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Aryl Ferrophites – A New Class of Ligands for Asymmetric Catalysis

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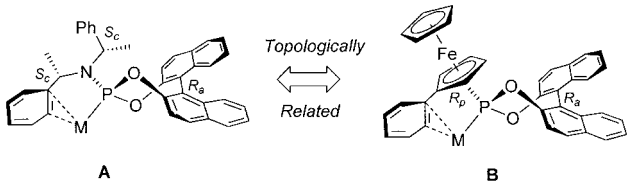
Enantiopure lithiated 1,2-ferrocenes, [CpFe{1,2-η^5-C_5H_3(Ar)(Li)}] (Ar = Ph, 4-$CF_3C_6H_4$, 1-$C_{10}H_7$), react readily with $PhOP(OR)_2$ to yield [CpFe{1,2-η^5-C_5H_3(Ar)$P(OR)_2$}] (R = Ph, 1,1′-biphenyl-based, 1,1′-binaphthyl-based) efficiently. Traditional routes to these species, involving the use of chlorophosphites $ClP(OR)_2$ were found to be ineffective. These "ferrophite" ligands have been characterised by X-ray crystallography (4 examples) and shown to be effective in both nickel-catalysed addition of $AlMe_3$ to PhCHO (up to 77 % *ee*) and copper(I)-catalysed additions of organoaluminium reagents to enones (up to 92 % *ee*).

Introduction

Phosphoramidites $[(RO)_2PNR_2]$ are recent additions to the set of so-called "privileged" ligands[1] leading to superlative asymmetric catalysis when coordinated to a range of metal centres for a variety of processes.[2] The very high levels of enantioselectivity that are often realised with these ostensively monodentate ligands are not expected if free rotation about the P–M_{cat} bond in the active catalyst [L_nM_{cat}-$P(OR)_2(NR_2)$] is present. Recently, it has been suggested that phosphoramidites can attain a (*P*,*C*=*C*) chelate coordination mode **A** in certain reactions including: nickel-catalysed alkene dimerisation,[3] ruthenium-catalysed cyclopropanation[4] and nickel-promoted additions of $AlMe_3$ to aldehydes.[5] In connection with the latter, we were interested in providing supportive evidence for a (*P*,*C*=*C*) contact and simultaneously in discovering new ligands both for this process and others. We believed that the ferrocene fragment **B** should be an analogue of **A** and set out to synthesise suitable examples of this ligand type, which we called "ferrophites". Throughout this manuscript (*R*) planar, axial and centrosymmetric stereochemical chemistry are distinguished by the descriptors (R_p), (R_a) and (R_c), respectively, for clarity.



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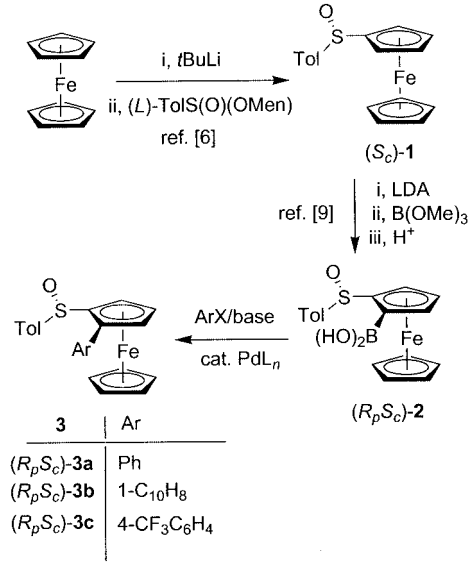
Results and Discussion

Ligand Synthesis: Kagan has introduced a powerful methodology for the preparation of planar chiral 1,2-disubstituted ferrocenes based on the use of sulfoxide auxiliaries.[6] Our synthetic route began with (S_c)-**1** prepared from ferrocene by Kagan's method by use of the known Andersen sulfoxide (Scheme 1).[7] All of the ligands in this paper could be prepared in either enantiomeric series, but are shown throughout as originating from natural L-menthol for consistency. The planar chirality of the ferrocenes is assigned in agreement with Schlögl's modified method.[8] Stereoselective lithiation and trapping with $B(OMe)_3$ allows access to (R_pS_c)-**2** using literature procedures.[9] Optimal coupling of (R_pS_c)-**2** with suitable ArX (X = I, Br) occurred with 8 mol-% $Pd(dppf)Cl_2$ and sodium hydroxide promotion[9] at reflux within 4 hours to give good yields for both sterically encumbered and electron-deficient aryl halides (R_pS_c)-**3a**–**c** (Scheme 1). Other catalyst systems, including $Pd(PPh_3)_4$/CsF and $Pd(OAc)_2$/X-Phos[10]/$K_3PO_4 \cdot H_2O$, were ineffective. It was not possible to prepare an electron-rich aryl derivative by using 4-$(MeO)C_6H_4I$ under any of these conditions. For example, the use of $Pd(dppf)Cl_2$ led only to low yields of (R_pS_c)-**3a** by presumed phenyl transfer from the dppf ligand. This is in contrast to the work of Johannsen who was able to couple 2-$(MeO)C_6H_4I$ to (R_pS_c)-**2** using a closely related methodology. In accordance with literature results the formation of (R_pS_c)-**3a** from (S_c)-**1** proceeds with very high selectivity.[6,11]

The sulfoxide auxiliary of (R_pS_c)-**3a** was cleaved under Kagan's conditions[6] to afford the derived organolithium species (S_p)-**4a** (Scheme 2). The change in stereochemical descriptor is caused only by the peculiarities of the CIP nomenclature (C has greater priority than Li). Such species

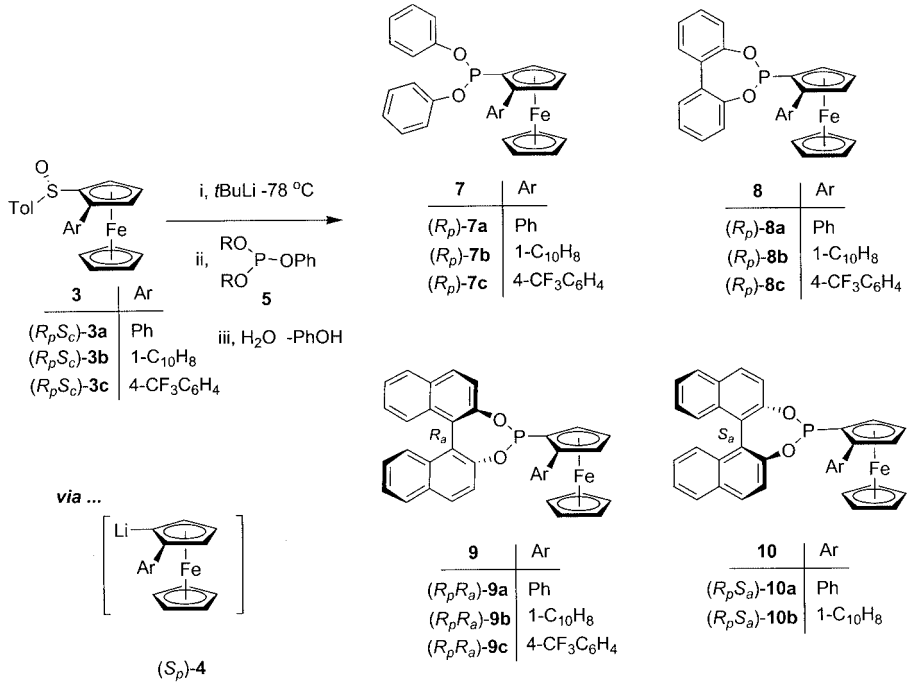


Scheme 1.

