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Synthesis, structures and *rac*/*meso* isomerization behaviour of bisplanar chiral bis(phosphino-η^5-indenyl)iron(II) complexes

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Abstract

Syntheses of the phosphinoindenes 1-(diphenylphosphino)-3-methylindene (**1b**), 3-(diphenylphosphino)-2-methylindene (**1c**), 1-(diphenylphosphino)-2,3-dimethylindene (**1d**), 4,7-dimethyl-3-(diphenylphosphino)indene (**1e**), 1-(diphenylphosphino)-3,4,7-trimethylindene (**1f**) and 3-(diisopropylphosphino)indene (**1i**) were carried out by treatment of the appropriate indenide with the appropriate chlorophosphine. The silylphosphinoindene 3-(diphenylphosphino)-1-(trimethylsilyl)indene (**1h**) was prepared by treatment of the indenide of 3-(diphenylphosphino)indene (**1a**) with trimethylsilylchloride. These indenes, in addition to **1a**, were then used, after deprotonation with BuLi, to prepare the corresponding indenyl ferrocenes, **2a**–**2e**, **2h** and **2i**, by treatment with ferrous chloride in a 2:1 ratio. These compounds were characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy, as well as by mass spectrometry, except for the highly-sensitive diisopropylphosphine **2i** that could only be characterized by ^{31}P NMR spectroscopy. All of these ferrocene complexes are bisplanar chiral systems that can potentially form *rac* and *meso* isomers. In all cases both isomers were observed but for **2b** and **2h** only one could be isolated. The *rac* isomers of complexes **2a**, **2b**, **2d**, and **2e**, as well as the *meso* isomer of **2e**, were studied by X-ray crystallography. Only complexes **2a** and **2i** were observed to undergo *rac*/*meso* isomerization processes at ambient temperature in THF solvent. We were unable to prepare the sterically congested hexamethylferrocene **2f**. Generally, it was found that increasing substitution on the indenyl ring increases the reactivity and sensitivity of the ferrocene.

Keywords: Phosphine; Ferrocene; X-ray structure; Planar chiral; Synthesis; Indenyl

1. Introduction

Ferrocenylphosphines continue to be intensively investigated for their utility in homogeneous catalysis; chiral derivatives are of particular interest for asymmetric catalysis [1,2]. The introduction of a chiral substituent to a ferrocene core or the use of heterotopic, planar chiral ligands is usually used to create the chirality. Despite the large number of planar-chiral ferrocenyl phosphines that have been reported and used in asymmetric catalysis, no racemization has been observed in any of these systems. Compounds containing two planar chiral units may exhibit *rac* and *meso* isomers. We recently reported the preparation of the diindenyl analogue of 1,1′-bis(diphenylphosphino)ferrocene (dppf), [(1-PPh_2-η^5-C_9H_6)$_2$Fe], and the characterization of its *rac* and *meso* isomers by X-ray crystallographic studies of their tetracarbonylmolybdenum complexes [3]. Non-hydrocarbon-functionalized diindenyl ferrocenes are very sparse, especially in comparison to the cyclopentadienyl system: there are only a few silyl [4], boryl [5] and amino [6] complexes known in addition to *ansa*-carboryl [7], *ansa*-dimethylsilyl [8] and *ansa*-ferrocenyl [9] complexes. A patent claiming 7-methoxy-1-(diphenylphosphino), 7-(ethoxycarbonyl)-1-(diphenylphosphino), 7-phenyl-1-(diphenylphosphino), and 1-(dicyclohexylphosphino) diindenyliron complexes has also appeared [2]. The number of non-*ansa* diindenyl iron complexes that have been crystallographically characterised to date is remarkably small [4,10–13]. Further studies on [(1-PPh_2-η^5-C_9H_6)$_2$Fe] have shown that this indenyl ferrocene undergoes a facile isomerization in THF from the *meso* isomer to the *rac* isomer at ambient temperatures [14,15]. Deuterium labeling studies, crossover experiments, activation parameter

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measurements (including the activation volume), salt and solvent effects all point to a mechanism involving THF coordination, indenyl ring-slippage, and indenide dechelation with phosphine coordination to give a zwitterionic intermediate. To further understand the factors influencing this unprecedented ferrocene isomerization process, we sought to prepare a number of derivatives to look at both their isomerization behaviour and their structural features. We report here the preparation, isolation and structure of a number of methyl and trimethylsilyl derivatives. Some of this work has previously been communicated [14].

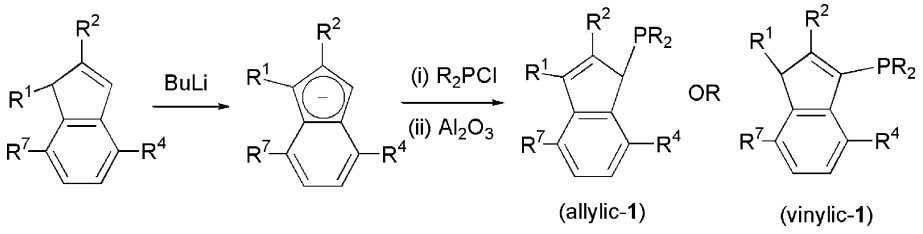
2. Results and discussion

2.1. Synthesis and characterization of the phosphinoindenes

The indenyl phosphine ligand precursors were prepared by a typical procedure of deprotonation of the appropriate indene with BuLi in diethyl ether, followed by treatment with the corresponding chlorophosphine (Scheme 1). Filtration of the product mixture through a short column of alumina was used to remove salts and any phosphine oxide. It also ensures that the thermodynamically-favored isomer of the product indene is isolated. 3-(Diphenylphosphino)indene was previously prepared by Anderson and coworkers [16] and 1,3-bis(diphenylphosphino)indene (**1g**) was previously reported by McGlinchey and coworkers [17] and isolated and characterized by us [3].

Generally, it is found that phosphino substituents prefer to be in the vinylic 3-position of the indene ring, rather than the allylic 1-position. This has been observed in 3-indenyldiphenylphosphine (**1a**) [16], bis(3-indenyl)phenylphosphine [18], tris(3-indenyl)phosphine and their derivatives [19], and is the case here for 2-methyl-3-(diphenylphosphino)indene (**1c**), 4,7-dimethyl-3-(diphenylphosphino)indene (**1e**) and 3-(diisopropylphosphino)indene (**1i**). However, in the presence of a competing methyl group, the methyl group has a stronger preference for the vinylic position than the phosphine group, as exhibited by compounds 1-(diphenylphosphino)-3-methylindene (**1b**), 1-(diphenylphosphino)-2,3-dimethylindene (**1d**) and 1-(diphenylphosphino)-3,4,7-trimethylindene (**1f**). Interestingly, trimethylsilyl may have a lower preference for the vinylic position than diphenylphosphino, since **1h** has vinylic phosphine and allylic silyl groups; however, this compound was not passed through alumina due to its sensitive nature and may not have been isolated as the most thermodynamically-stable isomer.

In addition to mass spectrometry, indenes **1** were characterized by ^{1}H, ^{13}C and ^{31}P NMR spectroscopies. The most readily identifiable peak in the ^{1}H NMR spectra of these compounds is that of H1. This lies at 3.2–3.6 ppm with an integral of two protons for the 3-substituted phosphino indenes and at 4.3–4.5 ppm with an integral of one proton for the 1-phosphino indenes. The aromatic benzo resonances lie in the range 6.6–7.7 ppm along with the phenyl resonances. In cases where these resonances are well separated, they could be assigned by observation of an NOE from H1 to H7 followed by ^{1}H–^{1}H COSY spectroscopy. Similarly, an NOE could be observed from H1 to the methyl on C7 for the 4,7-dimethyl-substituted indenes and the methyl on C2 for the 2-methyl-substituted indenes. H2 is usually upfield of the other aromatic resonances at 5.9–6.2 ppm, except for the diisopropylphosphine **1i** (6.71 ppm)



	R^1	R^2	R^4	R^7	R	Most stable isomer
1a	H	H	H	H	Ph	vinylic
1b	Me	H	H	H	Ph	allylic
1c	H	Me	H	H	Ph	vinylic
1d	Me	Me	H	H	Ph	allylic
1e	H	H	Me	Me	Ph	vinylic
1f	Me	H	Me	Me	Ph	allylic
1g	PPh_2	H	H	H	Ph	-
1h	$SiMe_3$	H	H	H	Ph	vinylic
1i	H	H	H	H	^{i}Pr	vinylic

Scheme 1. Synthesis of the methyl- and trimethylsilyl-substituted phosphinoindenes.

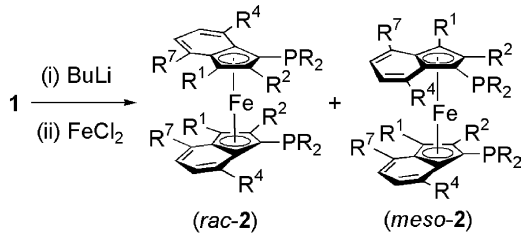
and the trimethylsilyl derivative **1h** (6.39 ppm), although these are still upfield of the benzo resonances. The 2- and 3-methyl resonances are found at 1.9–2.1 ppm whereas the 4- and 7-methyl resonances are found downfield of these at 2.2–2.7 ppm.

In the ^{13}C NMR spectra, C1 is readily identifiable at 47–52 ppm with $^{1}J_{PC} = 20$–25 Hz for the allylic phosphines **1b**, **1d** and **1f** and at 38–45 ppm with $^{3}J_{PC} = 2$–6 Hz for the vinylic phosphines **1c**, **1e** and **1i**. For the trimethylsilyl derivative **1h**, the resonance for C1 is found at 47.9 ppm with a three-bond coupling to phosphorus of 4 Hz. Where possible, ^{13}C assignments were aided by ^{1}H–^{13}C HSQC and ^{1}H–^{13}C HMBC experiments. The C4 and C7 benzo resonances at 118–124 ppm lie upfield of C5 and C6 (123–130 ppm), except when they are methylated, in which case they occur at 128–131 ppm. The phenyl resonances are generally downfield of the benzo resonances. The resonance for C2 occurs at approximately 130 ppm for the allylic phosphines of **1a**, **1b** and **1f**. Methylation gives a small downfield shift to 133.5 ppm for **1d** whereas the vinylic phosphino indenes give a larger downfield shift to approximately 142 ppm for **1a**, **1e**, **1h** and **1i**. Methylation of a vinylic phosphino indene gives a further downfield shift to 159.7 ppm for **1c**. The 4- and 7-methyl carbons lie in a narrow range at 18–21 ppm whereas the 2- and 3-methyl carbons lie upfield at 10–17 ppm.

