Synthesis, characterization and diastereoselective coordination of a planarly chiral, hybrid ferrocene ligand, (S_p)-2-(diphenylphosphino)ferrocenecarboxylic acid

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Hydrolytic cleavage of the dihydrooxazole ring in (S_p)-2-{2-(diphenylphosphino)ferrocenyl}-4-(1-methylethyl)-4,5-dihydrooxazole affords the planarly chiral functionalized phosphine, (S_p)-2-(diphenylphosphino)-ferrocenecarboxylic acid, (S_p)-Hpfc, in two steps and 65% yield. (S_p)-Hpfc, all intermediates and the corresponding phosphine oxides were characterized by elemental analysis, multinuclear NMR and IR spectroscopy, and by optical rotation measurements. Solid-state structures of the phosphine oxides were further studied by X-ray crystallography to reveal extensive hydrogen bonding of various types. Neutralization of (S_p)-Hpfc with *tert*-BuOK followed by metathesis of the *in situ* obtained salt with [{RuCl(μ-Cl)(η^6-*p*-cymene)}$_2$] gives a chelate complex [RuCl(pfc-κ^2*O*,*P*)(η^6-*p*-cymene)], **5**, as a kinetic 1 : 1 mixture of diastereoisomers. Upon standing in solution, the diastereomeric mixture undergoes a spontaneous resolution to yield the thermodynamically preferred diastereoisomer (R_{Ru},S_p)-**5** whose configuration was corroborated by X-ray crystallography; the (R_{Ru},S_p)-**5** diastereoisomer was obtained in 82% yield by crystallization. The epimerization is likely initiated by a reversible Ru–O bond cleavage and suggests a hemilabile coordination of the (S_p)-pfc$^-$ anion. However, according to NMR spectra pure (R_{Ru},S_p)-**5** does not undergo diastereoisomer interconversion in a solution, which is in agreement with an unfavourable geometric arrangement of the (S_{Ru})-epimer.

In spite of challenging advances in the synthesis and catalytic applications of planarly chiral η^6-arene tricarbonylchromium(0)[1] and cymantrene[2] complexes, enantioselective homogeneous catalysis with organometallic ligands is still dominated by ferrocene compounds.[3] Among others, the development of chiral ferrocene ligands was initiated by the discovery of selective *ortho*-metalation[4] of (*N*,*N*-dimethylaminomethyl)ferrocene[5] and its diastereoselective variant using C-chiral (1-ferrocenylethyl)dimethylamine (Chart 1, **A**).[6] An approach combining successive *ortho*-lithiation/functionalization and replacement of the dimethylamino group resulted in the latter case in the synthesis of numerous ferrocene derivatives with mixed central and planar chirality (Chart 1, **B**), which were used as effective catalyst components, even on the industry scale.[7] Since then, other chiral directing groups have been used to synthesize planarly chiral ferrocenes by the diastereoselective *ortho*-metalation approach.[8] More recently, and very likely stimulated by successful applications of dihydrooxazole-modified triphenylphosphine[9] (Chart 1, **C**), this methodology was extended to C-chiral ferrocene 4,5-dihydrooxazoles (or oxazolines)[10] to provide functionalized ferrocene oxazolines[11] (Chart 1, **D**), which were tested as ligands in various transition-metal catalyzed reactions.[12]

However, besides being an excellent chiral auxiliary group, the oxazoline ring may also be looked upon as a carboxyl-protecting group, which can be built up from readily available β-aminoalcohols and efficiently deprotected to give carboxylic acids after a synthetic transformation of the protected molecule.[10a,13] In this way, application of the protecting group approach towards 2-phosphinoferrocene oxazolines yields phosphinocarboxylic acids,[14] which have been successfully applied in catalysis.[15]

We have recently reported the synthesis of 1′-(diphenylphosphino)ferrocenecarboxylic acid (Hdpf)[16] and also demonstrated its ability to bind transition metals in various coordination modes.[17] This article describes the preparation, spectral characterization and solid-state structures of the planarly chiral isomer of Hdpf, (S_p)-2-(diphenylphosphino)ferrocencarboxylic acid (Hpfc) and related phosphine oxide derivatives. Furthermore, diastereoselective synthesis of a ruthenium complex with an O,P-chelating pfc$^-$ anion, [RuCl(pfc-κ^2*O*,*P*)(η^6-*p*-cymene)], is presented and factors influencing the course of complex formation are discussed with respect to the solid-state structure of the preferred diastereoisomer.