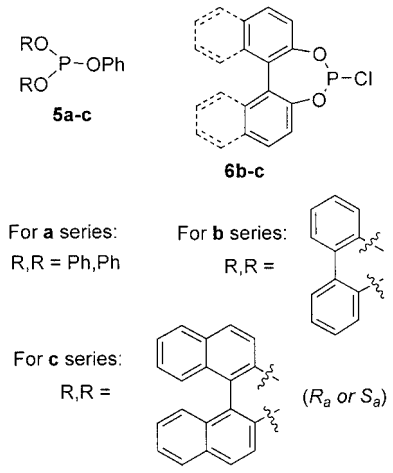
are known to react readily and stereospecifically with *chlorophosphanes* R_2PCl (R = Ph, *c*-C_6H_{11}). However, the reaction of (S_p)-**4a** with *chlorophosphite* $(RO)_2PCl$ species proved very inefficient, at best only traces of the desired product, even after prolonged heating of the reaction mixtures, were attained. This seems to be a general problem in the preparation of ferrocenyl-based phosphites,[12] as published literature procedures to these compounds are few and normally involve the preparation of reactive PCl_2-functionalised ferrocenes prior to subsequent reaction with alcohols.[13] Some time ago, Luetkens et al. reported that the reaction of MeMgX with $P(OPh)_3$ is one of the most efficient and clean routes to PMe_3[14] chemistry that can be extended to the use of MeLi. We speculated that the equivalent reaction of (S_p)-**4a** with $P(OPh)_3$ would favour the formation of the desired ferrophite ligand (R_p)-**7a**. Indeed, addition of $P(OPh)_3$ to organolithium species (S_p)-**4a** resulted in an almost immediate (<2 min at –78 °C) colour change in the reaction mixture from deep orange-red to pale orange-yellow, in contrast to the inefficient chlorophosphite reactions. On workup the desired product (R_p)-**7a** was isolated as an orange oil (69%). Compounds (R_p)-**7b**,**c** were similarly prepared in 33 and 56% yield, respectively (Scheme 2).

We were encouraged by these results to attempt the equivalent reaction of the anions **4a**–**c**, both with 1,1-binaphthol- and 1,1-biphenol-derived phosphites. The precursor phosphites were easily prepared by the reaction of PCl_3 with the appropriate diol in the presence of NEt_3, to yield the chlorophosphites **6b**–**c** (Scheme 3). Subsequent addition of phenol and further NEt_3 allowed the isolation of **5b**–**c** in moderate yield (53–74% based on the diol) after column chromatography on silica. Compounds **5** were used within 72 hours and handled under inert atmosphere when in solution, as they are sensitive to hydrolysis to phosphorus(v) species.

Reaction of **5b**–**c** with the organolithiums **4a**–**c** proceeded in a modular fashion to complete a small library of ferrophite ligands (Scheme 2). Overall, compounds **8**–**10** were isolated in 8–71% yield depending on the workup conditions. Some of the ligands showed appreciable sensitivity to acid-catalysed hydrolysis in the order **7** ≈ **9** < **8** < **10** with (R_pR_a)-**9a** being particularly robust but (R_pS_a)-**10a** being very easily hydrolysed. It is of note that the diastereomeric (S_a) axial compounds **10** had to be chromato-



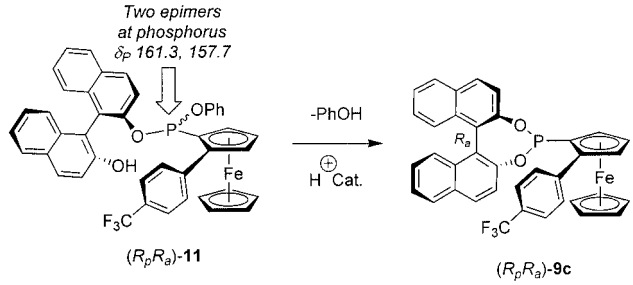
Scheme 2.



Scheme 3.

graphed on basic alumina to avoid complete decomposition, and that only (R_pS_a)-**10b** was isolated in analytically pure form after further crystallisation. Removal of the phenol by-product from the crude reaction mixtures dramatically improves the sample stabilities as this acts as a proton source (pK_a 10.0), catalysing the hydrolytic transformation of Fc-P(OR)$_2$ to Fc-PH(=O)(OR) (Fc = ferrocenyl fragment). The sensitivity of the ligands to hydrolysis accounts for the low yields of compounds (R_p)-**8b** (15%) and (R_pS_a)-**10b** (8%) as in all cases, monitoring the reaction mixtures by ^{1}H NMR spectroscopy and TLC indicated that the initial formation of the ligand was clean and rapid.

Mechanism for the Formation of the Ligands: Given the dramatic rate difference in the reaction of the anion (S_p)-**4** with P–OPh vs. P–Cl bonds, the coupling of **4c** with (R_a)-**5c** was closely monitored as this pair reacted somewhat more slowly than the rest (although the coupling was still fast and efficient). The selective formation of an initial intermediate was evident by TLC (R_f = 0.12, 4:1 hexane/Et_2O). On quenching the reaction mixture slowly evolved, and the intermediate was replaced by a new product (R_f = 0.44), later identified as the previously isolated final product (R_pR_a)-**9c** by both spectroscopic and crystallographic techniques. Repeated attempts to crystallise the initial kinetic product were unsuccessful and led only to its decomposition. It could be confirmed that conversion of the intermediate required the presence of acid, as deliberate addition of traces of HCl to C_6D_6 solutions led to very rapid formation of (R_pR_a)-**9c**. Spectroscopic studies (^{1}H-, ^{13}C-, ^{31}P NMR) of the crude (R_f = 0.12) intermediate revealed the presence of two very similar species, both of which contained binaphthyl and aryl-ferrocene fragments, in an approximately 3:1 ratio. Crucially, the *dry* solution IR spectra of the intermediate revealed the presence of a strong, sharp ν(OH) stretch at 3542 cm^{-1}. We believe that initial cleavage of one of the P–ONaphthyl bonds in (R_a)-**5c**, as it is attacked by the nucleophile (S_p)-**4c** followed by protonation with water, leads to the formation of (R_pR_a)-**11** as a mixture of two epimers at phosphorus as an initial kinetic product. Subsequent acid-catalysed elimination of phenol leads to thermodynamically favoured (R_pR_a)-**9c** (Scheme 4). It is likely that the formation of the other ferrophites proceeds through a similar mechanism, but in these cases the acid-catalysed rearrangements are much faster and these are attained within minutes in the presence of the phenol generated upon aqueous quench of the reaction mixture.



Scheme 4.

Crystallographic Studies: While the ^{1}H, ^{13}C NMR spectra of the compounds **7**–**10** were in agreement with the proposed structures, the ^{31}P NMR shifts (δ_P = 173.4–206.3 ppm) were somewhat higher than what we initially anticipated for these compounds. To ensure that the correct connectivity had been realised, crystallographic studies were carried out on compounds (R_p)-**8a**, (R_pR_a)-**9a**, (R_pR_a)-**9c** and (R_pS_a)-**10b** and their structures are shown in Figure 1, Figure 2, Figure 3 and Figure 4 together with selected bond length and angle data.

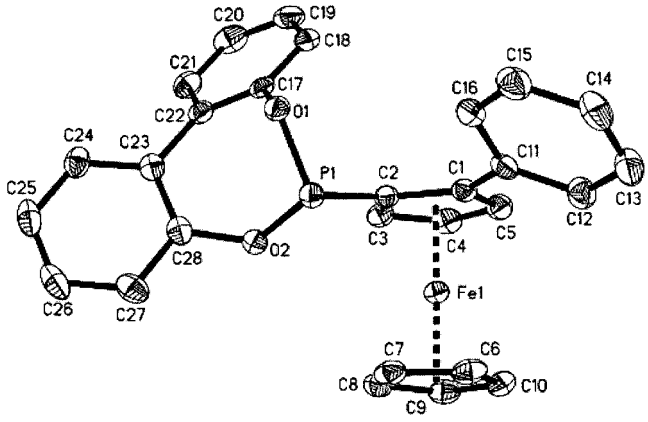


Figure 1. View of molecular structure of (R_p)-**8a** with ellipsoids drawn at 50% probability level. Selected bond lengths and angles: P1–C2 1.809(2), P1–O1 1.6575(13), P1–O2 1.6671(14), C1–C11 1.483(3) Å; C1–C2–P1 124.38(14), C2–P1–O1 102.28(7), C2–P1–O2 94.31(8)°.

