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Stereospecific Synthesis, Structural Characterisation and Resolution of 2-Phospha[3]ferrocenophane Derivatives – a New Chiral Scaffold

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The first 2-phospha[3]ferrocenophanes containing stereogenic carbon atoms in the three-atom bridge have been synthesised from phenylphosphane by stereospecific ring-closing phosphanation reactions. Either α-substituted 1,1′-bis-(hydroxymethyl)ferrocenes or the corresponding 2-oxa-[3]ferrocenophanes have been used as diastereomerically pure starting materials. The resolution of 1,2,3-triphenyl-[2]phosphaferrocenophane has been achieved by chromatographic separation of the diastereomeric adducts of a chiral cyclopalladate complex. The X-ray crystal structures of two 2-phospha[3]ferrocenophane-borane complexes are also reported.

The emergence of monodentate, bulky, electron-rich phosphanes is a recent, noteworthy issue in the field of organometallic catalysis. Tris(*tert*-butyl)phosphane, biphenyl-(di-*tert*-butyl)- and dicyclohexylphosphane are prototypical compounds of this class. By showing their great potential in palladium-promoted coupling reactions,[1] the pioneering work of Nishiyama, Fu and Buchwald stimulated the active search for new catalytic applications[2] as well as for new ligand structures. Among others, the synthesis and use of ferrocenyl-based phosphanes have been considered, which combine the steric bulk of the organometallic moiety with the electron-donating properties of alkyl and/or ferrocenyl phosphorus substituents.[3] Representative examples are given in Figure 1.

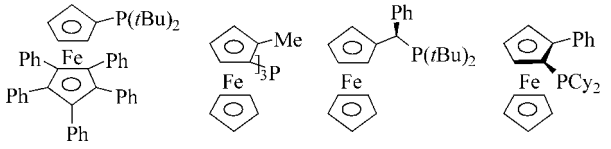
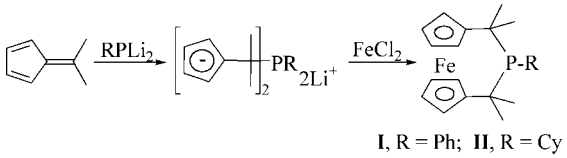


Figure 1. Ferrocenylphosphanes.

An especially attractive and favourable feature of ferrocenylphosphanes for routine bench use is their higher resistance to air oxidation with respect to other ligands with similar bulk and electron-donating ability. This is the basis of, for instance, the impressive development of ferrocenyl-based phosphanes in enantioselective catalysis,[4] and it motivates new studies in these series.

In this context, our purpose is to expand the field of monodentate, electron-rich ferrocenylphosphanes, and especially that of chiral species, to include unprecedented or neglected scaffolds. In most known ferrocenyl phosphanes, a phosphorus function and the cyclopentadienyl ring are either directly bonded or separated by a one-carbon spacer (representative examples of monodentate derivatives are shown in Figure 1). In only a few cases have two[3d,5,6] or three[3c] ferrocene moieties been connected to the same phosphorus atom, and ferrocenophane frameworks bearing phosphorus functions in a carbon-tethering chain are especially uncommon. Thus, ferrocenophane moieties of this series have been selected in this work as target compounds.

It may be interesting to recall here that, among phosphorus-containing ferrocenophanes, 1-phospha[1]ferrocenophanes are moderately stable compounds that have been extensively studied mainly as precursors for high-molecular-weight poly(ferrocenes) by thermal or photochemical ring-opening polymerisation.[7] Similarly, incorporation of phosphorus in the two-atom chain of [2]ferrocenophanes has been used to generate strained starting materials for the synthesis of polymeric materials.[8] On the other hand, three- to five-atom tethers are known to afford stable phosphorus derivatives. Thus, for instance, the synthesis and coordinating properties of a 3-phospha[5]ferrocenophane have been reported.[9] Concerning phosphorus-containing [3]ferrocenophanes, most known compounds have three heteroatom bridges. These include 1,3-distanna-,[10] 1,3-dithia-[11] and 1,3-diaza-2-phospha[3]ferrocenophanes.[12] The first [3]ferrocenophanes where phosphorus is included in a



I, R = Ph; **II**, R = Cy

Scheme 1.

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carbon tether have only recently been isolated from the reaction of 6,6′-dimethylfulvene with, successively, the dilithiated phosphanes $PhPLi_2$ or $CyPLi_2$, and $FeCl_2$ (Scheme 1).[13]

Results and Discussion

Synthesis and Characterisation of 2-Phospha[3]ferrocenophanes

As far as we know, no chiral, enantiomerically pure phosphaferrocenophanes where either phosphorus or phosphorus-containing chains link the two cyclopentadienyl rings are known to date.[14] Thus, in this work, 2-phospha-[3]ferrocenophane derivatives of the general formula **1** (Figure 2), including optically pure compounds, have been targeted as new bulky, rigid and electron-rich phosphanes for use in organometallic catalysis.

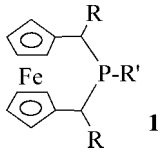

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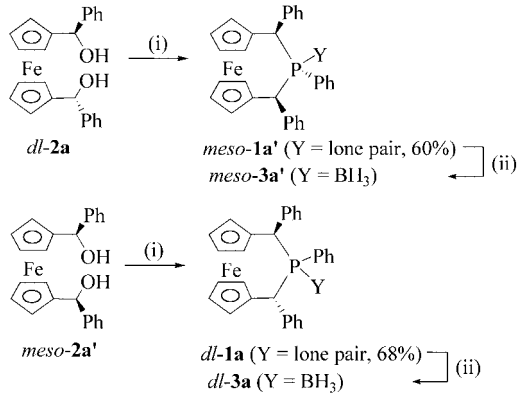
Figure 2. 2-Phospha[3]ferrocenophane derivatives **1**.

A key prerequisite for the synthesis of chiral derivatives is establishing reliable, stereospecific synthetic approaches to the [3]ferrocenophane scaffold; then convenient resolution procedures must be defined. The synthetic approach to 2-phospha[3]ferrocenophane shown in Scheme 1 is unlikely to be applied to the stereoselective synthesis of the targeted phospha[3]ferrocenophanes **1**, given that mixtures of all possible stereoisomers of **1** are expected to form as a result of such a procedure. Thus, alternative approaches that start from preformed, suitably substituted ferrocenes have been considered in this work. Known methods for the formation of P–C bonds from ferrocenylmethyl derivatives have been tested and adapted to the synthesis of the ferrocenophane derivatives **1**.

Since the pioneering work of Kumada and Hayashi, ferrocenylmethyl acetates or the corresponding ammonium salts have been routinely used for the synthesis of (ferrocenylmethyl)phosphanes through reactions with secondary phosphanes.[15] Starting from α-substituted derivatives, these highly stereospecific reactions take place with retention of the carbon configuration, because of the high configurational stability of the intermediate carbocation.

Although the use of primary phosphanes in such reactions has scarcely been reported,[6,16] the method might provide stereospecific access to 2-phospha[3]ferrocenophanes starting from 1,1′-bis(α-acetoxymethyl)ferrocenes. In preliminary experiments, however, the reaction of 1,1′-bis(α-acetoxybenzyl)ferrocene with phenylphosphane in usual experimental conditions (room temp. in acetic acid) afforded only trace amounts of the expected compounds, together with supposedly polymeric, insoluble material. We thus turned our attention to alternative starting materials and found that suitable reactants and conditions for the stereospecific synthesis of **1** must be selected for each of the targeted phosphanes. Especially, the availability of diastereomerically pure starting materials is a key prerequisite for these reactions.

For R = Ph, high-yield, stereospecific synthesis of **1a** and **1a′** has been performed from the *meso* and *dl* diols **2a′** and **2a** respectively, by their reactions with $PhPH_2$ in acetic acid (Scheme 2).



Reagents and conditions: (i) $PhPH_2$, 1 equiv., AcOH, 0°C to r.t. (ii) excess BH_3·THF

Scheme 2.

Diol **2a** can be obtained easily, albeit in an expensive and redundant way, by CBS reduction[17] of the corresponding diketone, 1,1′-dibenzoylferrocene. Alternatively,[18–20] diol **2a** can be obtained from the 1:1 mixture of the *meso* and *dl* diols produced by $NaBH_4$ reduction of 1,1′-dibenzoylferrocene, by repeated crystallisations from ethyl acetate/hexane. The *meso* diol **2a′** was obtained by fractional crystallisation of the *meso*/*dl* (2:1) diastereomeric mixture, which is produced when the same diketone is reduced with $LiAlH_4$ in ether.