The ^{31}P chemical shifts for the allylic phosphines **1b**, **1d** and **1f** lie closely together at −5 to +2 ppm (compared to −4.3 ppm for the unsubstituted 1-(diphenylphosphino)indene **1a**) [16] whereas the vinylic phosphines are further upfield and are more sensitive to substitution on the indene ring: compared to vinylic-**1a** at −22.3 ppm [16], substitution with methyl at the 2-position, **1c**, gives an upfield shift to −29.3 ppm whereas the 4,7-dimethyl derivative **1e** exhibits a downfield shift to −16.9 ppm. The 1-trimethylsilyl derivative **1h** has a small downfield shift to −21.5 ppm. The chemical shift of the diisopropylphosphine **1i** (−9.2 ppm) is consistent with a 3-indenyl substituent: the equation $\delta = \Sigma n\alpha_E - 4.8$ for phosphines (with α_E(3-indenyl) = −18.0 and α_E(*i*-Pr) = 8.1) gives a calculated chemical shift of −6.6 ppm for the 3-indenyl phosphine compared to +13.3 ppm for the 1-indenylphosphine (α_E(1-indenyl) = 2) [19].

2.2. Synthesis and characterization of the ferrocenes

The ferrocenes were all prepared by treatment of the phosphinoindenide (formed by deprotonation of the indene with BuLi) with anhydrous ferrous chloride in THF (Scheme 2). Generally, all of the ferrous chloride has reacted after approximately 2 h of stirring at ambient temperature. Purifications of the ferrocenes were carried out by filtration through a Celite column using a solvent appropriate for the ferrocene. In each case, the possibility exists for the formation of both *rac* and *meso*



	R^1	R^2	R^4	R^7	R
2a	H	H	H	H	Ph
2b	Me	H	H	H	Ph
2c	H	Me	H	H	Ph
2d	Me	Me	H	H	Ph
2e	H	H	Me	Me	Ph
2f	Me	H	Me	Me	Ph
2g	PPh_2	H	H	H	Ph
2h	$SiMe_3$	H	H	H	Ph
2i	H	H	H	H	^{i}Pr

Scheme 2. Synthesis of the methyl- and trimethylsilyl-substituted phosphinoindenyl ferrocenes.

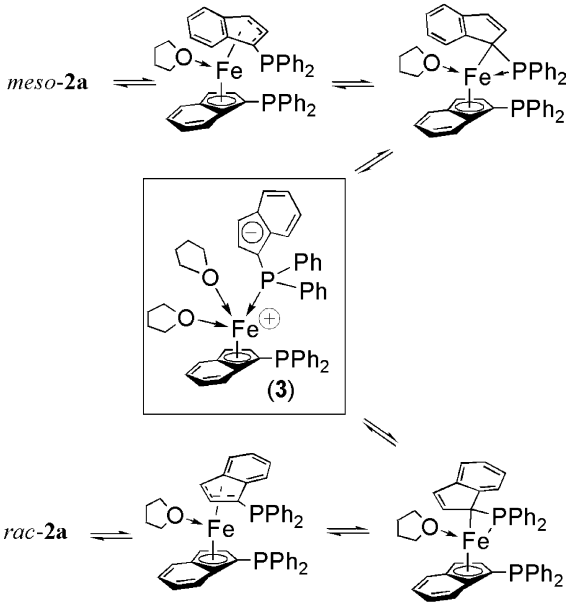
isomers due to the bisplanar chiral nature of the complexes. Since the *rac*/*meso* isomerization processes have not been observed in the non-coordinating solvents chloroform, dichloromethane or diethyl ether, these are generally used for the filtration and isolation steps.

The reaction of lithium 1-(diphenylphosphino)indenide with ferrous chloride initially produces a 1:1 mixture of two phosphorus-containing compounds, as shown by peaks in the ^{31}P NMR spectrum at −22.26 and −26.53 ppm. Overnight, the peak at −26.53 ppm almost disappears leaving essentially only one product. Recrystallization of this compound from CH_2Cl_2/diethyl ether gave crystals suitable for X-ray crystallography that showed the compound to be the *rac* isomer of **2a** (see below). If the reaction is stopped after 2 h by removal of solvent, the *rac*/*meso* product mixture can be isolated. In the ^{1}H NMR spectrum, the H2 and H3 protons have distinct chemical shifts from each other and for each isomer: For the *rac* isomer, they are widely spaced at 3.07 and 4.92 ppm for H2 and H3, respectively (a difference of 1.85 ppm), whereas for the *meso* isomer, they are closely spaced (and lie between those of the *rac* isomer) at 3.48 and 3.81 ppm for H2 and H3, respectively (a difference of 0.33 ppm). Clearly, the ring currents are having a significant effect on these protons.

In THF solvent, the *meso* isomer is observed to undergo an isomerization to the *rac* isomer with $\Delta H^{\ddagger} = 58 \pm 4$ kJ mol^{-1}, $\Delta S^{\ddagger} = -140 \pm 15$ J K^{-1} mol^{-1} and $\Delta V^{\ddagger} = -12.9 \pm 0.8$ cm^3 mol^{-1} [4]. At 23 °C, $k_{obs} = 1.59(3) \times 10^{-5}$ s^{-1} [14,15]. The isomerization does not go to completion, indicating that the reverse process of *rac* to *meso* isomerization does occur, but with a slower rate constant. Thus, the *meso*/*rac* equilibrium lies on the side of the *rac* isomer. In THF at

23 °C, $K = [meso\text{-}\mathbf{2a}]/[rac\text{-}\mathbf{2a}] = 0.074(5)$ [15]. Our preferred mechanism involves THF coordination with indenide ring-slippage and then dechelation of the indenide and coordination of the phosphine to form the key zwitterionic intermediate **3** (Scheme 3). It has also been found that the most facile hydrolysis mechanism is also via zwitterion **3** [15], which one would expect to be more readily protonated than a non-polar ferrocene **2**. As a consequence, it is found that *meso*-**2a** hydrolyses much more readily than *rac*-**2a**.

The synthesis of the 3-methyl analogue **2b**, from **1b**, gave the two isomers in a 3:1 ratio as indicated by peaks at −24.50 and −26.25 ppm in the ^{31}P NMR spectrum after 2 h. This ratio did not change after stirring at ambient temperature overnight. The use of higher temperatures led to hydrolysis reactions with no observable isomerization. Upon workup, only one compound, that with the downfield chemical shift, was isolated and



Scheme 3. Preferred mechanism for *rac*/*meso* isomerization of phosphinoindenyl ferrocenes.

X-ray crystallography, see below, showed this to be the *rac* isomer. The ^{1}H NMR spectrum contains a resonance at 3.61 ppm for H2, downfield of both isomers of **2a**. As with **2a**, the *meso* isomer appears to be the most reactive isomer.

Ferrocene **2c**, containing methyl groups in the 2 and 2′ positions, was prepared from **1c** in THF and found to give two compounds, in a 2:3 ratio, at −17.41 and −19.68 ppm in the ^{31}P NMR spectrum. This ratio did not change after stirring at ambient temperature for 3 days. The major isomer has a chemical shift of 4.84 ppm for H3 whereas this peak occurs at 5.08 ppm for the minor isomer. Comparison of the ^{31}P and ^{1}H NMR spectra with **2a** and **2b** (Table 1), as well as the ^{13}C NMR spectra (see below), strongly suggest that the major isomer, with the upfield ^{31}P chemical shift, is the *meso* complex, however, this is not unambiguous.

The tetramethylferrocene **2d**, with methyl groups in the 2, 2′, 3 and 3′ positions, was prepared from **1d** and found to give the two isomers in a 5:2 ratio (−23.3 and −23.7 ppm). Unfortunately, only a few crystals of the *rac* isomer (see below) were isolated and we have been unable to unambiguously state which is the major isomer. Nonetheless, the chemical shifts of C5 and C6 (122.0 and 123.5 ppm, respectively) tend to suggest that the major isomer is *rac* since, for **2a**–**2c**, these resonances occur at 121.2–123.1 ppm for the *rac* isomers and 124.0–125.0 ppm for the *meso* isomers. Solutions of this compound were found to be very sensitive and we were unable to observe any isomerization process.

Bis(1-(diphenylphosphino)-4,7-dimethyl-η^5-indenyl)-iron(II) (**2e**) was made from indene **1e** and found to give a 1:1 isomeric mixture with peaks in the ^{31}P NMR spectrum at −16.46 and −21.47 ppm. Crystallization from dichloromethane/diethyl ether afforded dark-red crystals which ^{31}P NMR spectroscopy showed to contain both isomers. As different NMR samples gave different ratios of the two isomers, we concluded that different crystals containing each isomer were present, however, we were unable to visually discriminate between the two sets of crystals. Random selection of

Table 1
^{31}P NMR chemical shifts and ^{1}H NMR chemical shifts for H2 and H3 of the ferrocenes in $CDCl_3$

Compound	^{31}P		H3		H2	
	rac	*meso*	*rac*	*meso*	*rac*	*meso*
2a	−22.26	−26.53	4.92	3.81	3.07	3.48
2b	−24.69	−26.35	–	–	3.61	Not observed
2c	−17.60	−20.10	5.08	4.84	–	–
2d	−23.81[a]	−23.21[a]	–	–	–	–
2e	−16.86	−22.17	5.31	4.02	3.13	3.85
2h	−28.49[a]		–	–	3.84[a]	
2i	−3.27	−8.89	Not observed	Not observed	Not observed	Not observed
2j	−16.81	−23.90	5.34	4.07	3.27	3.90
	−22.20	−25.61	4.98	3.85	3.11	3.55

[a] Assignment to the *rac* or *meso* isomer is ambiguous.

crystals allowed us to eventually obtain X-ray structures of both isomers (see below) as well as identify the separate NMR spectra. Again, the compound with the downfield chemical shift was found to be the *rac* isomer. As with **2a**, the ^{1}H NMR chemical shifts of the H2 and H3 protons are quite distinctive: The *rac* isomer has widely-spaced resonances at 3.13 and 5.31 ppm for H2 and H3, respectively (a difference of 1.98 ppm), whereas the *meso* isomer has closely-spaced resonances, in between those of the *rac* isomer, at 3.85 and 4.02 ppm for H2 and H3, respectively (a difference of 0.17 ppm). We based our NMR assignments of the isomers on these resonances since similar trends were unambiguously identified in **2a**.

We investigated possible isomerization processes in **2e** by taking a number of NMR samples of the crystalline mixture, to ensure that we did not accidentally start with the thermodynamic mixture, and then heated each sample to 40 °C for 24 h. We did not observe any change in the isomeric ratio under these conditions. We suggest that the increased steric protection of the iron centre and the electron-donating ability of the methyl groups are preventing nucleophilic attack at the iron center by solvent THF molecules.

Numerous unsuccessful attempts have been made to prepare the bis(trimethyldiphenylphosphino) derivative **2f** from indene **1f**. Presumably steric crowding is preventing its formation. We have also generally observed that increasing substitution in indenylferrocenes decreases the stability and increases the reactivity of the complexes once they are formed.