It should be noted that (S_p)-Hpfc has already been reported twice as an intermediate in the synthesis of

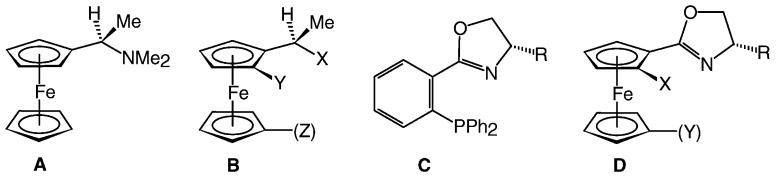


Chart 1

diamidodiphosphine ligands for allylic substitution—however, full experimental details or characterization data were *not* provided in either case.[18]

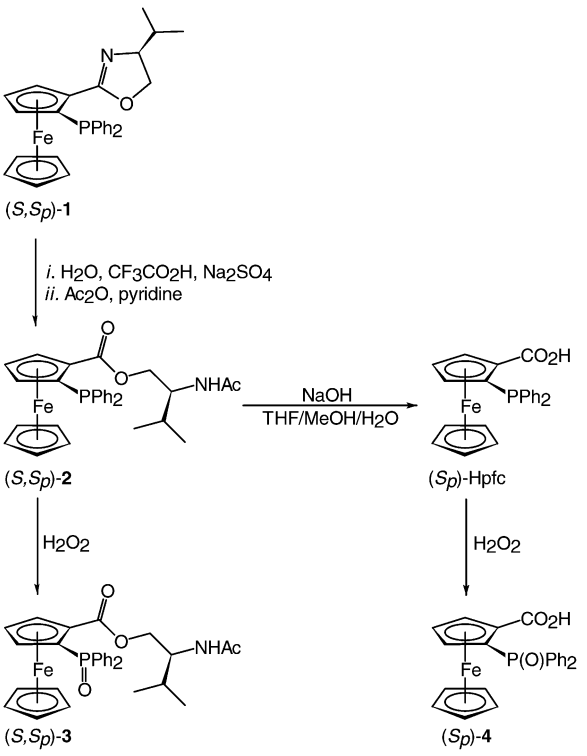
Results and discussion

Syntheses and characterization

(S_p)-Hpfc was prepared by the standard oxazoline ring-opening protocol[19] from oxazoline (S,S_p)-**1** (Scheme 1): the oxazoline was first reacted with a trifluoroacetic acid–water mixture in THF to give an unstable ammonium salt intermediate, which was without isolation converted to a stable ester amide (S,S_p)-**2** using an acetic anhydride–pyridine mixture (70% yield). A subsequent saponification of the ester amide with 1 M sodium hydroxide in a ternary water–methanol–THF mixture finally afforded (S_p)-Hpfc in 93% yield after chromatography.

Possessing a defined reference chirality centre inherent in (S)-valinol, the ester amide (S,S_p)-**2** was considered suitable to crystallographically confirm the configuration at the chirality plane. However, repeated attempts to obtain X-ray quality crystals met with no success since the compound tenaciously forms a glassy solid upon recrystallization. Fortunately, this is not the case of the analogous phosphine oxide (S,S_p)-**3**, which was obtained by hydrogen peroxide oxidation of the parent phosphine (Scheme 1). Similarly, the oxidation of (S_p)-Hpfc, which is also obtained as a non-crystallizing orange solid material, gives quantitatively the corresponding phosphine oxide (S_p)-**4**, whose solid-state structure was determined.