In the structure of (R_p)-**8a**, the biphenyl unit adopts a (R_a) configuration in the solid state. This suggests perhaps that this configuration is the lowest energy atropisomer. This supposition is supported by the comparison of two structures from the separate diastereomeric 1,1′-binaphthyl series: (R_pR_a)-**9a** vs. (R_pS_a)-**10b**. In the latter there is significant steric congestion between the binaphthyl ring and the aryl substituent which is avoided in the former. Relief of this strain is likely to be the driving force for the facile hydrolysis of compounds **10** and is the probable cause of our inability to isolate compound (R_pS_a)-**10a** pure. In (R_pS_a)-

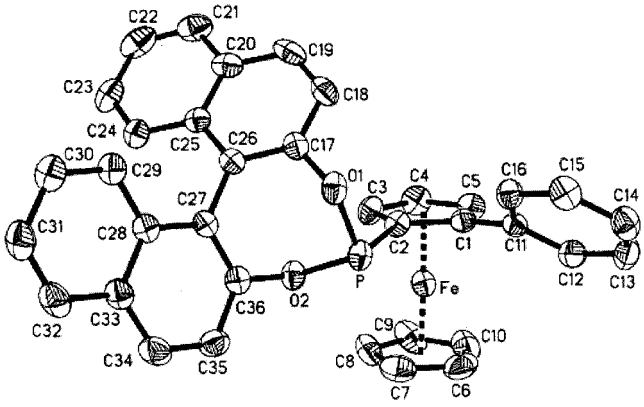


Figure 2. View of molecular structure of (R_pR_a)-**9a** with ellipsoids drawn at 50% probability level. Selected bond lengths and angles: P–C2 1.804(2), P–O1 1.6581(14), P–O2 1.6680(15), C1–C11 1.478(3) Å; C1–C2–P 122.45(14), C2–P–O1 102.91(8), C2–P–O2 96.19(8)°.

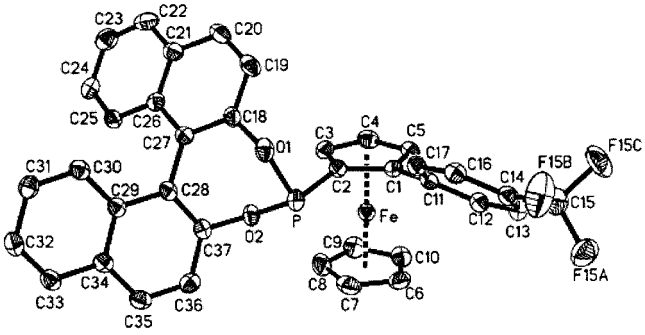


Figure 3. View of molecular structure of one of the two independent molecules of (R_pR_a)-**9c** with ellipsoids drawn at 50% probability level. Selected bond lengths and angles: P–C2 1.797(3), P–O1 1.663(2), P–O2 1.665(2), C1–C11 1.479(4) Å; C1–C2–P 123.5(2), C2–P–O1 103.81(12), C2–P–O2 95.80(12)°.

10b, the centroid–centroid distance between the naphthyl ring C11–C20 and one of the binaphthyl rings C21–C30 is 3.65 Å and the interplanar angle between the two rings is 15.2°. These are both in the range expected for a π stacking

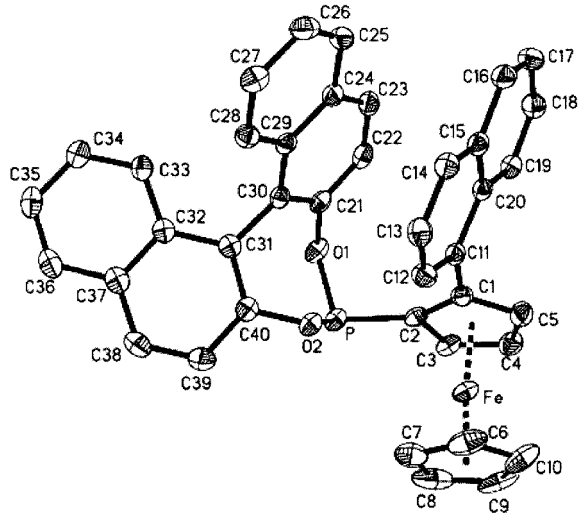
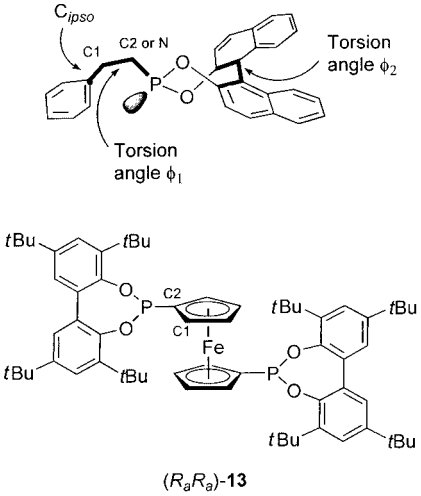
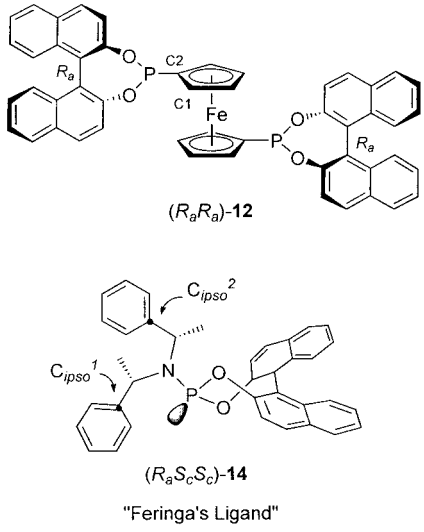


Figure 4. View of molecular structure of (R_pS_a)-**10b** with ellipsoids drawn at 50% probability level. Selected bond lengths and angles: P–C2 1.8030(15), P–O1 1.6544(11), P–O2 1.6617(11), C1–C11 1.489(2) Å; C1–C2–P 138.33(11), C2–P–O1 104.72(6), C2–P–O2 99.68(6)°.

interaction. We speculate that the higher stability of compound **10b** relative to compound **10a** is due to this interaction. As the ferrophites had been designed as analogues of Feringa's ligand (shown as its metal complex in structure **A**) it is appropriate to compare their ground-state geometries with that of the other ferrocenyl phosphites for which crystallographic data are available: Feringa's ligand itself, Reetz's **12**[13b] and Pastor's **13**[12a] (Scheme 5). For the purposes of the comparison it is useful to define C_{ipso} and the two torsion angles φ_1 and φ_2 whose values for the separate ligands are given in Table 1.

The data of Table 1 suggests that the ferrophites should present a structurally similar architecture to Feringa's ligand on metal binding, however there are notable differences. The first difference between the ligands is, as expected, the longer P–C2 bond length in the ferrophites com-





Scheme 5.

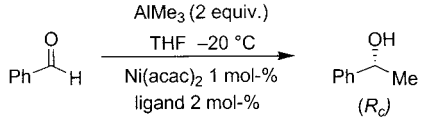
Table 1. Structural comparison of ferrophites with related ligands.

Compound	Code[a]	P–C_{ave} [Å]	P–O_{ave} [Å]	P···C_{ipso} [Å]	φ_1 [°]	φ_2 [°]
(R_p)-**8a**	–[b]	1.8086	1.6623	3.418	–12.2	–43.3
(R_pR_a)-**9a**	–[b]	1.8038	1.6631	3.372	–17.0	–53.3
(R_pR_a)-**9b**	–[b]	1.799	1.662	3.426	–15.7	–52.3
(R_pS_a)-**10b**	–[b]	1.803	1.658	3.767	–12.6	55.0
(R_aR_a)-**12**	GEGQAK	1.802	1.664	–		–54.1
(S_aS_a)-**13**[c]	NOPXAR	1.805 (P–N)	1.656	–		54.5
($R_aS_cS_c$)-**14**	–[d]	1.659	1.663	3.167 ($C_{ipso}{}^1$)	60.9 ($C_{ipso}{}^1$)	–52.2
"Feringa"				3.778 ($C_{ipso}{}^2$)	112.7 ($C_{ipso}{}^2$)	
($R_aS_cS_c$)-**A**	–[e]	–	–	2.957–3.000[e]	45.9–50.0[e]	–

[a] Cambridge Crystallographic Database code. [b] This publication. [c] Crystallised from a racemate. [d] Coordinates via personal communication W. Leitner (see also ref.[4]). [e] Range seen for calculated intermediates (B1, B2, C1, C2; structure **A** M = Ni) in ref.[4].