The stereochemical course of the reactions of diols **2** with phenylphosphane (Scheme 2) follows the expected pattern: retention of the carbon configuration takes place in the first, intermolecular nucleophilic substitution step, while the intramolecular ring-closing reaction necessarily induces inversion of the carbon configuration. In both steps an iron-stabilised carbocation is formed after departure of the leaving group;[21] however, the entering nucleophiles approach the carbocation once from the face opposite the iron atom and once from the "iron face". Consequently, the *dl* diol **2a** affords the *meso* derivative, *anti*,*anti*-1,3-diphenyl-2-phospha[3]ferrocenophane **1a′**, while the *meso* diol **2a′** selectively affords the *dl* isomer **1a**.

The cyclisation reaction is best performed by adding phenylphosphane to an ice-cooled suspension of diols **2** in acetic acid and then warming the mixture to room temperature. Prolonged stirring of the diol in acetic acid should be avoided, in order to prevent epimerisation.

The [3]ferrocenophanes **1** are air-stable in the solid state and oxidise slowly in solution. These compounds, as well as the corresponding borane complexes **3**, have been fully

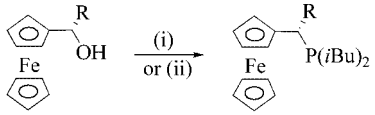
characterised. The crystal structure of the *dl* isomer **3a** has been determined by X-ray diffraction studies (see below). Phosphane **1a**′ and corresponding borane **3a**′ have been assigned as the *anti*,*anti* isomers, based on the small $^2J_{H-P}$ coupling (6.0 Hz) observed for the *CH*Ph protons in the ^{1}H NMR spectrum of **1a**′.[22] This isomer is expected to be the thermodynamically favoured one.

The use of ferrocenylmethyl alcohols as precursors for phosphanes has been rather infrequently reported,[3d,16,23] the alcohols usually being converted into acetates before their reaction with phosphorus nucleophiles. Thus, having ascertained the high stereoselectivity of the reaction between diols **2a** and phenylphosphane in acetic acid, we wondered if the method could also be applied to the stereoselective synthesis of simpler phosphanes, directly from enantiomerically enriched alcohols. As a representative example, the commercially available diisobutylphosphane has been reacted with (*S*)-α-ferrocenylpentan-1-ol **4a**[24] and (*S*)-α-(ferrocenyl)benzyl alcohol **4b**.[25] In both cases the targeted phosphane could be obtained stereoselectively when suitable experimental conditions were applied.

The (α-ferrocenyl-1-pentyl)diisobutylphosphane **5a** is formed with total retention of the carbon configuration when diisobutylphosphane is added to a solution of (*S*)-**4a** in acetic acid at room temperature. However, in the same conditions, the substitution reaction on the α-(ferrocenyl)-benzyl alcohol (*S*)-**4b** induces partial racemisation of the carbon centre. Racemisation can be avoided by immediately adding the phosphane to an ice-cooled suspension of the chiral alcohol **4b** in acetic acid. This procedure avoids prolonged contact of alcohol **4b** with the acidic medium and thus allows a stereospecific substitution reaction to take place with the phosphane.

These results corroborate previous data showing lack of stereochemical control in the substitution reaction between **4b** and imidazoles in acidic medium and almost total retention of the carbon configuration in the analogous substitution on α-ferrocenylethanol at room temperature.[26] On the other hand, however, a stereospecific reaction has been reported by Hu to take place between **4b** and phenylphosphane in acetic acid at room temperature.[3d]

Taken together, the results shown in Scheme 3 and literature data afford additional evidence that the stereochemical course of the substitution reactions on the α-substituted(ferrocenyl) alcohols **4** and most particularly on α-aryl-



(*S*)-**4a** R = Bu (*ee* = 98%)
(*S*)-**4b** R = Ph (*ee* = 94%)
(*S*)-**4b** R = Ph (*ee* = 96%)

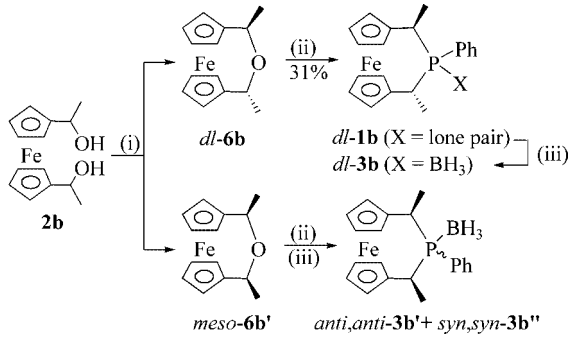
5a R = Bu, 90% yield, *ee* = 98%[(i)]
5b R = Ph, 65% yield, *ee* = 49%[(i)]
5b R = Ph, 86% yield, *ee* = 96%[(ii)]

Reagents and conditions: (i) slow addition of iBu$_2$PH (1 equiv.) to a solution of **4** in AcOH, at r.t. (ii) rapid addition of iBu$_2$PH (1 equiv.) to an ice-cooled suspension of **4** in AcOH.

Scheme 3.

substituted species depends on the nature of the entering nucleophile and/or on the precise experimental procedure, racemisation of the starting alcohol possibly being a competitive side reaction. Experimental conditions can be found where the substitution reaction overcomes the racemisation process induced by the acidic medium and the chiral alcohols **4** can be conveniently converted into the corresponding phosphanes by using nucleophilic phosphorus reagents.

Returning to our main aim, that is, the stereospecific synthesis of 2-phospha[3]ferrocenophanes, we next considered synthetic approaches to phosphanes **1b** (R = Me). In this case, the question arises of the availability of suitable, diastereomerically pure starting materials.[27] It is well known that the diastereomeric mixture of the 1,1′-bis(α-hydroxyethyl)ferrocenes **2b/2b**′ obtained by reduction of 1,1′-diacetylferrocene cannot be separated either by chromatography or by crystallisation. On the other hand, according to Yamakawa and Hisatome,[18] the corresponding diastereomeric 2-oxa[3]ferrocenophanes **6b/6b**′ are easily separable by column chromatography. The cyclic ethers **6**[28] have thus been selected as starting materials for the synthesis of phosphanes **1b**, which have been isolated as their borane complexes **3b**, according to the method shown in Scheme 4.



Reagents and conditions: (i) HCl_{aq}, column chromatography on silica gel. (ii) $PhPH_2$, $BF_3{\cdot}Et_2O$, CH_2Cl_2. (iii) $BH_3{\cdot}THF$

Scheme 4.

Treatment of diol **2b** (1:1 isomeric mixture) with aqueous HCl induces the ring-closure reaction and quantitatively affords the diastereomeric ethers **6**, which are easily separated by column chromatography on silica gel with hexane/ethyl acetate (9:1) as the eluent. The *meso*-**6b**′ isomer was eluted first (R_f = 0.47), followed by the *dl* isomer **6b** (R_f = 0.35).[29]

For the direct conversion of the cyclic ethers **6** into phosphanes, we envisioned a reaction with phenylphosphane in the presence of acid catalysts. Addition of the acid catalyst to the bridging oxygen atom is expected to generate a ferrocene-stabilised carbocation,[30] which should then react with the nucleophilic phosphane to afford a phosphonium salt intermediate. A second, intramolecular, acid-catalysed, nucleophilic substitution between the corresponding phosphane and the residual hydroxy function should then lead to the expected phospha[3]ferrocenophane **1b**. The use of both Brønsted and Lewis acid catalysts (HBF_4, CF_3CO_2H,

$BF_3{\cdot}Et_2O$, $SnCl_4$) has been considered. Boron trifluoride proved to be the best catalyst, affording the desired 2-phospha[3]ferrocenophanes **1b** in about 30% yield. The final phosphane–borane complexes are easily purified by column chromatography, given that the only side-products formed in the reaction are insoluble and probably polymeric.

The substitution reaction takes place with total stereoselectivity with respect to the carbon configuration, through a conceivably double inversion process. A single diastereoisomer is obtained from the *dl* ether **6b**, while a mixture of the *anti*,*anti* and *syn*,*syn* isomers **3b′** and **3b′′** respectively are formed from *meso*-**6b′**.

X-ray Crystal Structures of the Borane Complexes of 2-Phospha[3]ferrocenophane

As compounds **1** and **3** are the first known, stereochemically defined, phosphorus-bridged ferrocenophanes, the molecular structure of one of them, the *dl*-triphenyl-substituted derivative **3a**, has been investigated by X-ray diffraction studies. Suitable single crystals of **3a** were obtained by slow crystallisation from ethyl acetate/hexane. The ORTEP drawing is presented in Figure 3.

