (s, 5H), 4.34–4.60 (bm, 2H), 7.80–8.05 (m, 2H), 7.10–7.40 (m's, 6H). Anal. Calc. for $C_{26}H_{28}Cl_2FeNPPd$: C, 50.57; H, 4.57; N, 2.27. Found: C, 50.60; H, 4.62; N, 2.21%. (The stereochemistry refers to the bound ligand.)

(**4a**)$_2PdCl_2$: ^1H NMR ($CDCl_3$): 0.84–0.94 (m's, 6H), 1.27 (bm's, 4H), 1.44 (ms, 4H), 2.90 (m, 2H), 4.54 (s, 5H), 4.56 (m, 4H), 4.59 (s, 5H), 5.17 (m, 2H), 5.23 (m, 2H), 5.30 (4H, $2.CH_2Cl_2$). Anal. Calc. for $C_{42}H_{46}Cl_2Fe_2P_2Pd.2CH_2Cl_2$: C, 51.07; H, 4.87. Found: C, 51.84; H, 4.92%.

5 $PdCl_2$: ^1H NMR ($CDCl_3$): 2.76 (s, 3H), 3.03 (d, 1H), 3.47 (s, 3H), 3.93 (d, 1H), 3.76 (m, 1H), 3.93 (s, 5H), 4.20 (m, 1H), 4.32 (s, 5H), 4.32 (m, 1H), 4.68 (m, 1H), 5.37 (m, 1H). Anal. Calc. for $C_{29}H_{30}Cl_2Fe_2NPPd$: C, 48.95; H, 4.25; N, 1.75. Found: C, 47.61; H, 4.12; N, 1.73%.

The rhodium(I) complex of (NBD) and the ligand **3a** was prepared by the standard method [23] [(S,S-**3a**)Rh(NBD)]ClO_4. ^1H NMR 1.55 (m's, 2H), 2.06 (d, 3H), 2.65 (2s, 6H), 3.27 (bs, 1H), 3.65 (q, 1H), 3.84 (bs, 1H), 4.02 (bs, 1H), 4.06 (s, 5H), 4.14 (bs, 1H), 4.26 (bs, 1H), 4.30 (s, 1H), 4.59 (m, 2H), 5.28 (bs, 1H), 5.43 (bs, 1H), 7.29 (t, 1H), 7.30–7.40 (m's, 2H), 7.47–7.52 (m, 3H), 7.52–7.60 (m, 3H). Anal. Calc. for $C_{33}H_{36}ClFeNO_4PRh$: C, 53.87; H, 4.94; N, 1.91. Found: C, 52.61; H, 4.82; N, 1.83%.

3.4. X-ray crystallographic analyses of *3a.PdCl$_2$* and *(4)$_2$.PdCl$_2$.2CH$_2$Cl$_2$*

Crystallographic data are given in Table 1. The final unit-cell parameters were obtained by least-squares on the setting angles for 25 reflections with 2θ = 22.6–27.8° for **3a** $PdCl_2$ and 39.9–45.0° for (**4**)$_2$.$PdCl_2$.$2CH_2Cl_2$. The intensities of three standard reflections, measured every hour throughout the data collection, showed only small random variations for **3a**.$PdCl_2$ and uniform decay by 23.0% for (**4a**)$_2$.$PdCl_2$.$2CH_2Cl_2$. The data were processed, [24] corrected for Lorentz and polarization effects, decay (for (**4**)$_2$.$PdCl_2$.$2CH_2Cl_2$), and absorption (analytical method).

The structures were solved by conventional heavy atom methods, the coordinates of the heavy atoms being determined from the Patterson function and those of the remaining atoms from subsequent differ-

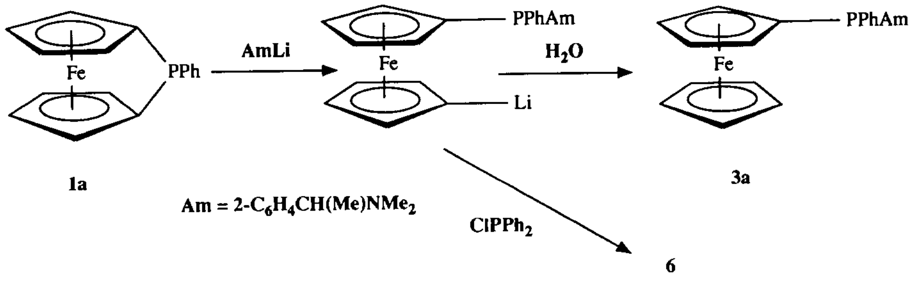

Table 4
Final positional (fractional × 10^4; Pd, Fe, Cl, P × 10^5) and isotropic thermal parameters ($U \times 10^3$ Å^2) with estimated standard deviations in parentheses