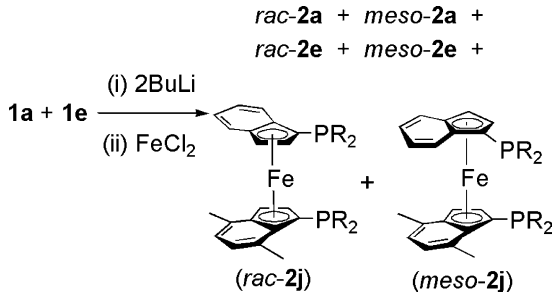
We have previously reported that treatment of 1,3-bis(diphenylphosphino)indenide with ferrous chloride in THF produces a single peak in the ^{31}P NMR spectrum consistent with the desired ferrocene, **2g** [3]. However, upon removal of solvent and extraction of the products, we find that the ferrocene has decomposed into **2a** and other species. It appears that concentration of this species leads to its decomposition. It may be that other molecules of **2g** act as nucleophiles to give reactive zwitterionic species to begin hydrolysis-type processes. Treatment of the sterically similar 3-(diphenylphosphino)-1-(trimethylsilyl)indene (**1h**) with BuLi followed by ferrous chloride also initially gives the expected product peaks in the ^{31}P NMR spectrum (at −25.3 and −27.3 ppm), in a 3:2 ratio of the two isomers. Like **2g**, this material is quite sensitive, however, one of the isomers is more stable than the other (probably the *rac* isomer) and we were able to isolate this in reasonable yield (31%). It seems that steric factors again lead to sensitive indenylferrocene systems. Similarly, we note that we have recently prepared and isolated bis(1,3-bis(trimethylsilyl)-η^5-indenyl)iron(II) and that it suffers from significant steric strain [4].

The ferrocene formed from the diisopropylphosphine **1i**, **2i**, was found to be extremely air, moisture and heat sensitive. We were unable to obtain satisfactory ^{1}H and ^{13}C NMR data due to the formation of paramagnetic decomposition products. However, we were able to observe, by ^{31}P NMR spectroscopy, an isomerization process, presumably from *meso* to *rac* (the *rac* isomer again lies downfield of the *meso* isomer: −3.27 ppm versus −8.89 ppm, respectively). At 23 °C, $k_{obs} = 1.75(30) \times 10^{-5}$ s^{-1} and, at 30 °C, $k_{obs} = 3.05(2) \times 10^{-5}$ s^{-1}. These rates are very similar to those observed for the isomerization of *meso*-**2a** to *rac*-**2a** ($1.59(3) \times 10^{-5}$ and $3.01(9) \times 10^{-5}$ s^{-1}, respectively) and suggest that the nucleophilicity of the phosphine, diisopropyl versus diphenyl, is not important in the rate-determining step and is consistent with this step involving coordination of THF solvent and indenide ring-slippage.

Since we have only been able to observe *rac*/*meso* isomerization in the two least-sterically-crowded systems, **2a** and **2i**, we sought to make a smaller increase in the steric bulk of the system by preparing a mixed-ligand system derived from indenes **1a** and **1e**, namely, {4,7-dimethyl-1-(diphenylphosphino)-η^5-indenyl}{1-(diphenylphosphino)-η^5-indenyl}iron(II) (**2j**) (Scheme 4). From the addition of ferrous chloride to a 1:1 mixture of the indenides of **1a** and **1e** we observed eight ferrocenyl phosphine signals in the ^{31}P NMR spectrum of the product solution. The two isomers of each of **2a** and **2e** account for four of these, and the other four can then be assigned to the *rac* and "*meso*" isomers of **2j**. It should be noted that the "*meso*" isomer actually exists as two enantiomers due to the differing centers of planar chirality. After stirring the product mixture for 24 h, all of the *meso*-**2a** had isomerized to *rac*-**2a**, as expected, however, there was no other change in the relative intensities of the signals. Surprisingly, the addition of just two methyl groups on one benzo ring is appears to be a sufficient increase in steric bulk to significantly slow the rate of isomerization.

2.3. NMR spectra of the ferrocenes

Generally, there are few consistent trends in the relative ^{13}C NMR spectra of the various isomers. The most useful information to be gained from the ^{13}C NMR



Scheme 4. Preparation of mixed diindenyl ferrocene **2j**.

spectra is that, for both **2a** and **2e**, on going from the *rac* to the *meso* isomer there is a consistent downfield shift of 2 ppm for both C5 and C6 and 4–5 ppm for both C4 and C7. Consistent with the trends in the P and H2 chemical shifts of **2c**, the relative chemical shifts of C5 and C6 for the two isomers of **2c** also suggest that the major isomer is *meso* and the minor isomer is *rac*. In the ^{31}P NMR spectra, so far as we can be certain of our assignments, the chemical shift of the *rac* isomer is always 2–6 ppm upfield of the *meso* isomer (Table 1).

2.4. X-ray structural analyses

Crystallographic and refinement data for complexes *rac*-**2a**, *rac*-**2b**, *rac*-**2d**, *rac*-**2e** and *meso*-**2e** are given in Table 2 with selected bond distances and angles given in Table 3. The solid-state structures of these compounds were determined for two reasons: to confirm the identity of the isomer and to look for possible explanations for the apparent preference of the *rac* isomer over the *meso* isomer in **2a**.

Compound *rac*-**2a** lies on a crystallographic C_2 axis whereas *rac*-**2e** does not. Nonetheless, the structures of *rac*-**2a** (Fig. 1) and *rac*-**2e** (Fig. 2) are very similar in that they have essentially the same conformation: the two benzo rings lie approximately on top of each other (RA = 20.8° and 12.1° for *rac*-**2a** and *rac*-**2e**, respectively, compared to 6.0° and 13.0° for diindenyliron(II) [10a]) in a π-offset arrangement to maximise π–π-stacking interactions [20] and the diphenylphosphino groups are on opposite sides of the molecule, presumably to minimise steric interactions. Fig. 3 shows the five molecules that we have crystallography characterized here looking down the centroid–centroid axis. From this view, it can be seen that two of the phenyl rings in both *rac*-**2a** and *rac*-**2e** (Figs. 3(a) and (d), respectively) effectively sandwich the H2 protons, which probably accounts for their large up-field shift in the ^{1}H NMR spectrum. The two other phenyl rings are oriented away from the ferrocene center. Interestingly, if the benzo rings in either compound were π offset in the other direction, but by approximately the same amount, the diphenylphosphino groups would be even further apart from each other without increasing the steric interactions between the phenyl groups and the other benzo ring. This appears to be the case in the only non-*ansa rac*

Table 2
Crystal data and structural refinement parameters for *rac*-**2a**, *rac*-**2b**, *rac*-**2d**, *rac*-**2e** and *meso*-**2e**

	rac-**2a**	*rac*-**2b**	*rac*-**2d**	*rac*-**2e**	*meso*-**2e**
Empirical formula	$C_{42}H_{32}FeP_2$	$C_{44}H_{36}FeP_2$	$C_{46}H_{40}FeP_2$	$C_{46}H_{40}FeP_2$	$C_{46}H_{40}FeP_2$
Formula weight (g mol^{-1})	654.47	682.52	710.57	710.57	710.57
Temperature (K)	168(2)	163(2)	183(2)	168(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	*Pbcn*	*C*2/*c*	$P\bar{1}$	$P\bar{1}$	*C*2/*c*
a (Å)	12.959(6)	15.569(16)	9.397(19)	12.652(7)	27.186(5)
b (Å)	12.396(5)	13.705(15)	14.16(3)	12.669(7)	12.532(3)
c (Å)	19.296(8)	17.401(18)	14.23(3)	14.304(8)	24.816(5)
α (°)	90	90	93.93(4)	67.521(7)	90
β (°)	90	110.40(3)	101.65(6)	87.440(7)	122.72(3)
γ (°)	90	90	90.03(6)	62.968(7)	90
Volume (Å^3)	3100(2)	3480(6)	1850(7)	1863.8(18)	7113(2)
Z	4	4	2	2	8
Density (calcd) (Mg/m^3)	1.402	1.303	1.276	1.270	1.331
Absorption coefficient (mm^{-1})	0.621	0.556	0.526	0.522	0.547
F (0 0 0)	1360	1424	744	748	2992
Crystal size (mm)	0.30 × 0.21 × 0.04	0.40 × 0.24 × 0.19	0.41 × 0. 15 × 0.07	0.75 × 0.25 × 0.05	0.40 × 0.36 × 0.27
θ Range (°)	2.11–26.44	2.04–26.31	1.98–26.46	1.96–26.47	1.79–26.61
Index ranges	$-16 \leqslant h \leqslant 16$, $-15 \leqslant k \leqslant 8$, $-23 \leqslant l \leqslant 23$	$-10 \leqslant h \leqslant 19$, $-16 \leqslant k \leqslant 17$, $-21 \leqslant l \leqslant 11$	$-11 \leqslant h \leqslant 10$, $-17 \leqslant k \leqslant 17$, $-17 \leqslant l \leqslant 17$	$-15 \leqslant h \leqslant 15$, $-15 \leqslant k \leqslant 15$, $-8 \leqslant l \leqslant 17$	$-33 \leqslant h \leqslant 26$, $-11 \leqslant k \leqslant 15$, $-21 \leqslant l \leqslant 31$
Reflections collected	37580	6664	22975	23327	21717
Independent reflections	3142	3209	7267	7376	7212
R(int)	0.1169	0.0416	0.0900	0.0631	0.0426
Completeness to θ	(26.44°) 98.3%	(26.31°) 90.7%	(26.46°) 95.0%	(26.47°) 95.9%	(26.61°) 96.7%
Absorption correction	Multi-scan	Multi-scan	Multi-scan	Multi-scan	Multi-scan
Maximum/minimum transmission	0.9756/0.8356	1.0000/0.8567	1.0000/0.7954	1.0000/0.8669	1. 0000/0.8534
Data/restraints/parameters	3142/0/204	3209/0/213	7267/0/446	7376/0/442	7212/0/446
Goodness-of-fit on F^2	0.966	0.892	1.053	0.921	1.022
R indices [$I > 2\sigma(I)$] (R, R_w)	0.0351, 0.0783	0.0373, 0.0788	0.1102, 0.3143	0.0464, 0.1041	0.0383, 0.0943
R indices (all data) (R, R_w)	0.0908, 0.1124	0.0652, 0.0840	0.2086, 0.3593	0.0978, 0.1165	0.0660, 0.1034
Final maximum/minimum Δρ (e Å^{-3})	0.308 and −0.427	0.339 and −0.369	2.047 and −0.415	0.722 and −0.324	0.298 and −0.301