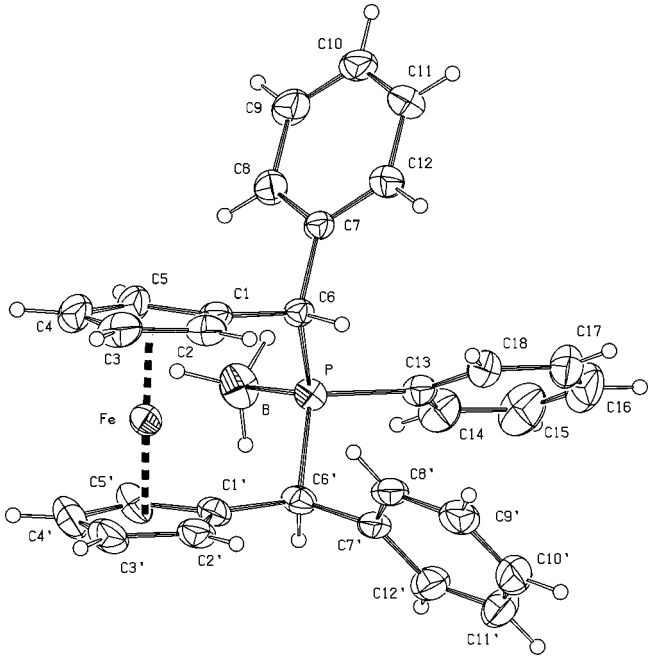


Figure 3. ORTEP drawing of *dl*-**3a**. Displacement ellipsoids are shown at the 30% probability level.

For comparison purposes, the carbon-unsubstituted *P*-phenylferrocenophane **3c** has been prepared from the corresponding oxa[3]ferrocenophane[31] and phenylphosphane (see Experimental Section) and structurally characterised (Figure 4). Comparative bond lengths and angles for compounds **3a** and **3c** are given in Table 1, together with relevant values for compound **I** from ref.[13]

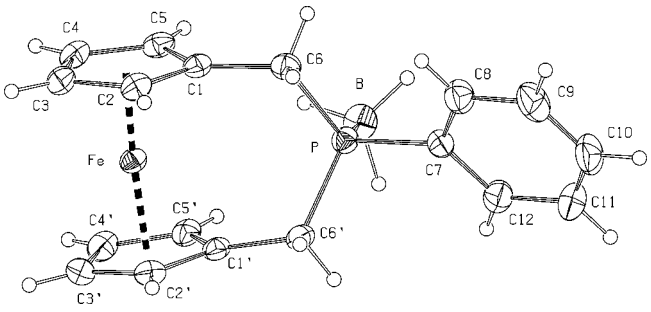


Figure 4. ORTEP view of the 2-phenyl-2-phospha[3]ferrocenophane borane complex **3c**. Displacement ellipsoids are shown at the 30% probability level.

Table 1. Selected bond lengths [Å] and angles [°] for **3a**, **3c** and **I** (see Scheme 1).

	dl-**3a**	**3c**	**I**[13]
P–C6	1.855(2)	1.826(3)	1.899(2)
P–C6′	1.878(2)	1.826(3)	1.900(2)
P–C13 or P–C7	1.813(3)	1.813(3)	1.844(2)
P–B	1.910(3)	1.929(4)	
C1–C6	1.510(3)	1.512(3)	1.516(3)
C1′–C6′	1.515(3)	1.508(3)	1.516(3)
Fe–C1	2.025(2)	2.024(3)	2.034(2)
Fe–C1′	2.016(2)	2.023(2)	2.045(2)
C6–P–C6′	108.28(9)	105.28(13)	109.16(9)
B–P–C13 or C7	110.20(14)	110.57(16)	
C7–C6–P	110.72(14)		118.5(2)
C7′–C6′–P	113.37(14)		104.8(2)

The crystal structures of **3a** and **3c** display roughly the same preferred arrangement and geometrical features as other 2-phospha[3]ferrocenophane derivatives.[13,32]

The Cp rings of **3** and, consequently, the C1–C6 and C1′–C6′ bonds are almost perfectly eclipsed in a synperiplanar conformation. The ferrocenophane scaffold therefore shows a symmetry plane including the iron and phosphorus atoms. This symmetry plane will be lost in **3a** because of the presence of the stereogenic α-carbon atoms. The mean values for the Fe–C distances are identical in the two complexes at 2.035 Å.

In **3a**, the plane of the phenyl ring bonded to C6 forms a dihedral angle of 74.8° with the Cp ring (pseudoaxial position), while the phenyl bonded to C6′ has a dihedral angle of 40.6° with the Cp plane (pseudoequatorial position). The phenyl substituent on phosphorus occupies an *anti* position with respect to the ferrocenyl moiety, which should minimise steric repulsions.

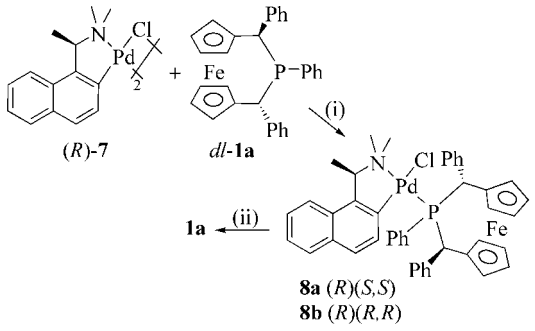
In both phosphane–borane complexes **3**, the cyclopentadienyl rings are slightly tilted toward each other, with dihedral angles of 4.8° and 5.6° for **3a** and **3c** respectively. Moreover, the angles around the phosphorus atom are very close to the expected tetrahedral value (109.5°). This suggests a very low degree of ring strain induced by the three-atom tether.

Resolution of *dl*-1,2,3-Triphenyl-2-phospha[3]ferrocenophane

The final aim of our work is to set up the 2-phospha[3]ferrocenophane unit as a new structural motif for the de-

sign of chiral ligands. Thus, within these first and preliminary studies, the last step has been the search for a suitable resolution procedure for the representative phosphane **1a**. For this resolution process we envisioned the use of *ortho*-palladate derivatives of optically active amines whose versatility as resolving agents for Lewis bases has been largely demonstrated.[33] The choice of the chiral amine auxiliary proved crucial. Attempts to separate diastereomeric palladium complexes derived from either α-methylbenzylamine, *N*,*N*-dimethyl-α-methylbenzylamine or 1-(α-naphthyl)ethylamine were unsuccessful, however better results were obtained with the (*R*)-configured cyclopalladate complex **7**.[34]

The (*R*)-configured cyclopalladate complex **7** was treated with the racemic 1,2,3-triphenyl-2-phospha[3]ferrocenophane *dl*-**1a** to afford a 1:1 mixture of the mononuclear diastereomeric complexes **8a** and **8b** by displacement of the chloride bridge (Scheme 5). Separation of the mixture proved to be straightforward: column chromatography on silica gel with a heptane/ethyl acetate (8:2) mixture as the eluent afforded **8a** and **8b** separately (R_f = 0.5 and 0.3 respectively in heptane/ethyl acetate, 6:4). An X-ray crystal structure of **8a** allowed assignment of the relative configuration of the phospha[3]ferrocene ligand with respect to the known (*R*) configuration of the amine fragment. In complex **8a** the 1,2,3-triphenyl-2-phospha[3]ferrocenophane has an (*S*,*S*) configuration (Figure 5).



Reagents and conditions: (i) acetone, r.t., 2h, chromatographic separation of the diastereomeric complexes **8**; (ii) dppe, CH_2Cl_2, r.t., 3h

Scheme 5.

Compared to the X-ray structures of compounds **3a** and **3c**, the special feature of the ferrocenophane moiety in **8a** is the synclinal staggered conformation of the cyclopentadienyl rings. The dihedral angle between the Cp rings is 11.7°, that is, slightly larger than in the corresponding borane complex **3c**. This distorted conformation may result from steric constraints in the hindered palladium complex.

Decomplexation of phosphane **1a** from **8** was performed according to the standard method, by reaction with the chelating diphosphane dppe, in dichloromethane, followed by separation on a short silica column. The optically active (*S*,*S*)-1,2,3-triphenyl-2-phospha[3]ferrocenophane **1a** obtained from **8a** gave $[a]_D$ = +392 (*c* = 0.2, $CHCl_3$).