All compounds were characterized by NMR and IR spectroscopy, elemental analyses and molar optical rotations. The ^{1}H NMR spectra of all compounds show a set of resonances typical for an unsymmetrically 1,2-disubstituted ferrocene unit, consisting of a sharp singlet (C_5H_5) and three characteristic multiplets due to the non-equivalent C_5H_3 protons. In ^{13}C NMR spectra, the signals of the ferrocene C_5H_3 carbon atoms are observed as phosphorus-coupled doublets whilst the C_5H_5 resonance usually remains uncoupled. The signals due to the diastereotopic phenyl rings appear as well resolved doublets with the J_{PC} scalar coupling constants similar to those of triphenylphosphine and triphenylphosphine oxide, respectively.[20]



Scheme 1

Solid-state structure of (S,S_p)-3

The molecular structure of compound (S,S_p)-**3** is shown in Fig. 1 and selected geometric parameters are listed in Table 1. Both the (S)-configuration at C(25) and Flack's enantiomorph parameter (see Table 4) corroborate the expected (S_p)-configuration at the ferrocene unit.

Compared to 1′-(diphenylphosphinoyl)ferrocenecarboxylic acid [P=O 1.487(2) Å][16] and 1,1′-bis(diphenylphosphinoyl)-ferrocene [P=O 1.493(2) Å],[21] (S,S_p)-**3** exhibits a shorter P–O bond length. However, the other parameters describing the geometry of the diphenylphosphinoyl moiety are similar in all the mentioned compounds. The arrangement of the ester amide side-chain is best described as consisting of two planar parts, [C(11)C(1)O(1)O(2)C(24)] and [C(30)C(29)O(4)NC(25)] (perpendicular distances of the plane-defining atom to the least-squares plane are shorter than 0.20 Å), which subtend a dihedral angle of 15.7(3)°. Such an arrangement seems to be brought about by the formation of an unsymmetric three-centred hydrogen bonds between the amide hydrogen and the O(2) and O(3) oxygen atoms [N–H(90)···O(3): N···O(3) 2.868(3), N–H(90) 0.86(2) Å, N–H(90)···O(3) 172(2)°; N–H(90)···O(2): N···O(2) 2.773(3) Å, N–H(90)···O(2) 103(2)°].

The intramolecular hydrogen bonding that controls the conformation of the ester amide side chain and very likely accounts for the remarkably different crystallization abilities of the phosphine-phosphine oxide pair (S,S_p)-**2** and (S,S_p)-**3**, leaves the ferrocene framework in (S,S_p)-**3** virtually intact. The carboxyl group plane is nearly coplanar with the adjacent cyclopentadienyl plane, the dihedral angle of the Cp[1] and [C(11)O(1)O(2)] least-squares planes being 5.4(3)°. The ferrocene cyclopentadienyl rings adopt a close-to-eclipsed conformation as evidenced by the torsion angle τ[C(1)–Cg[1]–Cg[2]–C(10)] of −7.9(2)° and are tilted at a dihedral angle of 1.7(1)°.

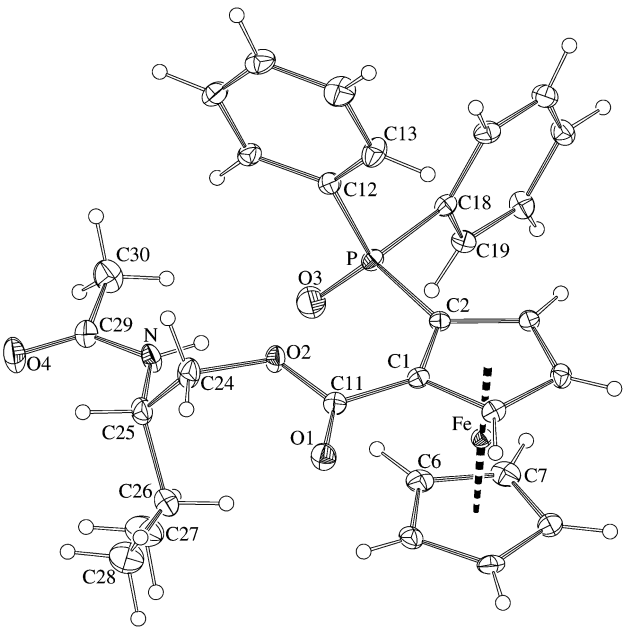


Fig. 1 Structure of (S,S_p)-**3** drawn at the 30% probability level. Ring atoms are labelled consecutively, hence, labels of only pivot and adjacent atoms are shown.