Table 3
Selected bond distances (Å) and angles (°) for *rac*-**2a**, *rac*-**2b**, *rac*-**2d**, *rac*-**2e** and *meso*-**2e**

	rac-**2a**	*rac*-**2b**	*rac*-**2d**	*rac*-**2e**[a]	*meso*-**2e**[a]
Fe–CNT	1.672	1.685	1.707, 1.693	1.666, 1.669	1.681, 1.681
Fe–C1	2.062(3)	2.064(3)	2.063(9), 2.083(9)	2.062(3), 2.056(3)	2.096(2), 2.052(2)
Fe–C2	2.045(3)	2.065(3)	2.102(11), 2.085(12)	2.041(3), 2.045(3)	2.048(2), 2.037(2)
Fe–C3	2.067(3)	2.089(3)	2.087(11), 2.073(12)	2.047(3), 2.057(3)	2.045(2), 2.067(2)
Fe–C8	2.090(3)	2.094(3)	2.112(9), 2.101(9)	2.116(3), 2.109(3)	2.094(2), 2.103(2)
Fe–C9	2.104(3)	2.113(3)	2.148(10), 2.091(10)	2.094(3), 2.104(3)	2.097(2), 2.112(2)
P–C1	1.829(3)	1.830(3)	1.852(9), 1.837(8)	1.832(3), 1.836(3)	1.840(2), 1.814(2)
CNT–Fe–CNT	179.6	177.03	175.84	178.8	175.4
Fe–C1–P	123.18(17)	130.06(13)	131.1(5), 131.2(4)	122.59(15), 126.90(15)	134.59(12), 125.82(12)
CNT–C1–P	176.07	174.11	168.30, 168.63	176.43, 178.82	171.45, 179.19
C1–CNT–CNT′–C1′	123.1	115.3	30.4	131.9	40.5
Slip-fold parameter Δ (Å)[b]	0.032	0.027	0.055, 0.018	0.051, 0.051	0.025, 0.047
Hinge angle HA (°)[c]	2.1	2.4	4.7, 3.3	2.6, 2.2	1.8, 2.7
Fold angle FA (°)[d]	0.9	2.5	5.2, 6.0	1.9, 1.9	1.2, 1.0
Rotation angle RA (°)[e]	20.8	28.7	118.8	12.1	40.5

[a] The second number refers to the equivalent parameter for the primed atoms.
[b] Δ = average distance of Fe to C8 and C9 minus average distance of Fe to C1 and C3.
[c] HA = angle between planes defined by [C1, C2, C3] and [C1, C3, C8, C9].
[d] FA = angle between planes defined by [C1, C2, C3] and [C4, C5, C6, C7, C8, C9].
[e] RA = angle formed by the intersection of two lines determined by the centroids of the five- and six-membered rings.

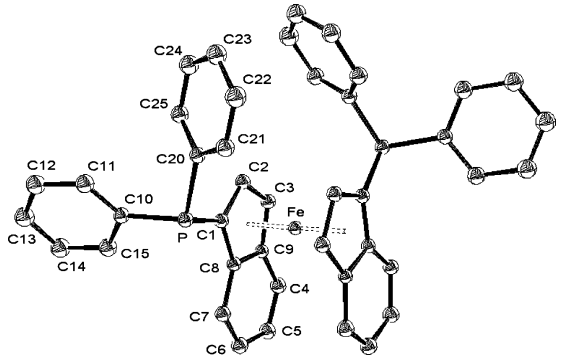


Fig. 1. ORTEP of *rac*-**2a** indicating the numbering of the atoms. The thermal ellipsoids have been drawn at 40% probability.

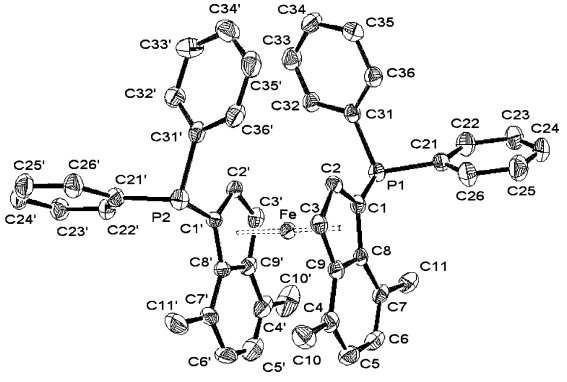


Fig. 2. ORTEP of *rac*-**2e** indicating the numbering of the atoms. The thermal ellipsoids have been drawn at 40% probability.

diindenyl ferrocene that has previously been crystallographically characterized, a bis(indeno[2.2]paracyclophane-9-ene) complex [13], in which the RA is 35.4°.

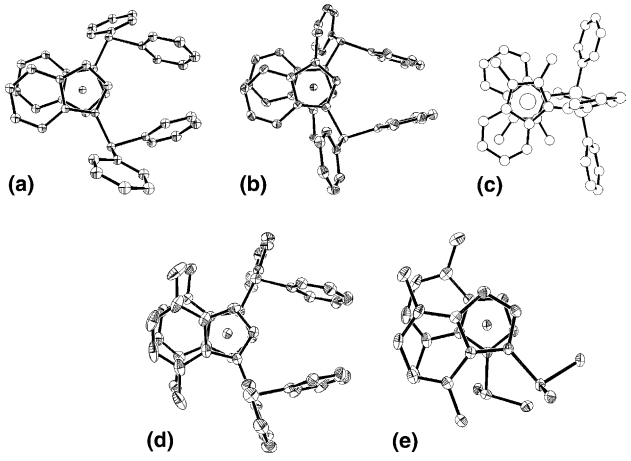


Fig. 3. Views down the CNT–CNT axes: (a) *rac*-**2a**, (b) *rac*-**2b**, (c) *rac*-**2d**, (d) *rac*-**2e** and (e) *meso*-**2e**. For clarity, only the *ispo*-Ph carbon atoms of the phenyl rings in *meso*-**2e** are shown.

Thus, it appears that this relative conformation of the indenyl rings in *rac*-**2a** and *rac*-**2e** is at least partially due to favourable edge-type CH–π hydrogen bonding interactions between the phenyl groups and the H2 atoms, as each H2 atom has three H···C distances of less than 3.0 Å: two to a phenyl group on the same ligand (the *ipso* atom and an *ortho* atom) and one to an *ortho* carbon atom on the other ligand (2.90, 2.69 and 2.98 Å, respectively, for *rac*-**2a** and 2.83, 2.95, and 2.97, respectively, for H2 of *rac*-**2e** and 2.81, 2.83 and 2.95 Å, respectively, for H2′ of *rac*-**2e**) [21].

Meso-**2e** is the first *meso*-diindenyl complex crystallographically characterized. As illustrated in Figs. 3(e) and 4, the π-offset stacking of the benzo rings is not ideal: RA (40.5°) is much larger than in *rac*-**2a**, *rac*-**2b**

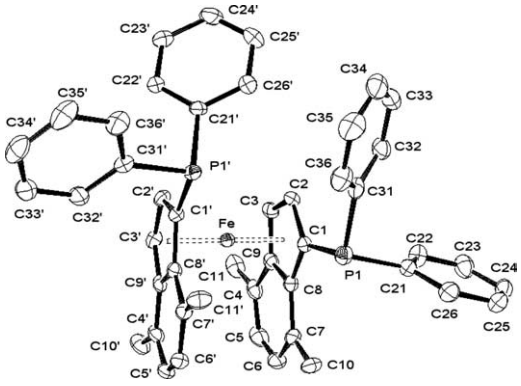


Fig. 4. ORTEP of *meso*-**2e** indicating the numbering of the atoms. The thermal ellipsoids have been drawn at 40% probability.

(see below) and *rac*-**2e** as well as in that of diindenyliron(II) [10a]. A better π-stacking would result in closer diphenylphosphino groups, but H26′ is already so close to C31–C36 as to be hydrogen bonding with this ring. As it is, steric interactions between the two diphenylphosphino groups and one of the methyl groups leads to a folding of the CNT–Fe–CNT angle away from linear to 175.4°; to one of the phosphino groups being bent back (CNT–C1–P = 171.5°); and to a long Fe–C1 distance (2.096(2) Å, which is over 0.03 Å longer than comparable distances in the other ring and the other compounds). There are also fewer CH–π interactions in this complex than in *rac*-**2a** and *rac*-**2e**: The H2 atoms each have two H···C distances of less than 3.0 Å, to the *ipso* and an *ortho* C atom of a phenyl group of the same ligand, but the orientations are not very favourable for hydrogen bonding. H26′ does, however, point directly at the centroid of C31–C36 and all of the H···C distances to this ring are less than 3.0 Å. It would appear that the π–π stacking, steric interactions and CH–π hydrogen bonding are all less favourable in this *meso* compound than in *rac*-**2a** and *rac*-**2e**.

Rac-**2b** (Figs. 3(b) and 5) has a similar conformation to *rac*-**2a** and *rac*-**2e**: the benzo rings lie in a π-offset arrangement (RA = 28.7°). The centroid–centroid view

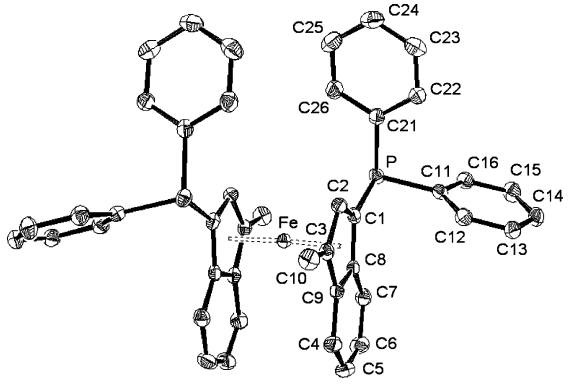


Fig. 5. ORTEP of *rac*-**2b** indicating the numbering of the atoms. The thermal ellipsoids have been drawn at 40% probability.

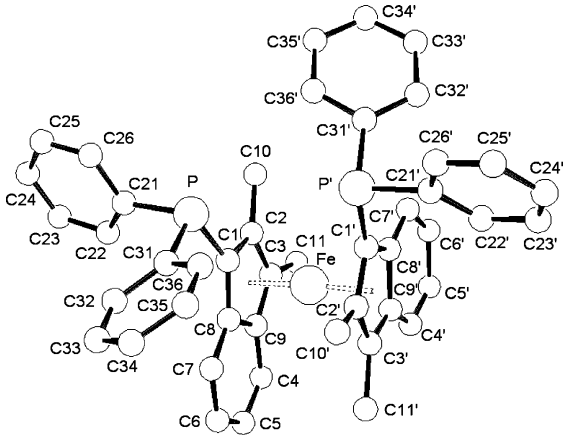


Fig. 6. PLUTO of *rac*-**2d** indicating the numbering of the atoms. The atoms have been drawn at 40% probability.

suggests that the H2 protons are again sandwiched between two of the phenyl rings, however, they are in fact pushed out of the Fe atom plane by the encroaching 3-methyl groups, such that the H2 atoms can each only hydrogen bond to one of the phenyl rings (the H2···C21 distance is 2.89 Å, all other H···C distances are greater than 3.0 Å). As with *rac*-**2a** and *rac*-**2e**, the other phenyl rings are oriented away from the ferrocene center.