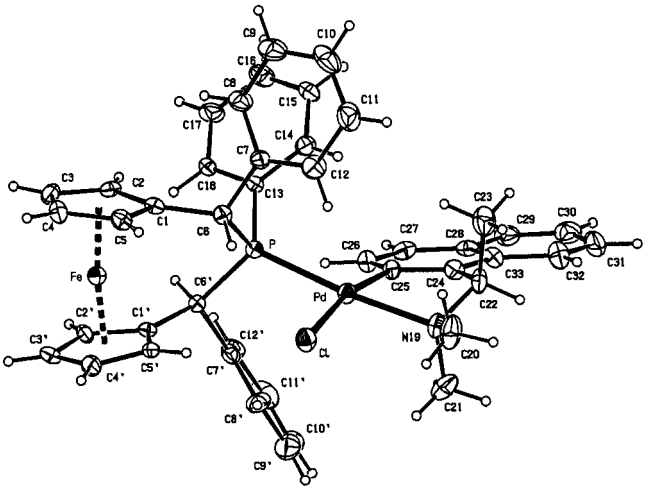


Figure 5. ORTEP view of the cyclopalladate complex **8a**. Displacement ellipsoids are shown at the 30% probability level.

Conclusions

This work demonstrates an unprecedented synthetic approach to the 2-phospha[3]ferrocenophane scaffold, which allows the stereospecific synthesis of α,α′-disubstituted derivatives. Moreover, optical resolution of the 2-phospha[3]-ferrocenophane **1a**, which contains stereogenic carbon atoms in the three-atom bridge, has been performed. These preliminary studies open the way to the development of a new family of phosphorus ligands based on the 2-phospha[3]ferrocenophane unit as a new chiral cyclic scaffold.

Experimental Section

NMR spectra were recorded with Bruker Avance 300 or Avance 500 spectrometers in $CDCl_3$ solutions. Chemical shifts are reported in ppm with reference to the residual solvent peak ($CHCl_3$) for ^1H and ^{13}C. Mass spectra were run on LCT Waters-Micromass (Electrospray) or on a MALDI-TOF Perseptive Biosystem Voyager DE-STR (HRMS). $[a]_D$ values were recorded with a Jasco P-1010 polarimeter at 20 °C. All reactions were carried out under argon.

General Procedure for the Synthesis of the 1,2,3-Triphenyl-2-phospha[3]ferrocenophanes 1a,1a′ and Their Borane Complexes 3a,3a′: The known 1,1′-bis(hydroxybenzyl)ferrocenes **2a** and **2a′** were obtained according to literature methods.[18,19] NMR spectra are in good agreement with those reported previously.[17c,19] ^1H NMR ($CDCl_3$), *dl*-**2a**: δ = 4.17 (s, 2 H), 4.23 (s, 2 H), 4.28 (s, 2 H), 4.29 (2 H, OH), 4.46 (s, 2 H), 5.55 (s, 2 H, CHPh), 7.2–7.3 (10 H, Ph); *meso* **2a′**: δ = 4.12 (s, 2 H), 4.21 (s, 2 H), 4.25 (s, 2 H), 4.29 (2 H, OH), 4.33 (s, 2 H), 5.54 (s, 2 H, CHPh), 7.2–7.4 (10 H, Ph) ppm.

A Schlenk tube was charged with acetic acid (6 mL) and ice-cooled under argon for about 10 min. The 1,1′-bis(hydroxybenzyl)ferrocene **2** (0.2 g, 0.5 mmol) was added at once, followed by addition of phenylphosphane (60 μL, 0.6 mmol). The mixture was warmed slowly to room temperature while stirring for about 1 h. The solvent was removed under vacuum. In order to remove the residual solvents, degassed CH_2Cl_2 was added and removed again under vacuum to afford an orange solid. Starting from the *meso* isomer **2a′**, ^1H NMR of the crude mixture shows formation of *dl*-**1a** as the single diastereomer of the final product. Starting from *dl*-**2a**,

the thermodynamically favoured *anti*,*anti* isomer **1a′** has been obtained as the major product. Phosphanes **1a** and **1a′** have been purified by column chromatography under argon.

To obtain the borane complexes **3a** or **3a′**, the crude product isolated from the reaction above after removal of acetic acid was dissolved in THF. An excess of BH_3·THF adduct (1.6 mL, 1 M solution in THF) was added at room temperature. After evaporation of the solvent, the final product was purified by column chromatography.

***anti*,*syn*-1,2,3-Triphenyl-2-phospha[3]ferrocenophane (1a):** Complex **1a** was purified by column chromatography on silica gel with hexane/ethyl acetate (90:10) as the eluent (R_f = 0.5). It was obtained as an orange solid in 68% yield (160 mg). ^{1}H NMR ($CDCl_3$): δ = 4.00 (d, $J_{H,P}$ = 12.5 Hz, 1 H, CHPh), 4.09 (d, $J_{H,P}$ = 5.0 Hz, 1 H, CHPh), 4.13 (m, 1 H, Cp), 4.14 (m, 1 H, Cp), 4.15 (m, 1 H, Cp), 4.18 (m, 1 H, Cp), 4.22 (m, 1 H, Cp), 4.29 (m, 1 H, Cp), 4.34 (m, 1 H, Cp), 4.41 (m, 1 H, Cp), 6.80 (t, 2 H), 6.95 (4 H), 7.06 (4 H), 7.21 (3 H), 7.39 (d, J = 7.5 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 35.9 (d, $^1J_{P,C}$ = 18.6 Hz, PCH), 44.8 (d, $^1J_{P,C}$ = 24.0 Hz, PCH), 68.1 (CH_{Cp}), 68.3 (CH_{Cp}), 68.5 (d, $J_{P,C}$ = 6.3 Hz, CH_{Cp}), 68.8 (CH_{Cp}), 69.1 (CH_{Cp}), 69.5 (d, $J_{P,C}$ = 9.2 Hz, CH_{Cp}), 69.7 (CH_{Cp}), 70.4 (d, $J_{P,C}$ = 4.2 Hz, CH_{Cp}), 85.5 (d, $^1J_{P,C}$ = 7.4 Hz, C_{Cp}), 87.3 (d, $^1J_{P,C}$ = 15.5 Hz, C_{Cp}), 126.0, 126.1, 127.2, 127.3, 127.6, 128.3, 128.6, 128.7, 128.8, 133.2, 133.3, 134.5 (d, $^1J_{P,C}$ = 20.5 Hz, C_{Ph}), 137.5 (d, $^2J_{P,C}$ = 6.6 Hz, C_{Ph}), 141.4 (d, $^2J_{P,C}$ = 14.4 Hz, C_{Ph}) ppm. ^{31}P NMR ($CDCl_3$): δ = 26 ppm. MS (MALDI): *m*/*z* (%) = 472.1 (100) [M]. HRMS: calcd. for $C_{30}H_{26}FeP$ [M + H] 473.1099; found 473.1122.

Borane Complex of *anti*,*syn*-1,2,3-Triphenyl-2-phospha[3]ferrocenophane (3a): Column chromatography was performed with hexane/ethyl acetate, 80:20 (R_f = 0.4) to afford **3a** as a yellow-orange solid. ^{1}H NMR ($CDCl_3$): δ = 4.19 (m, 1 H, Cp), 4.21 (d, $J_{H,P}$ = 4.7 Hz, 1 H, CHPh), 4.24 (m, 1 H, Cp), 4.28 (m, 1 H, Cp), 4.34 (m, 1 H, Cp), 4.37 (m, 2 H, Cp), 4.46 (d, $J_{H,P}$ = 18.3 Hz, 1 H, CHPh), 5.19 (m, 2 H, Cp), 6.9–7.2 (13 H, Ph), 7.50 (2 H, Ph) ppm. ^{13}C NMR ($CDCl_3$): δ = 34.0 (d, $^1J_{P,C}$ = 27.3 Hz, PCH), 46.7 (d, $^1J_{P,C}$ = 26.3 Hz, PCH), 68.3 (CH_{Cp}), 68.4 (CH_{Cp}), 70.4 (CH_{Cp}), 70.5 (CH_{Cp}), 70.7 (CH_{Cp}), 71.0 (CH_{Cp}), 71.1 (CH_{Cp}), 81.7 (C_{Cp}), 83.8 (C_{Cp}), 127.1, 127.4, 127.5, 128.1, 129.6, 130.0, 130.1, 130.4, 132.3, 132.4 (CH_{Ph}), 136.6 (C_{Ph}) ppm. ^{31}P NMR ($CDCl_3$): δ = 55 ppm. HRMS (MALDI): calcd. for $C_{30}H_{25}FeP$ [M – BH_3] 472.1043; found 472.1031.