Table 1 Selected geometric data for compound (S,S_p)-**3**[a]

Fe–Cg^1	1.642(1)	Fe–C(Cp) ave.	2.04(1)
Fe–Cg^2	1.650(1)	C–C(Cp) ave.	1.42(1)
P–O(3)	1.458(2)	O(3)–P–C(2,12,18)	109.4(1)–118.9(1)
C(2)–P	1.801(2)	C–P–C[b]	102.6(1)–106.6(1)
P–C(12)	1.808(2)	C(1)–C(2)–P	129.4(2)
P–C(18)	1.813(2)	C(3)–C(2)–P	124.2(2)
C(1)–C(11)	1.482(3)	O(1)–C(11)–O(2)	125.1(2)
C(11)–O(1)	1.210(3)	C(5)–C(1)–C(11)	123.0(2)
C(11)–O(2)	1.336(3)	C(2)–C(1)–C(11)	128.9(2)
O(2)–C(24)	1.462(3)	C(11)–O(2)–C(24)	118.8(2)
C(24)–C(25)	1.513(4)	O(2)–C(24)–C(25)	109.2(2)
C(25)–C(26)	1.543(4)	C(24)–C(25)–C(26)	112.4(2)
C(26)–C(27)	1.525(5)	N–C(25)–C(24)	109.0(2)
C(26)–C(28)	1.514(5)	N–C(25)–C(26)	113.6(2)
C(25)–N	1.456(3)	C(25)–C(26)–C(27)	112.2(3)
N–C(29)	1.350(3)	C(25)–C(26)–C(28)	109.6(3)
C(29)–O(4)	1.222(3)	C(27)–C(26)–C(28)	111.2(3)
C(29)–C(30)	1.508(4)	C(25)–N–C(29)	122.5(2)
		N–C(29)–C(30)	114.8(2)
		O(4)–C(29)–N	123.7(2)
		O(4)–C(29)–C(30)	121.4(2)
C(11)–C(1)–C(2)–P			3.2(4)
C(2)–C(1)–C(11)–O(1)			173.6(2)
C(2)–C(1)–C(11)–O(2)			−8.0(3)
Cp^1,Cp^2	1.7(1)	Cp^1,Ph^1	80.8(1)
Ph^1,Ph^2	68.4(2)	Cp^1,Ph^2	84.2(1)

[a] Plane definitions: Cp^1, C(1–5); Cp^2, C(6–10); Ph^1, C(12–17); Ph^2, C(18–23). Cg^1 and Cg^2 are centroids of the rings Cp^1 and Cp^2, respectively. [b] C(2)–P–C(12,18) and C(12)–P–C(18) angles.

Table 2 Selected geometric data for compound (S_p)-**4**[a]

Fe–Cg^1	1.640(1)	Fe–C(Cp) ave.	2.04(1)
Fe–Cg^2	1.653(2)	C–C(Cp) ave.	1.42(2)
P–O(3)	1.456(3)	O(3)–P–C(2,12,18)	107.8(2)–119.1(2)
C(2)–P	1.796(3)	C–P–C[b]	101.6(2)–105.3(2)
P–C(12)	1.799(3)	C(1)–C(2)–P	128.1(2)
P–C(18)	1.819(4)	C(3)–C(2)–P	125.1(2)
C(1)–C(11)	1.479(5)	O(1)–C(11)–O(2)	125.3(3)
C(11)–O(1)	1.209(4)	C(5)–C(1)–C(11)	126.8(3)
C(11)–O(2)	1.332(4)	C(2)–C(1)–C(11)	124.7(3)
C(11)–C(1)–C(2)–P			5.7(4)
C(2)–C(1)–C(11)–O(1)			−8.9(5)
C(2)–C(1)–C(11)–O(2)			170.7(3)
Cp^1,Cp^2	1.8(2)	Cp^1,Ph^2	83.9(2)
Cp^1,Ph^1	78.4(2)	Ph^1,Ph^2	78.2(2)

[a] Planes are defined as follows: Cp^1, C(1–5); Cp^2, C(6–10); Ph^1, C(12–17); Ph^2, C(18–23). Cg^1 and Cg^2 are centroids of the cyclopentadienyl rings Cp^1 and Cp^2, respectively. [b] C(2)–P–C(12,18) and C(12)–P–C(18) angles.