Although the crystallographic analysis of *rac*-**2d** is poor ($R = 11.0\%$), its identity and conformation, illustrated in Figs. 3(c) and 6, is unambiguous and quite different from that of the other *rac* compounds. The five-membered rings are staggered and there is no π-offset stacking between the benzo rings (RA = 118.8°). The diphenylphosphino groups lie near each other (C1–CNT–CNT′–C1′ = 30.4°) with two of the phenyl rings in the plane of the ferrocene and oriented towards the six-membered ring rather than the methyl groups.

3. Conclusions

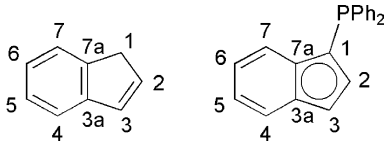
In this paper we have described a number of derivatives of the diindenyl analogue of dppf: a variety of methyl derivatives, one trimethylsilyl derivative, and a (diisopropylphosphino)indenyl analogue. All of these are bisplanar chiral systems with the potential to form both *rac* and *meso* isomers. In each case, a mixture of the two isomers was initially formed. For the 3-methyl and 3-trimethylsilyl derivatives, only one isomer, probably *rac*, was obtained upon workup. In the case of the non-functionalized phosphinoindenyl complexes, these were both observed to undergo a *meso* to *rac* isomerization process at similar rates, consistent with an isomerization mechanism involving solvent coordination and indenide ring-slippage in the rate determining step. The lack of isomerization in the other ferrocenes is attributed to steric effects since even the 4,7-dimethyl

derivative does not isomerize and a steric explanation seems more likely than an electronic one. Increasing functionalization was also found to increase the sensitivity of the ferrocene to such an extent that we were unable to prepare the bis(3,4,7-trimethyl) derivative.

Crystallographic studies of four *rac* compounds as well as the first non-*ansa meso* diindenyl ferrocene were carried out. Comparisons of the *rac*/*meso* pair of **2e** suggests that the *rac* isomer is favored due to a combination of better π-offset stacking, better intramolecular CH–π hydrogen bonding, and fewer intramolecular steric interactions.

4. Experimental

All manipulations and reactions were carried out under an inert atmosphere (Ar or N_2) by use of standard Schlenk line techniques. Reagent grade solvents were dried and distilled prior to use: diethyl ether and tetrahydrofuran from Na/benzophenone; dichloromethane and petroleum ether (50–70 °C fraction) from CaH_2. Diphenylphosphinoindene [16], bis(1-(diphenylphosphino)-η^5-indenyl)iron(II) [3,14], 1-methylindene [22] and 4,7-dimethylindene [23] were prepared by published procedures. 1,2-dimethylindene and 1,4,7-trimethylindene were prepared from 2-methylindene and 4,7-dimethylindene, respectively, by modifications of the route used to prepare 1-methylindene. All other reagents were purchased from Aldrich or Sigma Chemical Companies. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopy data were collected on a Varian UNITY-300 spectrometer operating at 300, 75 and 121 MHz, respectively. NOE, ^1H–^1H COSY, ^1H–^{13}C HSQC and ^1H–^{13}C HMBC experiments were run on a Varian INOVA-500 spectrometer operating at 500 and 125 MHz for ^1H and ^{13}C, respectively. Spectra were measured at ambient temperature with residue solvent peaks as internal standard for ^1H and $^{13}C\{^1H\}$ spectroscopy.Couplings in the ^{13}C NMR spectra are to phosphorus. $^{31}P\{^1H\}$ NMR spectroscopy chemical shifts were reported relative to external 85% H_3PO_4, positive shifts representing deshielding. EI mass spectra were collected on a Kratos MS80RFA mass spectrometer. Elemental analyses were carried out by Campbell Microanalytical Services, University of Otago, Dunedin.



4.1. Preparation of 1-(diphenylphosphino)-3-methylindene (*1b*)

To a solution of 1-methylindene (0.745 g, 5.72 mmol) in diethyl ether (40 ml) at −78 °C was added a solution of *n*-BuLi (3.57 ml, 1.6 M, 5.72 mmol). The solution was allowed to warm to ambient temperature and stirred for 2 h, in which time a white precipitate formed. The mixture was cooled to −78 °C, and PPh_2Cl (0.892 ml, 5.72 mmol) was added drop-wise. The mixture was allowed to warm to ambient temperature and stirred for 2 h. The reaction mixture was then filtered through alumina and the solvent was removed in vacuo to give 1.61 g (90%) of **1b** as a white, air-sensitive powder. ^1H NMR ($CDCl_3$): δ 7.67–6.85 (m, 14H, Ph*H* and H4–7), 6.12 (m, 1H, H2), 4.48 (m, 1H, H1), 2.11 (m, 3H, Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 145.71 (s, C3a), 144.47 (d, $^2J = 9$ Hz, C7a), 140.65 (d, $^3J = 6$ Hz, C3), 137.66 (d, $^1J = 19$ Hz, *i*-Ph), 137.21 (d, $^1J = 18$ Hz, *i*-Ph), 133.68 (d, $^2J = 20$ Hz, *o*-Ph), 133.12 (d, $^2J = 20$ Hz, *o*-Ph), 129.76 (d, $^2J = 4$ Hz, C2), 129.13 (s, *p*-Ph), 128.81 (s, *p*-Ph), 128.38 (d, $^3J = 7$ Hz, *m*-Ph), 128.07 (d, $^3J = 7$ Hz, *m*-Ph), 126.47 (s, C6), 124.51 (s, C5), 123.91 (d, $^3J = 5$ Hz, C7), 119.25 (s, C4), 47.08 (d, $^1J = 20$ Hz, C1), 12.95 (s, Me). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −4.98. Mass spectrum (EI, *m*/*z* (%)): 314 (82, M^+), 185 (100, Ph_2P^+), 128 (30, $C_9H_5Me^+$), 108 (6, PhP^+), 77 (8, Ph^+). HR-MS: M^+ Calc., 314.12244. Found, 314.12295.

4.2. Preparation of 3-(diphenylphosphino)-2-methylindene (*1c*)

2-Methylindene (1.00 g, 7.68 mmol) in diethyl ether (50 ml) was cooled to −78 °C and BuLi (4.8 ml of 1.6 M, 7.69 mmol) was added. After stirring at ambient temperature for 3 h, the solution was cooled to −78 °C and PPh_2Cl (1.38 ml, 7.69 mmol) was added. The solution was then stirred overnight at ambient temperature, filtered through a short alumina column and the solvent removed in vacuo to give **1c** (5.54 g, 94%) as a white powder. ^1H NMR ($CDCl_3$): δ 7.35 (m, 4H, *m*-PhH), 7.31 (d, $^3J_{HH} = 7$ Hz, 1H, H7), 7.2 (m, 6H, *o*-and *p*-PhH), 6.97 (dd, $^3J_{HH} = 7$ and 7 Hz, 1H, H6), 6.85 (dd, $^3J_{HH} = 7$ and 7 Hz, 1H, H5), 6.61 (d, $^3J_{HH} = 7$ Hz, 1H, H4), 3.45 (s, 2H, H1), 2.31 (s, 3H, Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 159.68 (d, $^2J = 30$, C2), 146.27 (s, C7a), 142.44 (d, $^2J = 3$ Hz, C3a), 136.09 (d, $^3J = 9$ Hz, C3), 132.49 (d, $^3J = 18$ Hz, *m*-Ph), 128.36 (d, $^2J = 6$ Hz, *o*-Ph), 128.02 (s, *p*-Ph), 125.83 (s, C5), 123.73 (s, C6), 123.15 (s, C7), 122.07 (d, $^3J = 2$ Hz, C4), 44.94 (d, $^3J = 6$ Hz, C1), 16.79 (d, $^3J = 20$ Hz, Me). The *i*-Ph carbon atoms were not observed. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −29.3. Anal. Calc. for $C_{22}H_{19}P$: C, 84.06; H, 6.09. Found: C, 81.23; H, 6.12%. Mass spectrum: (EI, *m*/*z* (%)): 314 (100, M^+), 185 (62, Ph_2P^+), 128 (16, $MeC_9H_5^+$). HR-MS: M^+ Calc., 314.12244. Found, 314.12359.

4.3. Preparation of 1-(diphenylphosphino)-2,3-dimethylindene (*1d*)

To a solution of 1,2-dimethylindene (0.717 g, 4.97 mmol) in diethyl ether (40 ml) at −78 °C was added a solution of *n*-BuLi (3.11 ml, 1.6 M, 4.97 mmol). The

solution was allowed to warm to ambient temperature and stirred for 2 h, in which time a white precipitate formed. The mixture was cooled to −78 °C, and PPh_2Cl (0.892 ml, 4.97 mmol) was added drop-wise. The mixture was then allowed to warm to ambient temperature and stirred for 2 h. The reaction mixture was filtered through alumina and the solvent removed in vacuo to leave a colourless oil, which solidified over a period of 1 h in vacuo to give 1.48 g (91%) of **1d** as a white, air-sensitive powder. ^{1}H NMR ($CDCl_3$): δ 7.57–6.64 (m, 14H, H4–7 and Ph), 4.33 (s, 1H, H1), 1.98 (s, 3H, CH_3(3)), 1.89 (s, 3H, CH_3(2)). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 146.4 (s, C3a), 142.9 (s, C7a), 138.2 (d, $^3J = 6$ Hz, C3) 137.0 (d, $^1J = 18$ Hz, *i*-Ph), 134.1 (d, $^2J = 20$ Hz, *o*-Ph), 134.1 (d, $^1J = 18$ Hz, *i*-Ph), 133.5 (d, $^2J = 4$ Hz, C2), 132.8 (d, $^2J = 20$ Hz, *o*-Ph), 129.1 (s, *p*-Ph), 128.4 (s, *p*-Ph), 128.2 (d, $^3J = 6$ Hz, *m*-Ph), 127.6 (d, $^3J = 7$ Hz, *m*-Ph), 126.2 (s, C6), 123.22 (s, C5), 123.2 (d, $^3J = 3$ Hz, C7), 118.1 (s, C4), 51.7 (d, $^1J = 24$ Hz, C1), 14.1 (d, $^3J = 8$ Hz, CH_3(2)), 10.1 (s, CH_3(3)). ^{31}P {^{1}H} NMR ($CDCl_3$): δ 1.76 (s). Mass spectrum (EI, *m*/*z* (%)): 328 (7, M^+), 201 (100, Ph_2PO^+), 142 (17, $C_9H_4Me_2^+$), 77 (12, Ph^+). HR-MS: M^+ Calc., 328.13809. Found, 328.13708.