***anti*,*anti*-1,2,3-Triphenyl-2-phospha[3]ferrocenophane (1a′):** Complex **1a** was purified by column chromatography on silica gel with hexane/ethyl acetate (90:10) as the eluent (R_f = 0.5). It was obtained in 60% yield (70 mg, starting from 0.25 mmol of **2a**) as an orange solid. ^{1}H NMR ($CDCl_3$): δ = 4.05 (d, $J_{H,P}$ = 6.0 Hz, 2 H, CHPh), 4.08 (m, 2 H, Cp), 4.26 (m, 2 H, Cp), 4.33 (m, 2 H, Cp), 4.88 (m, 2 H, Cp), 6.9 (t, 2 H), 7.0–7.1 (6 H), 7.2 (4 H), 7.2–7.3 (4 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 48.7 (d, $^1J_{P,C}$ = 15.8 Hz, PCH), 67.8, 68.7 (d, $J_{P,C}$ = 7.2 Hz, Cp), 69.8, 70.2 (d, $J_{P,C}$ = 3.9 Hz, Cp), 86.8 (d, $^1J_{P,C}$ = 12.8 Hz, C_{Cp}), 125.9, 127.6, 127.7, 128.1, 128.2, 129.0, 133.0, 133.3 (CH_{Ph}), 135.9 (d, $^1J_{C,P}$ = 16.0 Hz, PC_{Ph}), 141.5 (d, $^2J_{C,P}$ = 11.4 Hz, C_{Ph}) ppm. ^{31}P NMR ($CDCl_3$): δ = 21 ppm.

Borane Complex of *anti*,*anti*-1,2,3-Triphenyl-2-phospha[3]ferrocenophane (3a′): Column chromatography was performed with hexane/ethyl acetate (80:20) (R_f = 0.4) to afford 150 mg of **3a′** (63% yield) as a yellow-orange solid. ^{1}H NMR ($CDCl_3$): δ = 4.08 (m, 2 H, Cp), 4.19 (d, $J_{H,P}$ = 17.7 Hz, 2 H, CHPh), 4.20 (m, 2 H, Cp), 4.29 (m, 2 H, Cp), 5.17 (m, 2 H, Cp), 6.9–7.0 (6 H, Ph), 7.1 (4 H, Ph), 7.1–7.33 (3 H, Ph), 7.55 (t, 2 H, Ph) ppm. ^{13}C NMR (selected data, $CDCl_3$): δ = 45.8 (d, $^1J_{P,C}$ = 29.1 Hz, PCH), 68.6 (CH_{Cp}), 70.9 (CH_{Cp}), 71.1 (CH_{Cp}), 71.2 (CH_{Cp}), 83.1 (C_{Cp}), 126.8, 126.9, 127.6, 128.1, 128.2, 129.7, 129.8, 131.1, 132.4, 132.5 (CH_{Ph}), 136.5 (C_{Ph}) ppm. ^{31}P NMR ($CDCl_3$): δ = 51 ppm. MS (MALDI): *m*/*z* (%) = 472.1 (100) [M – BH_3].

(*S*)-1-Ferrocenylpentan-1-ol (4a):[24] A solution of borane–dimethyl sulfide complex (1.0 mL, 10 mmol) in anhydrous THF (about 10 mL) was prepared under argon. A fifth of this solution (2.2 mL) was added to a solution of (*R*)-2-methyl-CBS-oxazaborolidine in toluene (1 M, 3.0 mL, 3.0 mmol) under argon. The remaining BH_3–Me_2S solution and a solution of pentanoylferrocene (2.70 g, 10.0 mmol) in THF (10 mL) under argon were added simultaneously to this mixture at 0 °C. The addition was carried out over about 60 min. The mixture was stirred for another 60 min at 0 °C, then quenched by dropwise addition of methanol (2 mL) and satd. aqueous NH_4Cl (8 mL). The aqueous layer was extracted with diethyl ether. The organic phases were combined, washed with water and brine, and dried with magnesium sulfate. Purification by column chromatography (eluent: heptane/ethyl acetate, 5:1) gave (*S*)-1-ferrocenylpentan-1-ol as an amber-orange oil. Yield: 2.51 g (92%). ^{1}H NMR ($CDCl_3$): δ = 0.92 (t, $J_{H,H}$ = 7.0 Hz, 3 H, Me), 1.3–1.5 (m, 4 H, CH_2), 1.6–1.7 (m, 2 H, CH_2), 1.94 (d, $^3J_{H,H}$ = 3.5 Hz, 1 H, OH), 4.2 (m, 3 H, CH_{Cp}), 4.23 (s, 5 H, Cp), 4.27 (1 H, CH_{Cp}), 4.33 (m, 1 H, CHOH) ppm. HPLC [Chiralpak AD; *n*-hexane/isopropyl alcohol, 98:2, 1 mL/min; t_R/min = 17.2 (*R*), 23.7 (*S*)]: *ee* = 98%. $[\alpha]_D$ = +45 (c = 1, $CHCl_3$).

(*S*)-(α-Ferrocenylpentyl)diisobutylphosphane (5a): Diisobutylphosphane (4 mL) in hexane (10 wt.-% solution, about 1.8 mmol) was added to a degassed solution of (*S*)-1-ferrocenylpentan-1-ol (275 mg, 1.0 mmol) in degassed acetic acid (10 mL) under argon. The mixture was stirred overnight under argon at room temperature. The solvent and the remaining diisobutylphosphane were evaporated under vacuum. The residue was purified by chromatography on a short silica gel column, under argon. Elution with heptane/ethyl acetate (5:1) gave (*S*)-(1-ferrocenylpentyl)diisobutylphosphane as an amber-coloured oil. Yield: 360 mg (90%). ^{31}P NMR ($CDCl_3$): δ = –28 ppm. HRMS: calcd. for $C_{23}H_{38}FeP$ [M + H] 401.2041; found 401.2061. $[\alpha]_D$ = –39 (c = 0.1, $CHCl_3$); *ee* = 98%. NMR characterisation has been performed on the corresponding borane complex, **5a**·BH_3: ^{1}H NMR ($CDCl_3$): δ = 0.92 (d, ^3J = 6.6 Hz, 3 H, Me), 0.95 (d, ^3J = 6.6 Hz, 3 H, Me), 1.03 (t, 3 H, Me), 1.04 (d, ^3J = 6.9 Hz, 6 H, Me), 1.2–1.7 (7 H, CH_2, CH), 1.8–2.1 (5 H, CH_2, CH), 2.50 (ddd, J = 8.1, J = 6.6, J = 4.5 Hz, 1 H, CHP), 3.97 (1 H, CH_{Cp}), 4.08 (1 H, CH_{Cp}), 4.19 (s, 5 H, Cp), 4.2 (2 H, CH_{Cp}) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.0 (Me), 23.0 (CH_2), 24.0, 24.3, 24.6 (d, $J_{P,C}$ = 2.0 Hz), 24.7 (d, $J_{P,C}$ = 1.0 Hz), 25.1 (d, $J_{P,C}$ = 7.5 Hz), 25.3 (d, $J_{P,C}$ = 7.8 Hz), 31.1 (d, $^1J_{P,C}$ = 30.1 Hz, PCH_2), 31.4 (d, $J_{P,C}$ = 3.5 Hz, CH_2), 32.7 (d, $^1J_{P,C}$ = 30.3 Hz, PCH_2), 33.1 (d, $J_{P,C}$ = 3.5 Hz, CH_2), 36.0 (d, $^1J_{P,C}$ = 26.9 Hz, PCH), 66.9 (CH_{Cp}), 67.2 (CH_{Cp}), 67.9 (CH_{Cp}), 68.7 (CH_{Cp}), 69.0 (Cp), 88.7 (d, $J_{P,C}$ = 4.1 Hz, C_{Cp}) ppm. ^{31}P NMR ($CDCl_3$): δ = 23 ppm. $[\alpha]_D$ = –35 (c = 0.1, $CHCl_3$). The enantiomeric excess of **5a** was determined by HPLC analysis of the corresponding oxide, which was prepared as follows: (*S*)-(1-ferrocenylpentyl)diisobutylphosphane (100 mg, 0.25 mmol) was dissolved in acetone (about 2 mL), and hydrogen peroxide (35 wt.-% solution in water) was added. The mixture was stirred overnight at room temp. After addition of water, the aqueous phase was extracted with dichloromethane. The organic layer was washed with brine, dried with magnesium sulfate and concentrated to give (*S*)-(1-ferrocenylpentyl)diisobutylphosphane oxide as a red-brown oil. ^{1}H NMR ($CDCl_3$): δ = 0.98–1.07 (15 H, Me), 1.3–2.1 (12 H, CH_2, CH), 2.71 (ddd, J = 16.2, J = 6.6, J = 4.5 Hz, 1 H, CHP), 4.01 (1 H, CH_{Cp}), 4.16 (2 H, CH_{Cp}), 4.17 (s, 5 H, Cp), 4.22 (1 H, CH_{Cp}) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.0

(Me), 23.3 (CH_2), 23.5 (d, $J_{P,C}$ = 3.5 Hz), 23.6 (d, $J_{P,C}$ = 3.6 Hz), 24.5–25.0 (5 C), 30.1 (CH_2), 32.7 (d, J = 3.2 Hz, CH_2), 34.5 (d, J = 61.7 Hz, PCH_2), 36.1 (d, J = 61.8 Hz, PCH_2), 40.4 (d, J = 58.1 Hz, PCH), 66.9 (CH_{Cp}), 67.3 (CH_{Cp}), 67.7 (CH_{Cp}), 68.2 (CH_{Cp}), 68.8 (Cp), 88.3 (C_{Cp}) ppm. ^{31}P NMR ($CDCl_3$): δ = 49 ppm. HPLC (Chiralcel OD; *n*-hexane/2-propanol, 98:2, 1 mL/min) t_R/min = 10.0 (*R*), 11.3 (*S*).