Crystal structure of (S_p)-4

The molecular structure of the carboxyphosphine oxide (S_p)-**4** (Fig. 2, Table 2) is similar to the structure of (S,S_p)-**3**, particularly when the arrangement of the 2-(diphenylphosphinoyl)ferrocenyl moiety is considered. The two units differ only marginally in mutual rotation of the phenyl rings. Ferrocene cyclopentadienyls in (S_p)-**4** are eclipsed with a τ[C(1)–Cg^1–Cg^2–C(6)] torsion angle of −5.7(2)° and show a tilt of only 1.8(2)°. The dihedral angle subtended by the carboxyl plane [C(11)O(1)O(2)] and its parent cyclopentadienyl ring is 7.7(4)° but the orientation of the carboxyl group is exactly the opposite to that in (S,S_p)-**3**. This can be attributed to different solid-state interactions: whereas the amide (S,S_p)-**3** forms only intramolecular hydrogen bonds and its solid-state packing is molecular, the molecules of phosphine oxide (S_p)-**4** are involved in intermolecular hydrogen bonding in which the carboxyl OH group of one molecule is bonded to the phosphinoyl oxygen atom of a neighbouring molecule, thus forming infinite chains parallel to the crystallographic *a* axis [O(2)···O(3^i) 2.556(4), O(2)–H(90) 0.77(4) Å, O(2)–H(90)···O(3^i) 170(4)°; *i*: $1/2+x$, $1/2-y$, $1-z$].

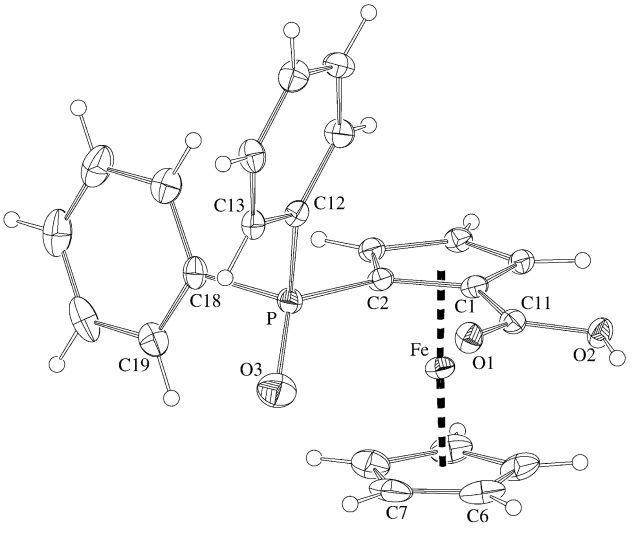
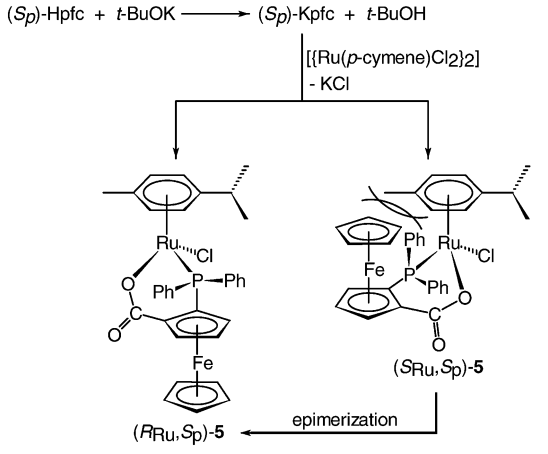


Fig. 2 Structure of (S_p)-**4** at the 30% probability level. For clarity, only labels of pivot and adjacent atoms in each ring are shown.

Preparation and structure of complex 5

Reacting [{RuCl(μ-Cl)(η^6-*p*-cymene)}$_2$] with (S_p)-Kpfc generated *in situ* from (S_p)-Hpfc and *tert*-BuOK in dichloromethane–methanol produces a chelate complex [RuCl(pfc-κ^2O,P)(η^6-*p*-cymene)], **5**. The metal centre in **5** is stereogenic due to its being surrounded by four different donors and, consequently, the formation of two diastereoisomers could be expected (Scheme 2). Surprisingly, the NMR analysis of a recrystallized sample revealed the presence of a single diastereoisomer whose absolute configuration was later determined as (R_{Ru},S_p) by X-ray crystallography (see below). Following the metathesis reaction by NMR spectroscopy (Fig. 3) has shown that both diastereoisomers are formed in a *ca.* 1 : 1 kinetic ratio (δ_P 22.3 and 28.8 in CD_2Cl_2) but the product distribution shifts slowly in favour of the thermodynamically preferred isomer (R_{Ru},S_p)-**5**. Once formed, the (R_{Ru},S_p)-isomer does not epimerize in chloroform-*d* or dichloromethane-d_2 solutions as indicated by the $^{31}P\{^1H\}$