pared with the P–N bond length in Feringa's ligand. Additionally, the torsion angle φ_1 is much smaller in the ferrophites as C1–C2 is conformationally locked in the cyclopentadienyl ring. Although the two differences (bond length vs. torsion angle) could potentially cancel each other out, the overall difference between the ferrophites and Feringa's ligand is an increased P···C_{ipso} distance in the ferrophite family, which consequently suggests a longer, and therefore weaker, C=C···M binding mode in catalysis. However, direct comparison with the free Feringa ligand **14** cannot be taken as representative of that in a putative η^2-*P,C=C* binding mode in the metal complexes. We therefore also compared the ferrophite ligand geometries with those calculated for motif **A** [M = Ni] by Hölscher and Leitner.[4] In these calculated structures φ_1 is reduced compared to free **14** leading to a reduced C_{ipso}···P distance, significantly smaller than in our ferrophite ligands. We therefore predicted that the ferrophites would not be quite as effective in nickel catalysis as the parent Feringa ligand. In the case of copper catalysis a bimetallic intermediate is thought to occur, and therefore, the increased P···C_{ipso} distance might now be an advantage; although the transition states in most copper-catalysed asymmetric 1,4-reactions are not very well understood. The flexibility seen by Feringa's ligand is in contrast to the more rigid structure of the ferrophite ligands. Only a few *P,C=C* coordination modes have been determined ex-

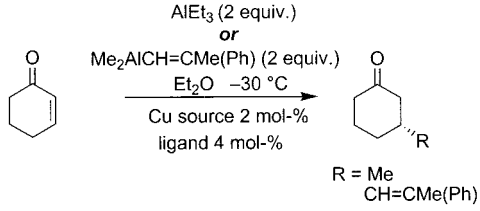
Table 2. Selected ligand comparisons in $AlMe_3$ 1,2-addition to PhCHO.[a]



Entry	Ligand	Yield/%	*ee* [%]
1	($R_aS_cS_c$)-Feringa **14**	60	**92**
2	(R_p)-**8a** [Ph, biphenyl]	96	16
3	(R_p)-**8b** [1-Nap, biphenyl]	92	28
4	(R_p)-**8c** [$CF_3C_6H_4$, biphenyl]	76	49
5	(R_pR_a)-**9a** [Ph, binaphthyl]	96	**73**
6	(R_pR_a)-**9a** [1-Nap, binaphthyl]	90	55
7	(R_pR_a)-**9c** [$CF_3C_6H_4$, binaphthyl]	95	**77**

[a] Addition of 2 equiv. of $AlMe_3$ to benzaldehyde and Ni(acac)$_2$/L in THF at –20 °C followed by 3 hours reaction at this temperature. Yield by GC against internal standard, *ee* by chiral GC.

Table 3. Selected ligand comparisons in organoaluminium 1,4-addition to cyclohexenone.[a]



Entry	Ligand	Cu source	Yield/%	*ee*/%
A. $AlEt_3$				
1	($R_aS_cS_c$)-Feringa **14**	CuTC	76	88
2	(*Rp*)-**8a** [Ph, biphenyl]	$Cu(OTf)_2$	92	59
3	(*RpRa*)-**9a** [Ph, binaphthyl]	$Cu(OTf)_2$	77	**92**
4	(*RpRa*)-**9b** [1-Nap, binaphthyl]	$Cu(OTf)_2$	58	78
5	(R_pR_a)-**9c** [$CF_3C_6H_4$, binaphthyl]	$Cu(OTf)_2$	78	87
B. $Me_2AlCH=CMe(Ph)$				
6	($R_aS_cS_c$)-Feringa **14**		54	75–76
7	(R_pR_a)-**9a** [Ph, binaphthyl]		[b]	**85**

[a] Addition of 1.4 equiv. of $AlMe_3$ to 2-cyclohexenone and Cu salt/L in Et_2O at –30 °C followed by 20 min reaction at this temperature. Yield by GC against internal standard, *ee* by chiral GC. [b] Comparable to that of ref.[16]

plicitly by X-ray diffraction: M–C contacts with the alkene carbon atoms in the range 2.3–2.6 Å are the norm,[15] but this is of course on the derived metal complexes and not a structural parameter of the free ligand.

Catalytic Studies: The efficacy of the new ferrophite ligands was ascertained by testing them in two reactions: nickel-catalysed addition of $AlMe_3$ to PhCHO (Table 2) and copper(I)-catalysed additions of organoaluminium reagents to enones (Table 3). The enantioselectivities realised with the ferrophite ligands in the 1,2-additions were lower than those attained with the optimal ($R_aS_cS_c$)-Feringa ligand **14** (compare Entries 1 vs. 2–7), although the yields were notably increased. However, the significant *ee* values from the ligands (R_pR_a)-**9a** and (R_pR_a)-**9c** might be taken as supportive of a putative *C=C···Ni* contact in the selective transition state of this reaction. Greater success was attained in asymmetric conjugate addition of organoaluminium reagents to enones. In this case, the greater rigidity of the ferrophite ligands engendered improved enantioselectivities over the Feringa phosphoramidite **14** (Table 3, Entry 1 vs. 2–5). This was particularly noticeable in our asymmetric carboalumination-conjugate addition procedure,[16] where we were able for the first time to attain synthetically useful enantioselectivity values (entries 6 vs. 7).

Conclusions

A new class of chiral ferrocenyl-based phosphite (ferrophite) ligands has been prepared with the aim of mimicking the π contacts thought to be realised in Feringa's phosphoramidite ligand **14**. The X-ray crystallographic data and the catalytic performance of the ferrophites provide some supportive evidence that such contacts are viable in the new ligands class, but these will not be as strong as in the phosphoramidite **14**. In nickel-catalysed 1,2-additions of $AlMe_3$ to aldehydes the sense of stereoinduction is identical for both ligand types despite their very different constitutions. However, the difference in the degree of stereoselectivity (up to 77% *ee* for the ferrophites vs. 92% *ee* for the optimal phosphoramidite ligand) supports the suggestion that any C=C···Ni contact engendered by the ferrophites is less strong than in the Feringa parent. In asymmetric conjugate addition of organoaluminium reagents to cyclohexenone, the ferrophites outperform Feringa's ligand **14** in the reactions tried thus far suggesting that they will find utility in this and other asymmetric reactions.

Experimental Section

General: All reactions involving air sensitive reagents were carried out under argon using standard Schlenk techniques and glassware was flame-dried before use. The spectrometers and other instrumentation used were as described previously.[17] Fluorine NMR shifts were referenced to $CFCl_3$ and phosphorus NMR shifts to phosphoric acid. Potential C–P couplings in the aromatic region of the carbon NMR spectra have not been listed due to spectral congestion in this region. Column chromatography and TLC analyses were performed on silica gel, Davisil and Merck Silicagel 60 $F_{254+366}$, respectively, or on basic alumina, Acros aluminium oxide, activated, basic, 50–200. Tetrahydrofuran was freshly distilled under argon from sodium and benzophenone or for larger-scale reactions was degassed and passed through a column of activated alumina. Petroleum ether refers to the fraction with b.p. 40–60 °C. All other reagents were used as received without further purification. The sulfoxide **1** was prepared in the (*R*) configuration by the methodology of Kagan.[6] Compounds **2**, **3a** and **3c** were prepared according to literature procedures.[9a]

Crystallographic Data: Yellow-orange crystals of (R_p)-**8a**, (R_pR_a)-**9a**, (R_pR_a)-**9c** were grown from dichloromethane/light petroleum ether and (R_pS_a)-**10b** from benzene. All single crystal diffraction data were collected using graphite-monochromated Mo-K_α X-radiation with either a Bruker SMART APEX (**8a**) or a SMART 1000 (**9a**, **9c**, **10b**) CCD-area detector diffractometer equipped with an Oxford Cryostream cooling device. All data were collected at 150 K. Details of the individual data collections and refinements are given in Table 1. All structures were solved by direct methods using SHELXS-97 for **8a** and SIR-92 for **9a**, **9c** and **10b**. All structures were refined by least-squares full-matrix refinement against F^2 using SHELXL-97 and all non-H atoms refined with anisotropic atomic displacement parameters (ADPs). Hydrogen atoms were geometrically placed and refined as part of a riding model. All atoms were refined as described above except for the atoms of the C_5H_5 ring in **10b** which were modelled over 2 sites with occupancies 0.820(5) and 0.180(5), the minor disorder component of which was refined with isotropic ADPs. Crystallographic data for all compounds are summarised in Table 4.

CCDC-295725 to -295728 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/datarequest/cif.