(*S*)-(α-Ferrocenylbenzyl)diisobutylphosphane (5b): (a) Phosphane **5b** was first prepared by following the same procedure used for the synthesis of **5a**. Starting from (*S*)-ferrocenylbenzyl alcohol **4b**[17a,30] (290 mg, 1.0 mmol, 94% *ee*), phosphane **5b** was obtained as a pale orange solid after chromatography (silica gel, heptane/ethyl acetate, 9:1). Yield 270 mg (65%); *ee* = 49%. (b) The same phosphane **5b** was then prepared as follows: (*S*)-ferrocenylbenzyl alcohol **4b** (1 mmol, 96% *ee*) was added to ice-cooled acetic acid (10 mL) under argon, and diisobutylphosphane was added immediately to the yellow suspension without waiting for the alcohol to be dissolved. The mixture was warmed slowly to room temperature. After overnight stirring, workup was performed as described above for **5a**. Phosphane **5b** was obtained in 86% yield (360 mg); *ee* = 96%. ^{1}H NMR ($CDCl_3$): δ = 0.77 (d, ^3J = 6.5 Hz, 3 H, Me), 0.83 (d, ^3J = 6.5 Hz, 3 H, Me), 0.85 (d, ^3J = 6.5 Hz, 3 H, Me), 0.92 (d, ^3J = 6.5 Hz, 3 H, Me), 1.1 (m, 3 H), 1.3 (m, 2 H), 1.38 (m, J = 6.5 Hz, 1 H, CHMe), 3.39 (d, $^1J_{H-P}$ = 5.0 Hz, CHP), 3.78 (s, 5 H, Cp), 4.08 (1 H, CH_{Cp}), 4.12 (1 H, CH_{Cp}), 4.14 (1 H, CH_{Cp}), 4.18 (1 H, CH_{Cp}), 7.2–7.4 (5 H, Ph) ppm. ^{13}C NMR ($CDCl_3$): δ = 23.8 (d, $^3J_{P,C}$ = 9.0 Hz, Me), 24.0 (d, $^3J_{P,C}$ = 9.2 Hz, Me), 24.2 (Me), 24.3 (Me), 26.18, 26.28, 26.38, 26.48 (*CH*Me), 38.7 (d, $^1J_{P,C}$ = 17.5 Hz, PCH_2), 38.8 (d, $^1J_{P,C}$ = 17.5 Hz, PCH_2), 48.3 (d, $^1J_{P,C}$ = 15.6 Hz, PCH), 66.2 (CH_{Cp}), 67.3 (d, $J_{C,P}$ = 5.2 Hz, CH_{Cp}), 68.1 (CH_{Cp}), 68.4 (Cp), 69.4 (CH_{Cp}), 91.2 (d, $^2J_{C,P}$ = 14.9 Hz, C_{Cp}), 126.1, 127.9, 129.0, 129.1 (CH_{Ph}) ppm. ^{31}P NMR ($CDCl_3$): δ = –14 ppm. HRMS: calcd. for $C_{25}H_{34}FeP$ [M + H] 421.1748; found 421.1738. The enantiomeric excess of the phosphane was determined by HPLC analysis of the corresponding oxide, which was prepared as described above. ^{1}H NMR ($CDCl_3$): δ = 0.88 (d, ^3J = 6.5 Hz, 3 H, Me), 0.90 (d, ^3J = 7.0 Hz, 3 H, Me), 0.93 (d, ^3J = 6.5 Hz, 3 H, Me), 0.99 (d, ^3J = 6.5 Hz, 3 H, Me), 1.3–1.5 (4 H), 1.8–1.9 (2 H, *CH*Me$_2$), 3.75 (d, $^1J_{H-P}$ = 12.5 Hz, CHP), 3.79 (s, 5 H, Cp), 4.15 (1 H, CH_{Cp}), 4.18 (1 H, CH_{Cp}), 4.31 (1 H, CH_{Cp}), 4.35 (1 H, CH_{Cp}), 7.34 (1 H, Ph), 7.43 (2 H, Ph), 7.54 (2 H, Ph) ppm. ^{13}C NMR ($CDCl_3$): δ = 23.7 (dd, 2 × *CH*Me), 24.4 (Me), 24.5 (Me), 24.9 (dd, 2 × Me), 36.5 (d, $^1J_{P,C}$ = 62.0 Hz, PCH_2), 36.6 (d, $^1J_{P,C}$ = 61.2 Hz, PCH_2), 49.9 (d, $^1J_{P,C}$ = 56.1 Hz, PCH), 66.9 (CH_{Cp}), 68.3 (d, $J_{C,P}$ = 2.2 Hz, CH_{Cp}), 68.5 (Cp), 68.6 (CH_{Cp}), 70.0 (d, $J_{C,P}$ = 2.1 Hz, CH_{Cp}), 85.6 (C_{Cp}), 127.2 (d, $J_{C,P}$ = 1.6 Hz, CH_{Ph}), 128.3, 128.4, 129.7, 129.8 (CH_{Ph}), 138.5 (d, $J_{C,P}$ = 3.3 Hz, C_{Ph}) ppm. ^{31}P NMR ($CDCl_3$): δ = 45 ppm. HPLC (Chiralpak AD column, *n*-hexane/2-propanol, 93:7, 1 mL/min) t_R/min = 8.3 (*S*), 13.9 (*R*).

Syntheses of the Borane Complexes of 1,3-Dimethyl-2-phenyl-2-phospha[3]ferrocenophane (6b, 6b′ and 3b)

(a) 1,3-Dimethyl-2-oxa[3]ferrocenophanes, 6b,b′:[28] 1,1′-Bis(acetyl)ferrocene (3.0 g, 11 mmol) was reduced with $NaBH_4$ in methanol. After hydrolysis and extraction in ether, the ether solution of crude 1,1′-bis(α-hydroxyethyl)ferrocene was acidified with aqueous HCl (1 N). After 1 h of stirring at room temperature, the organic layer was separated, dried with $MgSO_4$ and the final product was submitted to column chromatography. Elution with hexane/ethyl acetate (9:1) afforded 1.2 g (41% yield) of *meso*-**6b′** (R_f = 0.47), followed by 1.1 g (38% yield) of *dl*-**6b** (R_f = 0.35). *meso*-**6b′**: ^{1}H NMR ($CDCl_3$): δ = 1.54 (d, $^3J_{H,H}$ = 6.5 Hz, 6 H, Me), 3.84 (q, $^3J_{H,H}$ = 6.5 Hz, 2 H, C*H*Me), 4.05 (m, 2 H), 4.17 (m, 2 H), 4.27 (m, 4 H) ppm. HRMS: calcd. for $C_{14}H_{16}FeO$ 256.0551; found 256.0531. *dl*-**6b**: ^{1}H NMR ($CDCl_3$): δ = 1.48 (d, $^3J_{H,H}$ = 7.0 Hz, 6 H, Me), 4.12 (m, 4 H), 4.22 (m, 2 H), 4.24 (m, 2 H), 4.34 (q, $^3J_{H,H}$ = 7.0 Hz, 2 H, C*H*Me) ppm. HRMS: calcd. for $C_{14}H_{16}FeO$ 256.0551; found 256.0523.

(b) 3b: A solution of BF_3·Et_2O (0.28 mL, 2 mmol) in CH_2Cl_2 (5 mL) was added to a solution containing 1,3-dimethyl-2-oxa[3]-ferrocenophane (250 mg, 0.98 mmol) and phenylphosphane (0.12 mL, 1.1 mmol) in dichloromethane (20 mL) at room temperature. After two hours of stirring, an excess of BH_3·THF was added (2 mL, 1 M solution). The mixture was hydrolysed with water. The organic layer was dried with $MgSO_4$. After evaporation of the solvents, the crude product was purified by chromatography on silica gel with hexane/ethyl acetate (8:2) as the eluent. The borane complex **3b** was purified by column chromatography.