4.4. Preparation of 3-(diphenylphosphino)-4,7-dimethylindene (*1e*)

4,7-Dimethylindene (2.00 g, 13.9 mmol) in diethyl ether (100 ml) was cooled to −78 °C and BuLi (8.7 ml of 1.6 M, 13.9 mmol) was added. After stirring at ambient temperature for 3 h, the solution was cooled to −78 °C and PPh_2Cl (2.4 ml, 13.9 mmol) was added. The solution was then stirred overnight at ambient temperature, filtered through a short alumina column and the solvent removed in vacuo to give **1e** (4.10 g, 90%) as a white powder. ^{1}H NMR ($CDCl_3$): δ 7.4 (m, 10H, Ph*H*), 6.93 (s, 2H, H5 and H6), 5.94 (dt, $^3J_{HP} = 2$ Hz, $^3J_{HH} = 3$ Hz, 1H, H2), 3.29 (dd, $^4J_{HP} = 3$ Hz, $^3J_{HH} = 3$ Hz, 2H, CH_2), 2.42 (s, 3H, C4–Me), 2.32 (s, 3H, C7–Me). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 143.77 (d, $^3J = 5$ Hz, C7a), 143.58 (d, $^1J = 20$ Hz, C3), 143.09 (d, $^2J = 20$ Hz, C3a), 141.96 (s, C2), 136.95 (d, $^1J = 19$ Hz, *i*-Ph), 134.00 (d, $^2J = 20$ Hz, *o*-Ph), 130.28 (s, C7), 129.79 (d, $^3J = 3$ Hz, C4), 129.31 (s, C5 or C6), 128.76 (s, *p*-Ph), 128.49 (d, $^3J = 7$ Hz, *m*-Ph), 126.29 (s, C5 or C6), 38.61 (d, $^3J = 2$ Hz, C1), 20.64 (d, $^4J = 16$ Hz, C4–Me), 18.45 (s, C7–Me). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −16.9. Anal. Calc. for $C_{23}H_{21}P$: C, 84.12; H, 6.45. Found: C, 80.40; H, 6.36%. Mass spectrum: (EI, *m*/*z* (%)): 328 (100, M^+), 185 (82, Ph_2P^+), 143 (32, $Me_2C_9H_5^+$). HR-MS: M^+ Calc., 328.13809. Found, 328.13781.

4.5. Preparation of 1-(diphenylphosphino)-3,4,7-trimethylindene (*1f*)

To a solution of 1,4,7-trimethylindene (1.624 g, 10.76 mmol) in diethyl ether (50 ml) at −78 °C was added *n*-BuLi (6.41 ml, 1.6 M, 10.76 mmol). The solution was allowed to warm to ambient temperature and stirred for 2 h, in which time a white precipitate formed. The mixture was cooled to −78 °C, and PPh_2Cl (1.84 ml, 10.76 mmol) was added drop-wise. The mixture was allowed to warm to ambient temperature and stirred for 2 h. The reaction mixture was then filtered through alumina and the solvent was removed in vacuo to leave a colourless oily residue. The residue was washed with petroleum ether (2 × 25 ml) to give 2.28 g (62%) of **1f** as a white, air-sensitive powder. ^{1}H NMR ($CDCl_3$): δ 7.61–6.81 (m, 12H, H5, H6 and Ph), 6.08 (s, 1H, H2), 4.44 (s, 1H, H1), 2.61 (s, 3H, CH_3(4/7)), 2.27 (s, 3H, CH_3(4/7)), 1.96 (s, 3H, CH_3(3)). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 143.1 (d, $^2J = 6$ Hz, C7a), 142.6 (d, $^3J = 3$ Hz, C3), 141.3 (s, C3a), 138.3 (d, $^1J = 20$ Hz, *i*-Ph), 134.4 (d, $^2J = 20$ Hz, *o*-Ph) 133.4 (d, $^1J = 19$ Hz, *i*-Ph), 132.0 (d, $^2J = 16$ Hz, *o*-Ph), 130.8 (d, $^3J = 4$ Hz, C7), 130.3 (d, $^2J = 5$ Hz, C2), 129.1 (d, $^4J = 2$ Hz, C6), 128.6 (s, *p*-Ph), 128.4 (d, $^3J = 4$ Hz, *m*-Ph), 128.3 (s, C4), 127.7 (s, *p*-Ph), 126.5 (d, $^3J = 7$ Hz, *m*-Ph), 126.3 (d, ^{5}J = 2 Hz, C5), 46.3 (d, $^1J = 25$ Hz, C1), 19.5 (d, $^4J = 13$ Hz, CH_3(7)), 19.3 (s, CH_3(4)), 17.0 (s, CH_3(3)). ^{31}P {^{1}H} NMR ($CDCl_3$): δ −1.71 (s). Mass spectrum (EI, *m*/*z* (%)): 342 (15, M^+), 201 (100, Ph_2PO^+), 157 (39, $C_9H_4Me_3^+$), 142 (13, $C_9H_4Me_2^+$), 77 (14, Ph^+). HR-MS: M^+ Calc., 342.15374. Found, 342.15430.

4.6. Preparation of 3-(diphenylphosphino)-1-(trimethylsilyl)indene (*1h*)

To a solution of the phosphinoindene **1a** (1.027 g, 3.42 mmol) in diethylether (40 ml) at −78 °C was added *n*-BuLi (2.13 ml, 1.6 M, 3.42 mmol). The solution was allowed to warm to ambient temperature and stirred for 3 h. The mixture was then cooled to −78 °C, and Me_3SiCl (0.43 ml, 3.42 mmol) was added dropwise. The mixture was allowed to warm to ambient temperature, stirred for 2 h, and then filtered through Celite. The solvent was removed in vacuo to give an orange oily residue that was dissolved in petroleum ether (25 ml) and filtered to give an orange solution. Removal of solvent in vacuo yielded 0.97 g (76%) of **1h** as an orange air-sensitive oil. ^{1}H NMR ($CDCl_3$): δ 7.47–7.13 (m, 14H, H4–7 and Ph), 6.39 (dd, $^3J_{HH} = 2$ Hz, $^3J_{PH} = 4$ Hz, 1H, H2), 3.61 (d, $^3J_{HH} = 2$ Hz, 1H, H1), −0.52 (s, 9H, Si(CH_3)$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 146.1 (d, $^3J = 5$ Hz, C7a), 144.8 (d, $^1J = 18$ Hz, C3), 144.4 (d, $^2J = 4$ Hz, C2), 137.2 (d, $^2J = 11$ Hz, C3a), 136.6 (d, $^1J = 9$ Hz, *i*-Ph), 136.0 (d, $^1J = 9$ Hz, *i*-Ph), 133.8 (d, $^2J = 20$ Hz, *o*-Ph), 133.3 (d, $^2J = 19$ Hz, *o*-Ph), 128.7 (s, *p*-Ph), 128.4 (s, *p*-Ph), 128.3 (d, $^3J = 7$ Hz, *m*-Ph), 128.2 (d, $^3J = 7$ Hz, *m*-Ph), 124.7 (s, C5), 124.0 (s, C6), 122.6 (s, C7), 121.4 (d, $^3J = 4$ Hz, C4), 47.9 (d, $^3J = 4$ Hz, C1), −2.3 (s, Si(CH_3)$_3$). ^{31}P {^{1}H} NMR ($CDCl_3$): δ −21.54 (s). Mass spectrum: (EI, *m*/*z* (%)): 372 (6, M^+), 300 (85,

M^+–$SiMe_3$), 186 (20, $C_9H_5SiMe_3^+$), 185 (100, Ph_2P^+), 115 (15, $C_9H_7^+$), 73 (23, $SiMe_3^+$). HR-MS: M^+ Calc., 372.14632. Found, 372.14548.

4.7. Preparation of 3-(diisopropylphosphino)indene (*1i*)

Indene (1.5 ml, 12.9 mmol) in diethyl ether (30 ml) was cooled to −78 °C and BuLi (8.0 ml of 1.6 M, 12.9 mmol) was added. After stirring at ambient temperature for 3 h, the solution was cooled to −78 °C and P^iPr_2Cl (2.05 ml, 12.9 mmol) was added. The solution was then stirred overnight at ambient temperature, filtered through a short alumina column and the solvent removed in vacuo to give **1i** (5.54 g, 94%) as a yellow oil. ^1H NMR ($CDCl_3$): δ 7.64 (d, $^3J_{HH} = 8$ Hz, 1H, H4), 7.45 (d, $^3J_{HH} = 7$ Hz, 1H, H7), 7.27 (dd, $^3J_{HH} = 8$ Hz, $^3J_{HH} = 8$ Hz, 1H, H5), 7.18 (dd, $^3J_{HH} = 7$ Hz, $^3J_{HH} = 7$ Hz, 1H, H6), 6.71 (dt, $^3J_{HP} = 4$ Hz, $^3J_{HH} = 2$ Hz, 1H, H2), 3.52 (s, 2H, CH_2), 2.25 (qqd, $^3J_{HH} = 7$ Hz, $^3J_{HH} = 7$ Hz, $^2J_{HP} = 3$ Hz, 2H, C*H* Me_2), 1.13 (dd, $^3J_{HP} = 15$ Hz, $^3J_{HH} = 7$ Hz, 6H, Me), 1.02 (dd, $^3J_{HP} = 12$ Hz, $^3J_{HH} = 7$ Hz, 6H, Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 147.71 (d, $^1J = 18$ Hz, C3), 143.85 (d, $^3J = 4$ Hz, C7a), 141.47 (d, $^2J = 6$ Hz, C2), 139.07 (d, $^2J = 21$ Hz, C3a), 126.01 (s, C6), 124.57 (s, C5), 123.49 (s, C7), 121.35 (d, $^3J = 6$ Hz, C4), 39.76 (d, $^3J = 4$ Hz, CH_2), 22.49 (d, $^2J = 10$ Hz, Me), 20.32 (d, $^1J = 17$ Hz, *C*HMe_2), 19.29 (d, $^2J = 9$ Hz, Me). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −9.22. Microanalysis not attempted due to the oily nature of the material.

4.8. Preparation of rac-bis(1-(diphenylphosphino)-η^5-indenyl)iron(II) (*rac*-*2a*)

To a solution of indene **1a** (1.8 g, 6.0 mmol) in THF (50 ml) at −78 °C was added a solution of *n*-BuLi (3.75 ml, 1.6 M, 6.0 mmol). After 2 h, $FeCl_2$ (0.38 g, 3 mmol) was added and the reaction mixture stirred was stirred for 12 h at ambient temperature. The solvent was removed in vacuo and the residue was loaded onto a Celite column and washed with diethyl ether (to remove unreacted **1a**). Subsequent elution with dichloromethane yielded 1.26 g (64%) of *rac*-**2a** as a dark blue powder. Dark blue crystallographic-quality crystals were obtained by recrystallization from CH_2Cl_2/diethyl ether. ^1H NMR ($CDCl_3$): δ 7.4–6.4 (m, 28H, H4–7 and Ph), 4.92 (d, $^3J_{HH} = 2$ Hz, 2H, H3), 3.07 (d, $^3J_{HH} = 2$ Hz, 2H, H2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 139.8 (d, $^1J = 10$ Hz, *i*-Ph), 136.7 (d, $^1J = 7$ Hz, *i*-Ph), 135.2 (d, $^2J = 22$ Hz, *o*-Ph), 131.7 (d, $^2J = 18$ Hz, *o*-Ph), 129.3 (s, *p*-Ph), 128.3 (d, $^3J = 8$ Hz, *m*-Ph), 128.0 (d, $^3J = 5$ Hz, *m*-Ph), 127.6 (s, *p*-Ph), 124.1 (d, $^3J = 9$ Hz, C7), 123.6 (s, C4), 122.9 (s, C6), 122.5 (s, C5), 91.0 (d, $^2J = 25$ Hz, C7a), 90.3 (d, $^3J = 4$ Hz, C3a), 72.0 (d, $^2J = 4$ Hz, C2), 68.1 (d, $^1J = 9$ Hz, C1), 66.1 (d, $^3J = 4$ Hz, C3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −22.26 (s).