(R_pS_c)-2-(Tolyl-4-sulfinyl)-1-(4-trifluoromethylphenyl)ferrocene [CpFe{η^5-1,2-C_5H_3(4-$CF_3C_6H_4$)[S(O)-4-Tol]}] (3c): To a mixture of the boronic acid **2** (566 mg, 1.54 mmol), palladium(dppf) dichloride·DCM (100 mg, 0.12 mmol), 4-bromobenzotrifluoride (0.31 mL, 2.30 mmol) and toluene (50 mL) under argon was added sodium hydroxide (2 N, 1.5 mL). The solution was heated at reflux for 4 hours, then cooled and concentrated under reduced pressure. The crude oil was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate/dichloromethane, 7:2:1) to give the product (608 mg, 84%) as an orange crystalline solid. M.p. 73–75 °C. IR ($CHCl_3$): $\tilde{\nu}_{max}$ = 2985.4 ν(CH), 1616.3, 1322.5, 1120.3, 1069.0 (br), 1040.2 ν(SO) cm^{-1}. ^1H NMR (400.1 MHz, $CDCl_3$): δ = 7.89 (d, J = 8.0 Hz, 2 H, $C_6H_4CF_3$), 7.61 (d, J = 8.0 Hz, 2 H, C_6H_4Me), 7.56 (d, J = 8.0 Hz, 2 H, $C_6H_4CF_3$), 7.27 (d, J = 8.0 Hz, 2 H, C_6H_4Me), 4.74 (app. dd, J = 2.6, 1.5 Hz, 1 H, C_5H_3), 4.49 (app. t, J = 2.6 Hz, 1 H, C_5H_3), 4.27 (app. dd, J = 2.6, 1.5 Hz, 1 H, C_5H_3), 4.22 (s, 5 H, C_5H_5), 2.42 (s, 3 H, C_6H_4Me) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 141.4, 140.4 (br), 139.8, 129.9, 129.3, 129.1 (q, J = 32 Hz), 125.4, 125.3 (q, 273 Hz), 125.0 (q, 4 Hz), 93.0, 87.4, 72.2, 71.4, 70.8, 69.8, 21.4 ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –63.0 ppm. MS (ES): m/z (%) = 469 (10) $[M + H]^+$, 330 (70) $[M + H – S(O)tol]^+$. HRMS (ES):m/z found $[M + H]^+$ 469.0516. $C_{24}H_{20}F_3FeOS$ requires 469.0536. $C_{24}H_{19}F_3FeOS$ (468.32): calcd. C 61.55, H 4.09; found C 61.55, H, 4.22.

General Procedure for the Preparation of Phosphites. Biphenyl Phosphite 5b: Under argon, a mixture of biphenol (1.30 g, 6.98 mmol) and THF (10 mL) was cooled to –40 °C. To this solution was added a solution of phosphorus trichloride (0.98 mL, 11.2 mmol) in THF (9 mL). After 10 min, triethylamine (1.95 mL, 14.0 mmol) was

Table 4. Crystal data for the ligands.

Complex	(R_p)-**8a**	(R_pR_a)-**9a**	(R_pR_a)-**9c**	(R_pS_a)-**10b**
Empirical formula	$C_{28}H_{21}FeO_2P$	$C_{36}H_{25}FeO_2P$	$C_{37}H_{24}F_3FeO_2P$	$C_{40}H_{27}FeO_2P$
M_r	476.27	576.38	644.38	626.44
Cell setting, space group	orthorhombic, $P2_12_12_1$	monoclinic, $P2_1$	monoclinic, $P2_1$	orthorhombic, $P2_12_12_1$
a [Å]	9.9774(7)	10.0407(11)	11.2927(9)	11.5113(7)
b [Å]	10.7344(8)	12.1436(13)	11.9410(9)	14.7877(8)
c [Å]	20.7562(15)	11.8433(13)	22.073(2)	17.0437(10)
α [°]	90	90	90	90
β [°]	90	100.412(2)	96.277(2)	90
γ [°]	90	90	90	90
V [Å^3]	2223.0(3)	1420.3(5)	2958.6(7)	2901.3(5)
Z	4	2	4	4
D_x [Mg·m^{-3}]	1.423	1.348	1.447	1.434
μ (Mo-K_α) [mm^{-1}]	0.77	0.62	0.62	0.61
Temperature [K]	150(2)	150(2)	150(2)	150(2)
Crystal form, colour	block, orange	block, orange	column, orange	block, orange
Crystal size [mm]	0.50 × 0.39 × 0.26	0.78 × 0.65 × 0.63	0.56 × 0.26 × 0.18	0.66 × 0.59 × 0.50
T_{min}, T_{max}	0.707, 0.818	0.819, 1.000	–	0.826, 1.000
No. of measured, independent and observed reflections $I > 2\sigma(I)$	11902, 5021, 4873	8733, 5688, 5123	31692, 13311, 10376	26455, 6652, 6309
R_{int}	0.018	0.014	0.054	0.017
θ_{max} [°]	27.5	27.6	27.6	27.6
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.029, 0.072, 1.06	0.028, 0.070, 1.02	0.040, 0.092, 0.98	0.024, 0.062, 1.03
No. of relections	5021	5688	13311	6621
No. of parameters	289	362	794	419
$(\Delta/\sigma)_{max}$	0.001	0.001	0.003	0.002
$\Delta\rho_{max}$, $\Delta\rho_{min}$ [e·Å^{-3}]	0.33, –0.19	0.38, –0.17	0.58, –0.28	0.32, –0.15
Flack parameter	–0.015(12)	0.007(11)	0.00(1)	0.003(9)

added, and the reaction mixture warmed to room temperature. After a further 4 hours the mixture was filtered through a frit and concentrated under reduced pressure. The mixture was then diluted with THF (50 mL) followed by addition of triethylamine (1 mL, 7.16 mmol) and phenol (470 mg, 5.00 mmol). After 1 hour the mixture was evaporated to dryness. The product was purified by flash chromatography on silica gel (petroleum ether/Et_2O, 9:1, dry loaded) to give the product (1.20 g, 56% based on biphenol) as a white solid. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.54 (d, J = 1.5 Hz, 1 H, Ar), 7.52 (d, J = 1.5 Hz, 1 H, Ar), 7.43–7.31 (m, 6 H, Ar), 7.27–7.16 (m, 5 H, Ar) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = +144.9 ppm. Used immediately as attained.

Binaphthyl Phosphite 5c: Compound **5c** was prepared according to the general procedure. Purification by flash chromatography on silica gel (petroleum ether/Et_2O, 9:1, dry loaded) afforded 74% of **5c** as a white solid.^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 8.01 (d, J = 9.0 Hz, 1 H, Ar), 7.96–7.92 (m, 3 H, Ar), 7.58 (d, J = 9.0 Hz, 1 H, Ar), 7.48–7.34 (m, 7 H, Ar), 7.32–7.75 (m, 2 H, Ar), 7.20 (d, J = 8.5 Hz, 2 H, Ar), 7.17 (t, J = 7.0 Hz, 1 H, Ar) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 131.7, 131.3, 130.5, 129.9, 129.8 (2 C), 128.4, 128.3, 127.1, 127.0, 126.4, 126.2, 125.3, 125.0, 124.3, 121.7, 120.4, 120.3 ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = +146.1 ppm. Used immediately as attained.

General Method for Incorporation of the Phosphite. (R_p)-2-(Diphenoxyphosphanyl)-1-phenylferrocene [CpFe(η^5-1,2-C_5H_3(Ph){P(OPh)$_2$})] (7a): A solution of the sulfoxide **3a** (80 mg, 0.20 mmol) in THF (1 mL) was cooled to –78 °C under argon, then tBuLi (1.7 N *in* hexanes, 0.13 mL, 0.22 mmol) was added. After 5 minutes triphenyl phosphite (**5a**) (58 μL, 0.22 mmol) in THF (0.5 mL) was added, and an instant colour change from dark orange to yellow was observed. After 5 minutes the reaction was quenched by dropwise addition of H_2O (1 mL) and warmed to room temperature. The phases were separated and the organic layer dried ($MgSO_4$) and concentrated under reduced pressure. Purification by flash chromatography on silica gel (petroleum ether/Et_2O, 9:1) afforded 69% of (R_p)-**7a** as an orange oil. IR ($CHCl_3$): $\tilde{\nu}_{max}$ = 1593.3, 1488.1, 1162.4, 1106.5, 1071.8, 1023.8, 1001.4, 876.7 cm^{-1}. ^{1}H NMR (400.1 MHz, C_6D_6): δ = 7.96 (dd, J = 7.2, 1.2 Hz, 2 H, Ph-*o*), 7.45 (dd, J = 7.6, 1.2 Hz, 2 H, Ph-*o*), 7.32–6.85 (m, 11 H, Ph-*m*+*p*), 4.88 (m, 1 H, C_5H_3), 4.60 (m, 1 H, C_5H_3), 4.27 (app. t, J = 2.4 Hz, 1 H, C_5H_3), 4.12 (s, 5 H, C_5H_5) ppm. ^{13}C NMR (100.6 MHz, C_6D_6): δ = 156.6, 156.5, 154.9, 154.8, 152.0, 138.3, 130.0, 129.8, 129.6, 129.5, 129.4, 126.9, 124.2, 123.5, 123.3, 121.2, 121.2, 121.0, 120.9, 119.3, 119.2, 92.4 (d, J = 20 Hz), 76.2 (d, J = 15 Hz), 73.3 (d, J = 3.0 Hz), 71.0 (d, J = 2.4 Hz), 70.7 (d, J = 1.8 Hz), 70.5 (5 C) ppm. ^{31}P NMR (162 MHz, C_6D_6): δ = +174.3 ppm. MS (ES): *m*/*z* (%) = 479 (70) [M + H$^+$], 385 (30) [M – OPh$^+$], 262 (100) [M + H – P(OPh)$_2$]$^+$. HRMS (ES): *m*/*z* found [M + H]$^+$ 479.0872. $C_{28}H_{24}FeO_2P$ requires 479.0863.[α]$_D$ = –68.5 (c = 0.89, chloroform).