Borane Complex of *anti*,*syn*-1,3-Dimethyl-2-phenyl-2-phospha[3]ferrocenophane (3b): Complex **3b** was obtained in 31% yield (105 mg) as a yellow solid after column chromatography with hexane/ethyl acetate (9:1) as the eluent (R_f = 0.5). ^{1}H NMR ($CDCl_3$): δ = 1.15 (dd, ^3J = 12.5, ^3J = 7.5 Hz, 3 H, Me), 1.45 (dd, ^3J = 15.5, ^3J = 7.0 Hz, 3 H, Me), 2.83 (qd, ^3J = 7.5, $^2J_{H-P}$ = 3.0 Hz, 1 H, C*H*Me), 3.16 (dq, $^2J_{H-P}$ = 16.5, ^3J = 7.0 Hz, 1 H, C*H*Me), 4.04 (m, 1 H, CH_{Cp}), 4.11 (m, 1 H, CH_{Cp}), 4.14 (m, 1 H, CH_{Cp}), 4.16 (m, 1 H, CH_{Cp}), 4.23 (m, 1 H, CH_{Cp}), 4.25 (m, 1 H, CH_{Cp}), 4.72 (m, 1 H, CH_{Cp}), 4.87 (m, 1 H, CH_{Cp}), 7.54 (3 H, Ph), 7.87 (2 H, Ph) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.1 (d, $^2J_{P,C}$ = 6.9 Hz, Me), 16.8 (d, $^2J_{P,C}$ = 7.0 Hz, Me), 19.2 (d, $^1J_{P,C}$ = 32.4 Hz, *CH*Me), 29.4 (d, $^1J_{P,C}$ = 32.0 Hz, *CH*Me), 67.2 (CH_{Cp}), 67.6 (CH_{Cp}), 67.8 (d, $J_{P,C}$ = 4.1 Hz, CH_{Cp}), 69.8 (d, $J_{P,C}$ = 6.1 Hz, CH_{Cp}), 70.1 (CH_{Cp}), 70.2 (CH_{Cp}), 70.5 (CH_{Cp}), 71.6 (CH_{Cp}), 84.1 (C_{Cp}), 84.4 (C_{Cp}), 128.6, 127.8 (CH_{Ph}), 129.6 (d, $^1J_{C,P}$ = 43.3 Hz, C_{Ph}), 130.9 (d, $J_{C,P}$ = 2.2 Hz, CH_{Ph}), 132.1 (CH_{Ph}), 132.2 (CH_{Ph}) ppm. ^{31}P NMR ($CDCl_3$): δ = 57 ppm. HRMS: calcd. for $C_{20}H_{21}FeP$ [M – BH_3] 348.0730; found 348.0741.

Borane Complexes of *syn*,*syn*- and *anti*,*anti*-1,3-Dimethyl-2-phenyl-2-phospha[3]ferrocenophane (3b′ and 3b′′): The diastereomeric mixture of *anti*,*anti* and *syn*,*syn* isomers of the 1,3-dimethyl-2-phenyl-2-phospha[3]ferrocenophane borane complexes **3b′** and **3b′′** was characterised by mass spectrometry and ^{1}H NMR spectroscopy. ESI-MS: *m*/*z* (%) = 348 (100) [M]. A sample of pure *syn*,*syn*-**3b′′** was obtained by chromatography. *syn*,*syn*-**3b′′**: ^{1}H NMR ($CDCl_3$): δ = 1.37 (dd, ^3J = 15.9, ^3J = 7.5 Hz, 6 H, Me), 2.92 (dq, $^2J_{H-P} \approx {}^3J_{H,H}$ = 7.5 Hz, 2 H, C*H*Me), 4.12 (m, 2 H, CH_{Cp}), 4.17 (m, 4 H, CH_{Cp}), 4.23 (m, 2 H, CH_{Cp}), 7.5 (3 H, Ph), 8.2 (2 H, Ph) ppm. ^{13}C NMR ($CDCl_3$): δ = 17.7 (Me), 30.0 (d, $^1J_{P,C}$ = 32.9 Hz, *CH*Me), 67.6 (CH_{Cp}), 68.5 (CH_{Cp}), 69.9 (CH_{Cp}), 71.5 (d, J = 5.2 Hz, CH_{Cp}), 88.7 (C_{Cp}), 128.5, 131.4, 134.7 (CH_{Ph}) ppm. *anti*,*anti*-**3b′** was characterised from the mixture of isomers: ^{1}H NMR ($CDCl_3$): δ = 1.19 (dd, $^3J_{H-P}$ = 15.5, ^3J = 7.0 Hz, 6 H, Me), 2.85 (dq, $^2J_{H-P}$ = 16.5, $^3J_{H,H}$ = 7.0 Hz, 2 H, C*H*Me), 4.07 (m, 2 H, CH_{Cp}), 4.12 (m, 2 H, CH_{Cp}), 4.21 (m, 2 H, CH_{Cp}), 4.72 (m, 2 H, CH_{Cp}), 7.5 (3 H, Ph), 7.9 (2 H, Ph) ppm.

Synthesis of the Borane Complex of 2-Phenyl-2-phospha[3]ferrocenophane (3c): (a) 2-Oxa[3]ferrocenophane.[35] A solution of 1,1′-bis-(hydroxymethyl)ferrocene (107 mg, 0.43 mmol) in HCl (1 M)/ether (1:1, 12 mL) was stirred vigorously for 6 h. The layers were separated and the organic layer dried with $MgSO_4$, filtered and concentrated in vacuo. The crude product was purified by flash chromatography (hexane/ethyl acetate, 8:2) to yield 81 mg (82%) of the desired compound as an orange solid. ^{1}H NMR ($CDCl_3$): δ = 3.92 (s, 4 H, CH_2), 4.17–4.19 (CH_{Cp}, 8 H, A_2B_2) ppm. ^{13}C NMR

($CDCl_3$): δ = 64.6 (OCH_2), 69.9 (CH_{Cp}), 70.1 (CH_{Cp}), 83.2 (C_{Cp}) ppm.

(b) The same experimental procedure as for the synthesis of **3b** was applied, starting from 2-oxa[3]ferrocenophane. Compound **3c** was obtained in 17% yield as a yellow-orange solid. ^1H NMR ($CDCl_3$): δ = 2.55 (t, $J_{H,P} = J_{H,H}$ = 15.0 Hz, 2 H, CH_2), 2.65 (d, $J_{H,H}$ = 14.0 Hz, 2 H, CH_2), 4.02 (s, 2 H, CH_{Cp}), 4.11 (s, 2 H, CH_{Cp}), 4.22 (s, 2 H, CH_{Cp}), 4.61 (s, 2 H, CH_{Cp}), 7.56 (3 H, Ph), 7.91 (2 H, Ph) ppm. ^{13}C NMR ($CDCl_3$): δ = 22.5 (d, $^1J_{P,C}$ = 34.6 Hz, PCH_2), 68.0 (CH_{Cp}), 69.8 (CH_{Cp}), 70.8 (d, $J_{P,C}$ = 5.1 Hz, CH_{Cp}), 71.6 (CH_{Cp}), 78.5 (d, $^2J_{P,C}$ = 4.6 Hz, C_{Cp}), 128.9, 129.0 (CH_{Ph}), 130.3 (d, $^1J_{C,P}$ = 48.8 Hz, CPh), 131.3, 131.4 (CH_{Ph}) ppm. ^{31}P NMR ($CDCl_3$): δ = 46 ppm. HRMS (MALDI): calcd. for $C_{18}H_{17}PFe$ [M – BH_3] 320.0417; found 320.0412.

Resolution of *dl*-1,2,3-Triphenyl-2-phospha[3]ferrocenophane (1a): Complex **7** was obtained from the corresponding amine[36] and palladium(II) chloride, as described in the literature.[37] *anti*,*syn*-1,2,3-Triphenyl-2-phospha[3]ferrocenophane **1a** (100 mg, 0.21 mmol) and complex **7** (72 mg, 0.11 mmol) were dissolved in acetone (10 mL) under argon and the mixture was stirred at room temperature for 2 h. After evaporation of the solvent, the crude product was obtained as a diastereomeric mixture, which was separated by column chromatography on silica gel with a heptane/ethyl acetate (8:2) mixture as the eluent.