Atom	x	y	z	U_{eq}
3a · $PdCl_2$				
Pd	82394(2)	43700(2)	30343(2)	26
Fe	45267(6)	50559(4)	21715(3)	38
Cl(1)	99812(9)	36585(7)	24094(6)	43
Cl(2)	71793(11)	29585(7)	28170(7)	49
P	66411(9)	47985(6)	37854(5)	28
N	9182(3)	5690(2)	3186(2)	32
C(1)	5164(3)	4941(3)	3324(2)	33
C(2)	4365(4)	4154(3)	3129(2)	40
C(3)	3220(4)	4564(3)	2920(3)	47
C(4)	3296(4)	5575(3)	2982(2)	45
C(5)	4501(4)	5830(3)	3222(2)	37
C(6)	5910(5)	5015(5)	1340(3)	69
C(7)	5116(7)	4254(4)	1221(3)	80
C(8)	3949(7)	4628(5)	1069(3)	81
C(9)	4040(6)	5662(5)	1092(3)	71
C(10)	5250(6)	5875(4)	1272(3)	68
C(11)	6911(3)	5905(2)	4367(2)	31
C(12)	7780(3)	6593(3)	4125(2)	33
C(13)	8035(4)	7375(3)	4625(3)	45
C(14)	7464(4)	7480(4)	5353(3)	54
C(15)	6615(5)	6810(3)	5593(2)	50
C(16)	6347(4)	6025(3)	5113(2)	40
C(17)	6368(3)	3895(3)	4566(2)	34
C(18)	7345(4)	3350(3)	4835(3)	44
C(19)	7152(5)	2644(3)	5424(3)	53
C(20)	6032(6)	2500(3)	5736(3)	58
C(21)	5059(5)	3057(4)	5494(3)	59
C(22)	5220(4)	3754(4)	4902(2)	47
C(23)	8397(4)	6580(2)	3314(2)	34
C(24)	9932(5)	5898(3)	2444(3)	54
C(25)	10038(4)	5566(3)	3868(3)	48
C(26)	7502(4)	6758(3)	2652(3)	46
4a$_2$ · $PdCl_2$ · $2CH_2Cl_2$				
Pd	50000	50000	50000	31
Fe	16826(6)	76244(4)	57232(5)	30
P	32163(9)	63293(7)	33602(8)	30
Cl(1)	33241(10)	38271(7)	42037(10)	43
Cl(2) [a]	8773(3)	9156(2)	9375(3)	135
Cl(3) [a]	6989(4)	9166(2)	6282(2)	153
C(1)	1668(4)	6792(3)	3883(4)	35
C(2)	1197(4)	6178(3)	4789(4)	41
C(3)	−75(5)	6819(4)	4916(5)	54
C(4)	−396(5)	7803(4)	4127(5)	58
C(5)	665(5)	7795(4)	3475(4)	50
C(6)	3812(5)	7741(4)	7036(5)	59
C(7)	3148(5)	7294(4)	7844(4)	57
C(8)	1928(6)	8029(4)	7843(5)	62
C(9)	1779(7)	8971(4)	6996(6)	73
C(10)	2958(8)	8784(5)	6492(6)	80
C(11)	3783(4)	7594(3)	3061(4)	37
C(12)	4773(4)	7483(3)	2191(4)	42
C(13)	5165(6)	8576(4)	1976(6)	64
C(14)	6056(6)	8535(5)	1022(6)	70
C(15)	2480(4)	5814(3)	1498(3)	34
C(16)	3392(5)	5027(4)	1056(4)	50
C(17)	2885(7)	4633(4)	−370(5)	66
C(18)	1468(7)	5033(4)	−1358(5)	66
C(19)	568(6)	5811(5)	−935(5)	65
C(20)	1062(4)	6216(3)	489(4)	45
C(21)	7475(11)	8590(6)	7971(10)	118

[a] Coordinates × 10^4.

ence Fourier syntheses. The structure analysis of $(4)_2.PdCl_2.2CH_2Cl_2$ was initiated in the centrosymmetric space group $P\bar{1}$ on the basis of the E-statistics and the appearance of the Patterson function. This choice was confirmed by subsequent calculations. The $(4)_2.PdCl_2$ molecule lies on a crystallographic centre of symmetry. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were fixed in idealized positions ($C(sp^3)–H = 0.98$ Å, $C(sp^2)–H = 0.97$ Å, $U_H = 1.2\ U_{\text{bonded atom}}$). Secondary extinction corrections were not necessary. A parallel refinement of the mirror-image structure of **3a**.$PdCl_2$ gave significantly higher residuals, the R and R_w factor ratios being 1.066 and 1.060, respectively. Neutral atom scattering factors and anomalous dispersion corrections [25] were taken from the International Tables for X-ray Crystallography [25]. Atomic coordinates are listed in Table 4.

Tables of anisotropic thermal parameters, hydrogen atom coordinates and torsion angles, have been deposited at the Cambridge Crystallographic Data Centre.

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