(R_p)-2-(Diphenoxyphosphanyl)-1-(1-naphthyl)ferrocene [CpFe{η^5-1,2-C_5H_3(1-$C_{10}H_8$)[P(OPh)$_2$]}] (7b): Compound **7b** was prepared according to the general procedure. Purification by flash chromatography on basic alumina (petroleum ether/Et_2O, 9:1) afforded 33% of (R_p)-**7b** as an orange oil. IR ($CHCl_3$): $\tilde{\nu}_{max}$ = 1593.9, 1489.5, 1382.0, 1162.1, 1107.9, 1071.6, 1023.8, 1002.7, 876.2 cm^{-1}. ^{1}H NMR (500.1 MHz, C_6D_6): δ = 8.46 (dt, J = 7.0, 1.0 Hz, 1 H, $C_{10}H_7$), 8.20 (d, J = 8.0 Hz, 1 H, $C_{10}H_7$), 7.77–7.73 (m, 2 H, Ar), 7.47 (dd, J = 8.5, 7.5 Hz, 1 H, $C_{10}H_7$), 7.35–7.24 (m, 4 H, Ar), 7.17–7.11 (m, 2 H, Ph-*m*), 6.94 (t, J = 7.5 Hz + unresolved long range couplings, 1 H, Ph-*p*), 6.90–6.84 (m, 2 H, Ph-*m*), 6.75 (t, J = 7.5 Hz + unresolved long range couplings, 1 H, Ph-*p*), 6.66 (d, J = 8.5 Hz, 2 H, Ar), 4.96 (app. dd, J = 1.0, ≈ 0.6 Hz, 1 H, C_5H_3), 4.52 (app. q, J = 2.1 Hz, 1 H, C_5H_3), 4.35 (app. t, J = 2.5 Hz, 1 H C_5H_3), 4.29 (s, 5 H, C_5H_5) ppm. ^{13}C NMR (125.8 MHz, C_6D_6): δ = 156.8, 156.7, 155.3, 134.2. 134.1, 134.0, 130.5, 130.4, 130.0, 129.3,

128.5, 128.3, 126.7, 126.1, 126.0, 125.3, 123.4, 123.3, 120.9, 120.8, 119.6, 119.5, 93.3 (d, J = 27 Hz), 80.0 (d, J = 14 Hz), 75.1 (d, J = 4.5 Hz), 70.5, 70.2 (d, J = 2.0 Hz), 70.0 (d, J = 3.0 Hz) ppm. ^{31}P NMR (121.5 MHz, C_6D_6): δ = +177.9 ppm. MS (ES): m/z (%) = 529 (35) $[M + H]^+$, 435 (50) $[M - OPh]^+$, 312 (10) $[M + H - P(OPh)_2]^+$. HRMS (ES): m/z found $[M + H]^+$ 529.1023. $C_{32}H_{26}FeO_2P$ requires 529.1020. $[a]_D$ = –180.5 (c = 1.99, chloroform).

(R_p)-2-(Diphenoxyphosphanyl)-1-(4-trifluoromethylphenyl)ferrocene [CpFe{η^5-1,2-C_5H_3(4-$CF_3C_6H_4$)[P(OPh)$_2$]}] (7c): Compound **7c** was prepared according to the general procedure. Purification by flash chromatography on silica gel (petroleum ether/Et_2O, 19:1) afforded 56% of (R_p)-**7c** as an orange oil. IR ($CHCl_3$): $\tilde{\nu}_{max}$ = 1616.1, 1593.1, 1488.3, 1161.8, 1122.9, 1106.0, 1069.4, 1024.2, 1001.7, 877.7 cm^{-1}. ^{1}H NMR (400.1 MHz, C_6D_6): δ = 7.67 (d, J = 8.0 Hz, 2 H, Ph-*o*), 7.35–7.29 (m, 4 H, Ar), 7.12–7.08 (m, 2 H, Ar), 6.98–6.91 (m, 4 H, Ar), 6.90–6.86 (m, 1 H, Ph-*p*), 6.80–6.77 (m, 1 H, Ph-*p*), 4.75 (m, 1 H, C_5H_3), 4.38 (m, 1 H, C_5H_3), 4.15 (app. t, J = 2.5 Hz, 1 H, C_5H_3), 3.95 (s, 5 H, C_5H_5) ppm. ^{13}C NMR (100.6 MHz, C_6D_6): δ = 156.4, 156.3, 154.7, 142.7, 130.0, 129.5, 125.2 (2 C), 123.7, 123.5, 120.9, 120.8, 119.3, 119.3, 90.1 (d, J = 24 Hz), 76.5 (d, J = 19 Hz), 73.7 (d, J = 4 Hz), 71.6 (d, J = 4 Hz), 71.0 (d, J = 2 Hz), 70.6 (5 C) ppm. ^{31}P NMR (121.5 MHz, C_6D_6): δ = +173.4 ppm. ^{19}F NMR (282 MHz, C_6D_6): δ = –62.3 ppm. MS (ES) m/z (%) = 547 (35) $[M + H]^+$, 453 (50) $[M - OPh]^+$, 330 (10) $[M + H - P(OPh)_2]^+$. HRMS (ES): m/z found $[M + H]^{l+}$ 547.0716. $C_{29}H_{23}F_3FeO_2P$ requires 547.0737. $[a]_D$ = –37.2 (c = 1.01, chloroform).

(R_pR_a)-2-(3,5-Dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*′]biphenalen-4-yl)-1-phenylferrocene [CpFe{η^5-1,2-C_5H_3(Ph)[P($O_2C_{12}H_8$)]}] (8a): Compound **8a** was prepared according to the general procedure. Purification by flash chromatography on silica gel (petroleum ether/Et_2O, 19:1) afforded 49% of (R_pR_a)-**8a** as an orange crystalline solid. M.p. 147–149 °C. IR ($CHCl_3$): $\tilde{\nu}_{max}$ = 1600.2, 1497.3, 1447.6, 1165.3, 1096.2, 1033.8, 1001.1, 884.4 cm^{-1}. ^{1}H NMR (400.1 MHz, C_6D_6): δ = 7.87 (d, J = 8.0 Hz, 2 H, Ph-*o*), 7.27 (dt, J = 7.6, 2.0 Hz, 2 H, Ar), 7.21–7.16 (m, 3 H, Ph-*m* + Ar), 7.12–7.06 (m, 2 H, Ar), 7.00 (tdd, J = 7.5, 1.6, ≈ 0.8 Hz, 1 H, biphenyl-H4,4′ or 5,5′), 6.95 (td, J = 7.5, 1.1 Hz, 1 H, biphenyl-H4,4′ or 5,5′), 6.89 (td, J = 7.4, 1.8 Hz, 1 H, biphenyl-H4,4′ or 5,5′), 6.77 (dd, J = 7.6, ≈ 0.8 Hz, 1 H, biphenyl-H6 or 6′), 4.50 (m, 1 H, C_5H_3), 4.22 (m, 1 H, C_5H_3), 4.08 (s, 5 H, C_5H_5), 4.03 (app. t, J = 2.0 Hz, 1 H, C_5H_3) ppm. ^{13}C NMR (100.6 MHz, C_6D_6): δ = 152.4, 151.8 (2 C), 138.0, 133.0 (2 C), 132.0, 129.9, 129.8, 129.7, 129.6, 129.5, 128.9, 127.0, 125.2, 124.5, 122.6, 122.1, 93.8 (d, 21 Hz), 73.7, 71.6, 71.3, 70.9 (6 C, m) ppm, the CF_3 carbon atom was not apparent. ^{31}P NMR (121.5 MHz, C_6D_6): δ = +205.2 ppm. MS (ES): m/z (%) = 477 (50) $[M + H]^+$, 476 (100) $[M]^+$, 262 (50) $[M + H - P(O_2C_{12}H_8)]^+$. HRMS (ES): m/z found $[M + H]^+$ 477.0747. $C_{28}H_{22}FeO_2P$ requires 477.0707. $[a]_D$ = –149.8 (c = 1.00, chloroform).