Complex **8a** was eluted first (R_f = 0.5 in heptane/ethyl acetate, 6:4, 35 mg, 40% yield): ^1H NMR ($CDCl_3$): δ = 1.96 (d, $^3J_{H,H}$ = 6.5 Hz, 3 H, CH*Me*), 2.44 (s, 3 H, NMe), 3.08 (d, J = 3.5 Hz, 3 H, NMe), 4.1–4.2 (4 H, Cp, N*CH*Me), 4.35 (1 H, Cp), 4.44 (2 H, Cp), 4.48 (1 H, Cp), 5.42 (d, $^1J_{H\text{-}P}$ = 15.0 Hz, 1 H, CHPh), 5.62 (dd, 1 H, Naph), 5.92 (1 H, Cp), 6.48 (d, ^3J = 7.0 Hz, 1 H, Naph), 6.91 (t, J = 8.5 Hz, 1 H), 7.0–7.5 (Ar), 7.54 (d, J = 8.5 Hz, 1 H), 8.16 (d, J = 7.0 Hz, 2 H) ppm. ^{13}C NMR (selected data, $CDCl_3$): δ = 21.8 (CH*Me*), 43.4 (d, $^1J_{P,C}$ = 10.9 Hz, PCH), 46.2 (d, $^1J_{P,C}$ = 12.1 Hz, PCH), 48.0 (NMe), 50.3 (NMe), 67.3, 68.1, 68.3, 69.5, 70.5, 70.6, 70.7, 71.8, 72.1 (Cp, N*CH*Me), 84.0 (d, $^1J_{P,C}$ = 9.2 Hz, C_{Cp}), 86.2 (C_{Cp}), 121–129 (Ar), 137.4 [C-3′ (Naph)], 141.2, 145.9, 150.0 (C) ppm. ^{31}P NMR ($CDCl_3$): δ = 80.4 ppm. MS (MALDI): *m*/*z* (%) = 776 (100) [M – Cl]. HRMS (MALDI): calcd. for $C_{44}H_{41}FeNPPd$ 776.1361; found 776.1359. $[a]_D$ = +281 (c = 0.2, $CHCl_3$).

Complex **8b** was then eluted with R_f = 0.3 in heptane/ethyl acetate (6:4). ^1H NMR ($CDCl_3$): δ = 2.19 (d, $^3J_{H,H}$ = 6.5 Hz, 3 H, CH*Me*), 2.73 (s, 3 H, NMe), 3.13 (d, J = 3.5 Hz, 3 H, NMe), 4.18, 4.21, 4.23, 4.28, (Cp), 4.31 (m, N*CH*Me), 4.35, 4.39 (Cp), 4.77 (d, $^1J_{H-P}$ = 17.0 Hz, 1 H, CHPh), 5.47 (1 H, Cp), 5.65 (dd, $^3J_{H,H}$ = 8.5 Hz, $^4J_{H,P}$ = 5.0 Hz, 1 H, Naph), 6.02 (1 H, Cp), 6.12 (d, ^3J = 8.5 Hz, 1 H, Naph), 6.33 (d, $^1J_{H-P}$ = 6.5 Hz, 1 H, CHPh), 6.65 (2H), 6.88 (t, J = 7.5 Hz, 1 H), 7.0–7.5 (Ar), 7.67 (d, J = 8.5 Hz, 1 H), 7.84 (2H). ^{13}C NMR (selected data, $CDCl_3$): δ = 22.4 (CH*Me*), 37.7 (d, $^1J_{P,C}$ = 15.1 Hz, PCH), 46.6 (d, $^1J_{P,C}$ = 17.3 Hz, PCH), 48.7 (NMe), 50.9 (NMe), 69.0, 69.2, 69.3, 69.6, 70.1, 70.3, 70.7, 71.5, 73.5 (Cp, N*CH*Me), 82.1 (C_{Cp}), 83.9 (C_{Cp}), 123–131 (Ar), 136.2 (CH), 136.3 (CH), 137.2, 138.1, 147.0, 148.0 (C) ppm. ^{31}P NMR ($CDCl_3$): δ = 75.8 ppm. $[a]_D$ = –160 (c = 0.2, $CHCl_3$).

Complex **8a** (32 mg, 0.04 mmol) was treated with 1,2-bis(diphenylphosphanyl)ethane (15 mg) in CH_2Cl_2 (2 mL) at room temperature for 3 h. After evaporation, phosphane **1a** was isolated by filtration through a short silica gel column with heptane/ethyl acetate (8:2) as the eluent (R_f = 0.6). $[a]_D$ = +392 (c = 0.2, $CHCl_3$).

X-ray Crystal Structure Analyses: For the three structures, intensity data were measured with a Nonius Kappa-CCD area detector diffractometer using graphite-monochromated Mo-K_α radiation, in ϕ- and ω-scans, up to θ = 27.5° for compounds **3a** and **3c**, and only to 22° for **8c**. The structures were solved by direct methods with the program SHELXS86[38] and refined by full-matrix least-squares, on the basis of unique F^2, with the program SHELXL97.[39] The hydrogen atoms were located on difference Fourier maps and fitted at theoretical positions [d(C–H) = 0.93 or 0.98 Å], except those fixed to the B atom, which were refined. They were assigned an isotropic displacement parameter equivalent to 1.12 times that of the bonded atom.

Crystallographic Data for Compound 3a: A small brown-yellow prismatic crystal of 0.55 × 0.45 × 0.45 mm, cut from a larger one, was used. Empirical formula $C_{30}H_{28}BFeP$, M = 486.15, T = 293 K. Monoclinic system, centrosymmetric space group $P2_1/n$. The unit cell of parameters a = 7.401(4), b = 29.868(15), c = 11.186(6) Å, β = 93.75(2)°, V = 2467 Å^3 contains four molecules (Z = 4); d_{calcd} = 1.309 g cm^{-3}, F(000) = 1016, μ = 0.692 mm^{-1}, λ(Mo-K_α) = 0.71073 Å. A total of 9485 data were collected, giving 6901 monoclinic reflections, of which 4806 were unique.[40] Refinement of 307 parameters on F^2 led to $R_1(F)$ = 0.0382 calculated with the 3942 observed reflections having $I \geq 2\sigma(I)$ and to $wR_2(F^2)$ = 0.0946 considering all 4806 unique reflections. Goodness of fit = 1.050. The residual density was found to be between –0.36 and 0.29 e Å^{-3}.

Crystallographic Data for Compound 3c: A yellow prismatic crystal of 0.25 × 0.10 × 0.10 mm was used. Empirical formula $C_{18}H_{20}BFeP$, M = 333.97, T = 293 K. Monoclinic system, centrosymmetric space group $P2_1/a$. The unit cell of parameters a = 10.891(4), b = 7.472(4), c = 19.160(6) Å, β = 94.47(2)°, V = 1554 Å^3 contains four molecules (Z = 4); d_{calcd} = 1.427 g cm^{-3}, F(000) = 696, μ = 1.062 mm^{-1}, λ(Mo-K_α) = 0.71073 Å. A total of 14535 data were collected, giving 6478 monoclinic reflections, of which 3530 were unique. Refinement of 199 parameters on F^2 led to $R_1(F)$ = 0.0401 calculated with the 2292 observed reflections having $I \geq 2\sigma(I)$ and to $wR_2(F^2)$ = 0.0956 considering all 3530 unique reflections. Goodness of fit = 1.044. The residual density was found to be between –0.47 and 0.42 e Å^{-3}.

Crystallographic Data for Compound 8a: From very small crystals, a small orange needle of 0.20 × 0.05 × 0.012 mm was chosen. Empirical formula $C_{44}H_{41}ClFeNPPd{\cdot}C_7H_8$, M = 904.58, T = 293 K. Tetragonal system, chiral space group $I4_1$. The unit cell of parameters a = b = 27.112(7), c = 11.592(5) Å, V = 8521 Å^3 contains eight molecules (Z = 8); d_{calcd} = 1.410 g cm^{-3}, F(000) = 3891, μ = 0.90 mm^{-1}, λ(Mo-K_α) = 0.71073 Å. A total of 26093 reflections were collected, giving 5070 unique tetragonal reflections. In addition, a toluene molecule of crystallisation solvent was found per molecule. The absolute configuration was calculated from the anomalous dispersion effects in diffraction measurements. Refinement of 510 parameters on F^2 led to $R_1(F)$ = 0.0440 calculated with the 3891 observed reflections having $I \geq 2\sigma(I)$ and to $wR_2(F^2)$ = 0.0768 considering all 5070 unique reflections. Goodness of fit = 1.032. The residual density was found to be between –0.28 and 0.25 e Å^{-3}.

CCDC-636890 (for **3a**), -636891 (for **3c**) and -636892 (for **8a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.cccd.cam.ac.uk/data_request/cif.

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