4.9. Preparation of rac- and meso-bis(1-(diphenylphosphino)-η^5-indenyl)iron(II) mixture

Same procedure as for the preparation of *rac*-**2a**, except that the reaction solution is stirred for only 2 h before the solvent is removed in vacuo. The product contains a mixture of the *rac* and *meso* isomers in approximately a 1:1 ratio. Yields obtained for mixtures do not vary significantly from that obtained for the *rac* isomer. Data for *meso*-**2a**: ^1H NMR ($CDCl_3$): δ 7.53–6.88 (m, 28H, H4–7 and Ph), 3.81 (d, $^3J_{HH} = 2$ Hz, 2H, H3), 3.48 (d, $^3J_{HH} = 2$ Hz, 2H, H2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 139.1 (d, $^1J = 14$ Hz, *i*-Ph), 137.4 (d, $^1J = 11$ Hz, *i*-Ph), 135.4 (d, $^2J = 21$ Hz, *o*-Ph), 132.4 (d, $^2J = 20$ Hz, *o*-Ph), 129.0 (s, *p*-Ph), 128.2 (d, $^3J = 8$ Hz, *m*-Ph), 128.1 (d, $^3J = 10$ Hz, C7), 128.0 (d, $^3J = 3$ Hz, *m*-Ph), 127.9 (s, C4), 127.7 (s, *p*-Ph), 124.9 (s, C6), 124.3 (s, C5), 91.6 (d, $^2J = 22$ Hz, C7a), 90.3 (s, C3a), 74.5 (s, C2), 66.9 (d, $^1J = 13$ Hz, C1), 64.4 (s, C3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −26.53 (s).

4.10. Preparation of bis(1-(diphenylphosphino)-3-methyl-η^5-indenyl)iron(II) (*2b*)

To a solution of indene **1b** (0.352 g, 1.12 mmol) in THF (40 ml) at −78 °C was added a solution of *n*-BuLi (0.70 ml, 1.6 M, 1.12 mmol). After 3 h at ambient temperature, $FeCl_2$ (0.07 g, 0.56 mmol) was added and the reaction mixture stirred for 2 h to give two product peaks in a 3:1 ratio at −24.50 and −26.25 ppm, respectively, corresponding to the *rac* isomer and, presumably, the *meso* isomer, respectively. The ratio of products did not change after stirring overnight. The solvent was removed in vacuo and the residue was loaded onto a Celite column and washed with dichloromethane. Removal of the solvent in vacuo yielded a dark green powder containing both isomers (^{31}P NMR $CDCl_3$: δ −24.69 (*rac*), −26.35 (*meso*)) as well as free ligand and its oxide. Recrystallization from diethyl ether gave 0.16 g (43%) of *rac*-**2b** as a green powder. ^1H NMR ($CDCl_3$): δ 7.44–6.38 (m, 28H, H4–7 and Ph), 3.61 (s, 2H, H2), 2.38 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 139.2 (d, $^1J = 12$ Hz, *i*-Ph), 136.7 (d, $^1J = 10$ Hz, *i*-Ph), 134.9 (d, $^2J = 21$ Hz, *o*-Ph), 132.5 (d, $^2J = 19$ Hz, *o*-Ph), 129.1 (s, *p*-Ph), 128.2 (d, $^3J = 8$ Hz, *m*-Ph), 127.9 (d, $^3J = 6$ Hz, *m*-Ph), 127.7 (s, *p*-Ph), 127.1 (d, $^3J = 7$ Hz, C7), 123.4 (s, C4), 123.1 (s, C6), 121.2 (s, C5), 89.3 (d, $^2J = 19$ Hz, C7a), 89.1 (d, $^3J = 4$ Hz, C3a), 78.1 (s, C3), 74.5 (s, C2), 65.7 (d, $^1J = 11$ Hz, C1), 11.8 (d, $^4J = 9$ Hz, Me). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −24.69 (s). Anal. Calc. for $C_{44}H_{36}P_2Fe$: C, 77.42; H, 5.32. Found: C, 75.65; H, 5.55. Mass spectrum: (EI, *m*/*z* (%)): 682 (27, M^+), 312 (100, $MeC_9H_6PPh_2^+$), 185 (64, Ph_2P^+), 128 (18, $MeC_9H_6^+$), 108 (19, PhP^+). HR-MS: M^+ Calc., 682.16413. Found, 682.16511.

4.11. Preparation of bis(1-(diphenylphosphino)-2-methyl-η^5-indenyl)iron(II) (**2c**)

Indene **1c** (1.016 g, 3.2 mmol) was dissolved in THF (45 ml), cooled to −78 °C, and BuLi (2.0 ml, 1.6 M, 3.2 mmol) was added and the solution stirred for 2 h. $FeCl_2$ (0.204 g, 1.6 mmol) was then added and the reaction mixture stirred overnight to give two products, as observed by ^{31}P NMR with peaks at −17.41 and −19.68 ppm in a 1.0:1.4 ratio. This ratio did not change after stirring at ambient temperature for 3 days. The solvent was removed in vacuo and the solid redissolved in CH_2Cl_2 and filtered down a Celite column. The solvent was removed in vacuo to give a green-brown powder containing both isomers and free ligand. The major isomer was obtained as a green powder (0.614 g, 55%) in a pure form by filtration down a Celite column with diethyl ether and precipitation, after concentration, by addition of petroleum ether.

Major isomer of **2c**, probably *meso*: ^1H NMR ($CDCl_3$): δ 7.80 (m, 2H, p-Ph), 7.68 (d, $^3J_{HH} = 9$ Hz, H4), 7.46 (m, Ph), 7.2–7.0 (m, Ph and H5), 6.72 (dd, $^3J_{HH} = 6$, 8 Hz, H6), 6.41 (d, $^3J_{HH} = 9$ Hz, H7), 4.84 (s, H3), 0.77 (s, Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 137.16 (d, $^1J = 11$ Hz, *i*-Ph), 137.06 (d, $^1J = 11$ Hz, *i*-Ph), 134.97 (d, $^2J = 20$ Hz, *o*-Ph), 133.40 (d, $^2J = 20$ Hz, *o*-Ph), 128.93 (s, *p*-Ph), 128.5–128.0 (*m*-Ph, *p*-Ph, C4 and C7), 124.63 (s, C6), 124.23 (s, C5), 90.20 (d, $^2J = 22$ Hz, C7a), 88.46 (s, C3a), 87.44 (s, C2), 66.36 (s, C3), 65.50 (d, $^1J = 15$ Hz, C1), 9.36 (d, $^3J = 11$ Hz, Me). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −20.04 (s). $C_{44}H_{36}P_2Fe$: Calc.: C, 77.43; H, 5.32. Exptl: C, 76.19; H, 5.33. Mass spectrum: (EI, *m/z* (%)): 682 (40, M^+), 314 (100, $MeC_9H_6PPh_2^+$), 185 (83, Ph_2P^+), 128 (25, $MeC_9H_6^+$), 108 (15, PhP^+). HR-MS: M^+ Calc., 682.16413. Found, 682.16475.

Minor isomer of **2c**, probably *rac*: ^1H NMR ($CDCl_3$): δ 7.9–6.4 (aromatic), 5.08 (s, 2H, H3), 1.86 (s, 6H, Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 134.7 (d, $^2J = 20$ Hz, *o*-Ph), 133.7 (d, $^2J = 20$ Hz, *o*-Ph), 128.8 (s, *p*-Ph), 121.7 (s, C6), 121.2 (s, C5), 87.9 (s, C3a), 86.9 (s, C2), 68.6 (s, C3), 13.3 (d, $^3J = 10$ Hz, Me). Signals for C1, C4, C7, C7a, *i*-Ph, and *meta*-Ph were not resolved from those of the major isomer. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −17.60 (s).

4.12. Preparation of bis(1-(diphenylphosphino)-2,3-dimethyl-η^5-indenyl)iron(II) (**2d**)

To a solution of indene **1d** (0.867 g, 2.64 mmol) in THF (40 ml) at −78 °C was added a solution of *n*-BuLi (1.65 ml, 1.6 M, 2.64 mmol). After warming to ambient temperature and stirring for 2 h, $FeCl_2$ (0.167 g, 1.32 mmol) was added and the reaction mixture was stirred for a further 2 h to give a 2:5 ratio of two isomers (−23.3 and −23.7 ppm in the ^{31}P NMR spectrum). Stirring of the reaction solution for an additional 18 h gave no change of the isomer ratio. The solvent was removed in vacuo and the residue was loaded onto a Celite column and washed with petroleum ether (to remove unreacted **1d**). Subsequent washing with CH_2Cl_2, followed by removal of solvent in vacuo, yielded **2d** (0.392 g, 42%) as a green powder. The product was obtained as a 2:5 mixture of diastereomers. Recrystallization from diethyl ether gave a few purple crystals that X-ray crystallography showed to be the *rac* isomer. There was insufficient sample to unambiguously identify the isomers in the NMR spectra. The high sensitivity of the material to hydrolysis precluded good microanalytical results.

Major isomer of **2d**: ^1H NMR ($CDCl_3$): δ 7.68–6.38 (m, 28H, H4–7 and Ph), 1.96 (s, 6H, C3–Me), 1.50 (s, 6H, C2–Me), $^{13}C\{^1H\}$ NMR (C_6D_6): δ 138.5 (d, $^1J = 12$ Hz, *ipso*-Ph), 137.1 (d, $^1J = 11$ Hz, *ipso*-Ph), 135.9 (d, $^2J = 21$ Hz, *o*-Ph), 134.0 (d, $^2J = 19$ Hz, *o*-Ph), 129.0–127.2 (m, C7, *m*-Ph and *p*-Ph), 125.6 (s, C4), 123.5 (s, C6), 122.8 (s, C5), 88.8–88.1 (m, C3a and C7a), 86.0 (s, C2), 75.6 (s, C3), 67.2 (d, $^1J = 12$ Hz, C1), 11.2 (s, C3–Me), 8.5 (s, C2–Me). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −23.81 (s). Mass spectrum: (EI, *m/z* (%)): 710 (10, M^+), 525 (5, $[M–PPh_2]^+$), 326 (100, $Me_2C_9H_4PPh_2^+$).