(R_pR_a)-2-(3,5-Dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*′]biphenalen-4-yl)-1-(1-naphthyl)ferrocene [CpFe{η^5-1,2-C_5H_3(1-$C_{10}H_8$)-[P($O_2C_{12}H_8$)]}] (8b): Compound **8b** was prepared according to the general procedure. Purification by flash chromatography on silica gel (petroleum ether/Et_2O, 9:1) afforded 15% of (R_pR_a)-**8b** as an orange crystalline solid. M.p. 191–192 °C. IR ($CHCl_3$): $\tilde{\nu}_{max}$ = 1601.0, 1497.1, 1377.4, 1165.9, 1096.3, 890.7 cm^{-1}. ^{1}H NMR (400.1 MHz, C_6D_6): δ = 8.60 (d, J = 8.0 Hz, 1 H, Ar), 8.48 (d, J = 7.2 Hz, 1 H, Ar), 7.79 (d, J = 8.0 Hz, 1 H, Ar), 7.74 (d, J = 8.0 Hz, 1 H, Ar), 7.51–7.45 (m, 2 H, Ar), 7.42–7.35 (m, 2 H, Ar), 7.34–7.28 (m, 2 H, Ar), 7.18 (td, J = 7.6, 1.2 Hz, 1 H, Ar), 7.11–7.06 (m, 3 H, Ar), 6.99–6.95 (m, 1 H, Ar), 4.60–4.58 (br. m, 1 H, C_5H_3), 4.40–4.38 (br. m, 1 H, C_5H_3), 4.33 (s, 5 H, C_5H_5), 4.26 (app. t, J = 2.0 Hz, 1 H, C_5H_3) ppm. ^{13}C NMR (100.6 MHz, C_6D_6): δ = 155.0, 131.2, 130.6, 129.8, 129.3, 127.2, 126.4, 125.9, 125.8, 125.7, 125.2, 125.0, 124.4, 122.6, 122.0, 121.0, 120.6, 75.7, 71.3, 71.2, 70.7 (5 C), 69.8 ppm. ^{31}P NMR (121.5 MHz, C_6D_6): δ = +206.3 ppm. MS (ES): m/z (%) = 527 (100) $[M + H]^+$, 526 (5) $[M]^+$, 312 (100) $[M + H - P(O_2C_{12}H_8)]^+$. HRMS (ES): m/z found $[M + H]^+$ 527.0863. $C_{32}H_{24}FeO_2P$ requires 527.0863. $[a]_D$ = –209.0 (c = 1.00, chloroform).

(R_pR_a)-2-(3,5-Dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*′]biphenalen-4-yl)-1-(4-trifluoromethylphenyl)ferrocene [CpFe{η^5-1,2-C_5H_3(4-$CF_3C_6H_4$)[P($O_2C_{12}H_8$)]}] (8c): Compound **8c** was prepared according to the general procedure. Purification by flash chromatography on silica gel (petroleum ether/Et_2O, 19:1) afforded 26% of (R_pR_a)-**8c** as an orange crystalline solid. M.p. 73–75 °C. IR ($CHCl_3$): $\tilde{\nu}_{max}$ = 1615.8, 1325.5, 1165.7, 1120.8, 1096.4, 1069.3, 889.9 cm^{-1}. ^{1}H NMR (400.1 MHz, C_6D_6): δ = 7.69 (d, J = 8.0 Hz, 2 H, $C_6H_4CF_3$), 7.32 (d, J = 8.0 Hz, 2 H, $C_6H_4CF_3$), 7.27 (dd, J = 7.4, 1.9 Hz, 1 H, biphenyl-H3 or 3′), 7.26 (dd, J = 7.5, 1.7 Hz, 1 H, biphenyl-H3 or 3′), 7.19 (dt, J = 8.0, ≈ 0.8 Hz, 1 H, biphenyl-H6 or 6′), 7.11 (td, J = 7.5, 1.6 Hz, 1 H, biphenyl-H4,4′ or 5,5′), 7.01 (tdd, J = 7.5, 1.6, ≈ 0.8 Hz, 1 H, biphenyl-H4,4′ or 5,5′), 6.95 (td, J = 7.5, ≈ 0.8 Hz, 1 H, biphenyl-H4,4′ or 5,5′), 6.92 (td, J = 7.5, 1.6 Hz, 1 H, biphenyl-H4,4′ or 5,5′), 6.77 (dd, J = 7.5, ≈ 0.8 Hz, 1 H, biphenyl-H6 or 6′), 4.39 (m, 1 H, C_5H_3), 4.23 (m, 1 H, C_5H_3), 4.03 (app. t J = 2.4 Hz, 1 H, C_5H_3), overlapped by 4.02 (s, 5 H, C_5H_5) ppm. ^{13}C NMR (100.6 MHz, C_6D_6): δ = 152.2, 151.6 (2 C), 142.4, 132.8 (2 C), 131.9, 130.0 (2 C), 129.6 (3 C), 129.0, 125.5 (2 C), 125.1 (q, J = 218 Hz), 124.9, 122.5, 122.2, 91.6 (d, J = 20 Hz), 74.8, 74.3 (d, J = 34 Hz), 71.6, 71.5, 71.2 (5 C) ppm. ^{31}P NMR (121.5 MHz, C_6D_6): δ = +203.7 ppm. ^{19}F NMR (282 MHz, C_6D_6): δ = –62.3. MS (ES): m/z (%) = 545 (100) $[M + H]^+$, 544 (10) $[M]^+$, 330 (90) $[M + H - P(O_2C_{12}H_8)]^+$. HRMS (ES) m/z found $[M + H]^+$ 545.0557. $C_{29}H_{21}F_3FeO_2P$ requires 545.0581. $[a]_D$ = –85.4 (c = 1.08, chloroform).

(R_pR_a)-2-(3,5-Dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*′]dinaphthalen-4-yl)-1-phenylferrocene [CpFe{η^5-1,2-C_5H_3(Ph)[P($O_2C_{20}H_{12}$)]}] (9a): Compound **9a** was prepared according to the general procedure. Purification by flash chromatography on silica gel (petroleum ether/Et_2O, 9:1) afforded 71% of (R_pR_a)-**9a** as an orange crystalline solid. M.p. 218–220 °C. IR ($CHCl_3$): $\tilde{\nu}_{max}$ = 1589.5, 1462.2, 1360.0, 1324.5, 1106.5, 1070.3, 981.6, 950.0 cm^{-1}. ^{1}H NMR (500.1 MHz, C_6D_6): δ = 8.03 (d, J = 8.0 Hz, 2 H, Ph-*o*), 7.82 (t, J = 8.7 Hz, 2 H, Ar), 7.75 (t, J = 8.7 Hz, 2 H, Ar), 7.65 (t, J = 7.5 Hz, 2 H, Ar), 7.62 (d, J = 8.7 Hz, 1 H, Ar), 7.34 (t, J = 8.0 Hz, 2 H, Ph-*m*), 7.31–7.22 (m, 3 H, Ph-*p* + Ar), 7.20 (d, J = 8.7 Hz, 1 H, Ar), 7.13–7.07 (m, 2 H, Ar), 4.60 (dd, J = 3.9, 2.0 Hz, 1 H, C_5H_3), 4.18 (s, 5 H, C_5H_5), 4.00–3.98 (m, 2 H, C_5H_3) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 150.4, 150.3, 149.2, 149.1, 137.5, 133.0, 132.6, 131.6, 131.0, 130.5, 129.5, 129.4, 129.3, 128.4, 128.3, 127.0 (2 C), 126.8, 126.2, 126.0, 124.9, 124.6, 123.7, 123.6, 122.5, 121.7, 93.7 (d, J = 27 Hz), 74.0 (2 C), 72.9, 72.5, 70.7 (5 C, m) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = +189.3 ppm. MS (ES): m/z (%) = 577 (100) $[M + H]^+$, 576 (10) $[M]^+$, 262 (40) $[M + H - P(O_2C_{20}H_{12})]^+$. HRMS (ES) m/z found $[M + H]^+$ 577.0975. $C_{36}H_{26}FeO_2P$ requires 577.1020. $C_{36}H_{25}FeO_2P$ (576.41): calcd. C 75.01, H 4.37; found C 75.19, H 4.32. $[a]_D$ = –386.0 (c = 1.00, chloroform). X-ray crystal structure obtained.

(R_pR_a)-2-(3,5-Dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*′]dinaphthalen-4-yl)-1-(1-naphthyl)ferrocene [CpFe{η^5-1,2-C_5H_3(1-$C_{10}H_8$)-[P($O_2C_{20}H_{12}$)]}] (9b): Compound **9b** was prepared according to the general procedure. Purification by flash chromatography on silica

gel (petroleum ether/Et_2O, 9:1) afforded 61% of (R_pR_a)-**9b** as an orange crystalline solid. M.p. 210–212 °C. IR ($CHCl_3$): $\tilde{\nu}_{max}$ = 1589.5, 1462.9, 1372.1, 1327.3, 1108.1, 1070.3, 981.6, 950.0 cm^{-1}. ^1H NMR (400.1 MHz, C_6D_6): δ = 8.71 (d, J = 8.4 Hz, 1 H, Ar), 8.52 (ddd, J = 7.2, 2.0, 1.2 Hz, 1 H, Ar), 7.82–7.73 (m, 6 H, Ar), 7.68 (d, J = 8.8 Hz, 1 H, Ar), 7.62 (dd, J = 8.8, 0.4 Hz, 1 H, Ar), 7.58 (d, J = 8.8 Hz, 1 H, Ar), 7.56 (dd, J = 6.8, 1.2 Hz, 1 H, Ar), 7.50 (dd, J = 8.0, 7.2 Hz, 1 H, Ar), 7.43 (dd, J = 6.8, 1.2 Hz, 1 H, Ar), 7.30–7.24 (m, 3 H, Ar), 7.10 (dd, J = 6.8, 1.2 Hz, 1 H, Ar), 7.05 (dd, J = 6.8, 1.2 Hz, 1 H, Ar), 4.60 (app. dd, J = 3.6, 2.4 Hz, 1 H, C_5H_3), 4.30 (s, 5 H, C_5H_5), 4.10 (app. t, J = 2.4 Hz, 1 H, C_5H_3), 4.00 (app. dd, J = 2.4, 1.2 Hz, 1 H, C_5H_3) ppm. ^{13}C NMR (100.6 MHz, C_6D_6): δ = 150.8 (2 C), 149.9 (2 C), 134.2, 133.6 (2 C), 133.4 (2 C), 133.1, 131.8, 131.3, 130.7, 130.6, 129.5, 128.8, 128.5, 128.3, 127.2, 127.0, 126.4 (2 C), 126.2, 125.8, 125.7, 125.2, 124.8, 124.7, 123.0, 121.8, 94.1 (d, J = 30 Hz), 75.8 (d, J = 3.2 Hz), 70.8, 70.7, 70.0, 65.7 ppm. ^{31}P NMR (202.5 MHz, C_6D_6): δ = +189.0 ppm. MS (ES): m/z (%) = 627 (100) $[M + H]^+$, 626 (10) $[M]^+$, 312 (10) $[M + H – P(O_2C_{20}H_{12})]^+$. HRMS (ES) m/z found $[M + H]^+$ 627.1122. $C_{40}H_{28}FeO_2P$ requires 627.1176. $[\alpha]_D$ = –355.2 (c = 1.00, chloroform).

(R_pR_a)-2-(3,5-Dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*′]dinaphthalen-4-yl)-1-(4-trifluoromethylphenyl)ferrocene [CpFe{η^5-1,2-C_5H_3(4-$CF_3C_6H_4$)[P($O_2C_{20}H_{12}$)]}] (9c): Compound **9c** was prepared according to the general procedure. Purification by flash chromatography on silica gel (petroleum ether/Et_2O, 9:1) afforded 44% of (R_pR_a)-**9c** as an orange crystalline solid. M.p. 236–237 °C. ^1H NMR (500.1 MHz, C_6D_6): δ = 7.86–7.83 (m, 3 H, Ar), 7.80 (d, J = 8.2 Hz, 1 H, Ar), 7.77–7.75 (m, 2 H, Ar), 7.66–7.62 (m, 3 H, Ar), 7.47 (d, J = 8.2 Hz, 2 H, Ar), 7.31–7.27 (m, 2 H, Ar), 7.16 (d, J = 8.7 Hz, 1 H, Ar), 7.11–7.07 (m, 2 H, Ar), 4.74 (dd, J = 3.7, 2.0 Hz, 1 H, C_5H_3), 4.13 (s, 5 H, C_5H_5), 4.00–3.98 (m, 2 H, C_5H_3) ppm. ^{13}C NMR (100.6 MHz, C_6D_6): δ = 150.5, 150.6, 149.6, 149.6, 142.4, 133.4, 133.3, 131.9, 131.3, 130.9, 129.6, 129.5, 128.6 (2 C), 127.2, 127.0, 126.6, 126.4, 125.4, 125.3, 125.0, 124.8, 22.6, 121.7, 91.2 (d, J = 26 Hz), 74.7 (d, J = 3.0 Hz), 71.6 (2 C), 71.4, 71.0 (5 C) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = +187.6 ppm. ^{19}F NMR (282 MHz, C_6D_6): δ = –62.4 ppm. MS (ES): m/z (%) = 645 (30) $[M + H]^+$, 644 (20) $[M]^+$. HRMS (ES) m/z found $[M + H]^+$ 645.0892. $C_{37}H_{25}FeF_3O_2P$ requires 645.0894. $C_{37}H_{25}FeF_3O_2P$ (644.40): calcd. C 68.96, H 3.75; found C 68.57, H 3.77. $[\alpha]_D$ = –285.8 (c = 1.00, chloroform).

(R_pS_a)-2-(3,5-Dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*′]dinaphthalen-4-yl)-1-(1-naphthyl)ferrocene [CpFe{η^5-1,2-C_5H_3(1-$C_{10}H_8$)-[P($O_2C_{20}H_{12}$)]}] (10b): Compound **10b** was prepared according to the general procedure. A portion (250 mg) of the crude reaction mixture was purified by flash chromatography on basic alumina (petroleum ether/Et_2O, 4:1) to afford a mixture of the target compound and the proton-quenched product. Recrystallisation of the mixture (benzene) led to pure (R_pS_a)-**10b** as orange crystals (40 mg, 8%). The remainder of the crude reaction mixture by flash chromatography on silica gel led only to decomposition.^1H NMR (500.1 MHz, C_6D_6): δ = 8.26 (dd, J = 7.1, 1.1 Hz, 1 H, Ar), 7.66 (br. d, J = 7.0 Hz, 1 H, Ar), 7.69–7.63 (m, 3 H, Ar), 7.54 (d, J = 7.8 Hz, 1 H, Ar), 7.46 (dd, J = 8.6, 2.8 Hz, 1 H, Ar), 7.44–7.34 (m, 5 H, Ar), 7.32–7.22 (m, 3 H, Ar), 7.21–7.17 (m, 1 H, Ar), 7.14–7.10 (m, 1 H, Ar), 7.04–7.01 (m, 1 H, Ar), 6.99–6.95 (m, 1 H, Ar), 4.67–4.65 (m, 1 H, C_5H_3) 4.46 (s, 5 H, C_5H_5), overlapped by 4.48–4.45 (m, 1 H, C_5H_3), 4.28 (app. t J = 2.5 Hz, 1 H, C_5H_3) ppm; satisfactory ^{13}C NMR spectra could not be obtained due to degradation in solution: benzene (slow and only sparingly soluble) and chloroform (rapid). ^{31}P NMR (202 MHz, C_6D_6): δ = +196.8 ppm. MS (ES): m/z (%) = 667 (100) $[M + H_2O + Na]^+$, 645 (75) $[M + H_2O]^+$, 312 (20) $[M + H – P(O_2C_{20}H_{12})]^+$. HRMS (ES): m/z found $[M + H_2O + H]^+$ 645.1307. $C_{40}H_{30}FeO_3P$ requires 645.1277.

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