Minor isomer of **2d**: ^1H NMR ($CDCl_3$): δ 2.16 (s, 6H, C3–Me), 1.34 (s, 6H, C2–Me). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −23.21 (s).

4.13. Preparation of bis(1-(diphenylphosphino)-4,7-dimethyl-η^5-indenyl)iron(II) (**2e**)

Indene **1e** (1.38 g, 4.2 mmol) was dissolved in THF (40 ml), cooled to −78 °C, and BuLi (2.6 ml, 1.6 M, 4.2 mmol) added. The solution was then stirred for 2 h. $FeCl_2$ (0.27 g, 2.1 mmol) was added and the mixture stirred for 2 h to give two product peaks in the ^{31}P NMR spectrum at δ −16.46 and −21.47 in a 1:1 ratio. The solvent was removed in vacuo. The solid was redissolved in diethyl ether and filtered down a Celite column. The mauve solution was concentrated and cooled to afford the desired product **2e** (1.11 g, 73%) as dark red crystals. Although the crystals appeared to be identical, NMR of separate samples of crystals gave varying ratios of the *rac* and *meso* isomers. Random choosing of crystals eventually allowed us to obtain X-ray structures of both isomers. $C_{46}H_{40}P_2Fe$: Calc.: C, 77.78; H, 5.68. Exptl: C, 77.63; H, 5.88.

Rac-**2e**: ^1H NMR ($CDCl_3$): δ 7.5–6.7 (m, aromatic Hs), 6.45 (s, H5 and H6), 5.31 (d, $^3J_{HH} = 2$ Hz, H3), 3.13 (d, $^3J_{HH} = 2$ Hz, H2), 2.35 (s, Me), 2.10 (s, Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 140.71 (d, $^1J = 13$ Hz, *i*-Ph), 136.82 (d, $^1J = 10$ Hz, *i*-Ph), 135.22 (d, $^2J = 22$ Hz, *o*-Ph), 132.09 (d, $^3J = 3$ Hz, C7), 131.88 (d, $^2J = 18$, *o*-Ph), 129.41 (s, C4), 129.39 (s, *p*-Ph), 128.1–128.0 (*m*-Ph), 127.64 (s, *p*-Ph), 122.50 (s, C6), 120.60 (s, C5), 93.06 (d, $^3J = 4$ Hz, C3a), 91.35 (d, $^2J = 18$ Hz, C7a), 71.79 (d, $^2J = 5$ Hz, C2), 69.32 (d, $^1J = 14$ Hz, C1), 65.22 (d, $^3J = 6$ Hz, C3),

22.34 (d, $^4J = 20$ Hz, Me(7)), 19.03 (s, Me(4)). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −16.86 (s).

Meso-**2e**: ^1H NMR ($CDCl_3$): δ 7.5–6.7 (m, aromatic H, H5 and H6), 4.02, (d, $^3J_{HH} = 3$ Hz, H3), 3.85 (d, $^3J_{HH} = 3$ Hz, H2), 2.32 (s, Me), 2.14 (s, Me). $^{13}C\{^1H\}$($CDCl_3$): δ 141.10 (d, $^1J = 15$ Hz, *i*-Ph), 137.73 (d, $^1J = 13$ Hz, *i*-Ph), 136.41 (d, $^3J = 2$ Hz, C7), 136.38 (d, $^2J = 22$ Hz, *o*-Ph), 134.32 (s, C4), 131.73 (d, $^2J = 18$ Hz, *o*-Ph), 129.25 (s, *p*-Ph), 128.1–128.0 (*m*-Ph), 127.47 (s, *p*-Ph), 124.27 (s, C6), 122.93 (s, C5), 92.68 (d, $^3J = 3$ Hz, C3a), 90.50 (d, $^2J = 15$ Hz, C7a), 73.78 (d, $^2J = 3$ Hz, C2), 68.28 (d, $^1J = 18$ Hz, C1), 63.42 (s, C3), 22.78 (d, $^4J = 17$ Hz, Me(7)), 19.45 (s, Me(4)). $^{31}P\{^1H\}$($CDCl_3$): δ −22.17 (s).

4.14. Attempted preparation of bis(1-(diphenylphosphino)-3,4,7-trimethyl-η^5-indenyl)iron(II) (**2f**)

Numerous attempts were made to prepare this ferrocene using similar routes used to make the other ferrocenes, however, ^{31}P NMR of the brown product solutions showed mostly free ligand with only some minor peaks in the −20 ppm region.

4.15. Preparation of bis(1-(diphenylphosphino)-3-(trimethylsilyl)-η^5-indenyl)iron(II) (**2h**)

To a solution of indene **1h** (0.803 g, 2.16 mmol) in THF (35 ml) at −78 °C was added a solution of *n*-BuLi (1.35 ml, 1.6 M, 2.16 mmol). After warming to ambient temperature and stirring for 5 h, $FeCl_2$ (0.137 g, 1.08 mmol) was added and the reaction mixture stirred for a further 2 h to give two product isomers in a 3:2 ratio (−25.3 and −27.3 ppm in the ^{31}P NMR spectrum). The solvent was removed in vacuo and the green, oily residue loaded onto an alumina column. Elution, in the first instance with petroleum ether, followed by subsequent elution with 1:1 CH_2Cl_2/petroleum ether yielded a green oily residue, which contains both **1a**, resulting from loss of $SiMe_3$, and **2h**. The residue was dissolved in petroleum ether, filtered, and the solvent removed in vacuo to yield **2h** (0.23 g, 31%) as a green solid containing only the isomer with the upfield chemical shift. Stirring the reaction solution overnight only gave decomposition products. The product proved too unstable for microanalysis or mass spectroscopy.

^1H NMR ($CDCl_3$): δ 7.54–6.77 (m, 28H, H4–7 and Ph), 3.84 (s, 2H, H2), 0.23 (s, 18H, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 138.9 (d, $^1J = 15$ Hz, *ipso*- Ph), 137.5 (d, $^1J = 14$ Hz, *ipso*-Ph), 135.4 (d, $^2J = 20$ Hz, *o*-Ph), 132.9 (d, $^2J = 21$ Hz, *o*-Ph), 129.3 (s, *p*-Ph), 128.9–127.5 (m, C7, *m*-Ph and *p*-Ph), 124.8 (s, C4), 124.2 (s, C6), 123.8 (s, C5), 94.1 (s, C3a), 92.7 (d, $^2J = 16$ Hz, C7a), 78.7 (s, C2), 70.8 (d, $^1J = 13$ Hz, C1), 64.6 (s, C3), 0.8 (s, Me). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −28.49 (br, s).

4.16. Preparation of bis(1-(diisopropylphosphino)-η^5-indenyl)iron(II) (**2i**)

Indene **1i** (0.833 g, 3.6 mmol) was dissolved in THF (40 ml) and cooled to −78 °C. BuLi (2.2 ml, 1.6 M, 3.6 mmol) was then added and the solution stirred for 2 h. Ferrous chloride (0.23 g, 1.8 mmol) was then added and the reaction mixture stirred for 30 min to give a dark green solution. The solvent was removed in vacuo and the resulting black oily solid redissolved in CH_2Cl_2 and filtered down a Celite column. The product was a black oil and no yield was able to be calculated. Due to the extreme sensitivity of this product no ^1H, ^{13}C NMR spectra or microanalytical data were collected. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −3.27 (*rac*), −8.89 (*meso*).

4.17. Preparation of {4,7-dimethyl-1-(diphenylphosphino)-η^5-indenyl}{1-(diphenylphosphino)-η^5-indenyl}iron(II) (**2j**)

To a solution of **1a** (0.335 g, 1.12 mmol) and **1e** (0.366 g, 1.12 mmol) in THF (35 ml) at −78 °C was added a solution of *n*-BuLi (1.40 ml, 1.6 M, 2.24 mmol). After 2 h, $FeCl_2$ (0.142 g, 1.12 mmol) was added and the reaction mixture stirred for 2 h at ambient temperature. ^{31}P NMR indicates the presence of ten unique phosphorous environments (one peak for each of the free ligands in addition to eight signals arising from the ferrocenes: two for each of *rac*- and *meso*-**2j** and one for each of *rac*- and *meso*-**2a** as well as *rac*- and *meso*-**2e**). The solution was stirred for a further 24 h, before the solvent was removed in vacuo. The residue was dissolved in CH_2Cl_2 (20 ml) and filtered through Celite. Removal of the solvent in vacuo yielded a black powder (0.64 g) that was shown to contain, by ^{31}P NMR, a mixture of *rac*- and *meso*-**2j**, *rac*- and *meso*-**2e**, and *rac*-**2a** in a ratio of 4:3:1:2:1. All of the *meso*-**2a** had isomerized to *rac*-**2a**, but after that there was no other significant variation in these ratios with stirring of the mixture in THF for 3 days. An EI mass spectrum of the mixture showed a parent-ion peak for the mixed ferrocene **2j** at 682 *m/z*.

Rac-**2j**: ^1H NMR ($CDCl_3$): δ 5.34 (s, 1H, H3 (**1e**)), 4.98 (s, 1H, H3 (**1a**)), 3.27 (s, 1H, H2 (**1e**)), 3.11 (s, 1H, H2 (**1a**)). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −16.81 (s, **1e**), −22.20 (s, **1a**).

Meso-**2j**: ^1H NMR ($CDCl_3$): δ 4.07 (s, 1H, H3 (**1e**)), 3.90 (s, 1H, H2 (**1e**)), 3.85 (s, 1H, H3(**1a**)), 3.55 (s, 1H, H2 (**1a**)). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −23.9 (s, **1e**), −25.61 (s, **1a**).

4.18. X-ray structure determinations for rac-**2a**, rac-**2b**, rac-**2d**, rac-**2e** and meso-**2e**

Crystal data and experimental details are given in Table 2. For each compound, a crystal was attached to a thin glass fiber and mounted on a Siemens P4 SMART

diffractometer with a Siemens CCD area detector. Multi-scan absorption corrections were determined with SADABS and applied to the data [24]. Data processing was undertaken with SAINT [24] and the structures were solved by direct methods and refined by least-squares methods on F^2 using the SHELXTL program library [25]. Hydrogen atoms were placed in their calculated positions and refined isotropically riding with the atoms to which they are bonded. Non-hydrogen atoms were refined anisotropically, except for *rac*-**2d** for which they were refined isotropically.

5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre: CCDC No. 229441 for *rac*-**2a**; CCDC No. 229345 for *rac*-**2b**; CCDC No. 229346 for *rac*-**2d**; CCDC No. 229343 for *rac*-**2e**; and CCDC No. 229344 for *meso*-**2e**. Copies of the information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK. Fax: +44-1223-336-033 or by Email at deposit@ccdc.cam.ac.uk or from the www at http://www.ccdc.cam.ac.uk.

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