Scheme 2

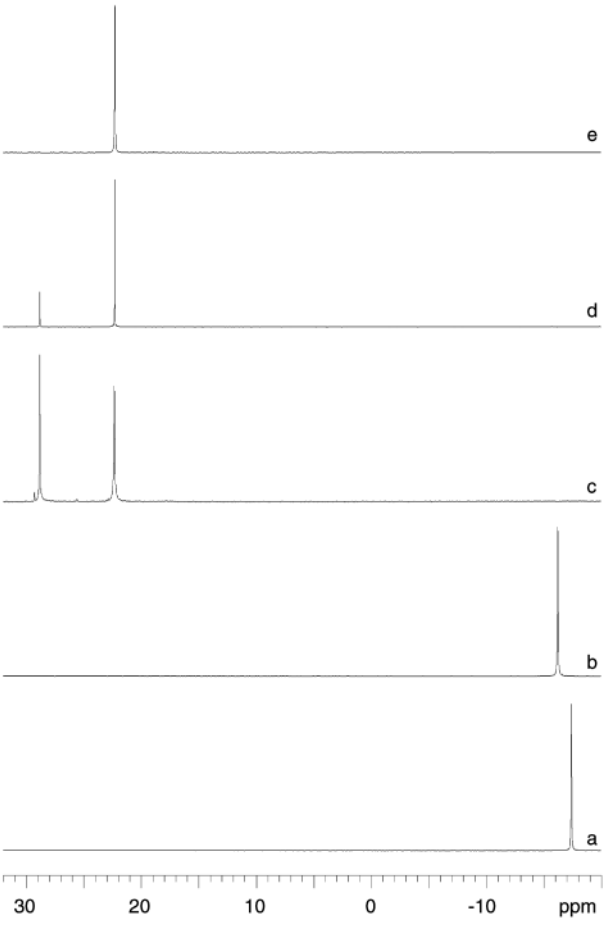


Fig. 3 $^{31}P\{^1H\}$ NMR spectra (CD_2Cl_2, 298 K) recorded to follow complex **5** formation: (a) (S_p)-Hpfc; (b) (S_p)-Kpfc prepared *in situ* from (S_p)-Hpfc and *tert*-BuOK; a mixture of (R_{Ru},S_p)-**5** (δ_P 22.3) and (S_{Ru},S_p)-**5** (δ_P 28.8) (c) after stirring (S_p)-Kpfc with [{RuCl(μ-Cl)(η^6-*p*-cymene)}$_2$] for 3 and (d) after standing overnight; (e) spectrum of a recrystallized sample [several days, (R_{Ru},S_p)-**5**].

NMR spectra. Pure (R_{Ru},S_p)-**5** can thus be obtained by simple recrystallization of the crude product from a dichloromethane–hexane mixture over several days (82% yield).

Apart from signals of the ferrocene ligand, the ^1H and $^{13}C\{^1H\}$ NMR spectra of (R_{Ru},S_p)-**5** exhibit diastereotopic and remarkably anisochronic resonances of the arene ligand. The fact that ^1H NMR signals of only the arene ligand are rather broad points to a hindered libration movement of the η^6-ligand that is slow on the NMR time scale (in $CDCl_3$ solution at room temperature).

Although no mechanistic study has been carried out, it may be expected that the isomerization mechanism is initiated by a pfc-κ^2*O*,*P* ⇄ pfc-κ*P* interconversion analogous to the fluxional behaviour of [Rh(CO)(dpf-κ^2*O*,*P*)(Hdpf-κ*P*)] in which the two forms of the Hdpf ligand rapidly interchange the acidic hydrogen atom.[17c] Involvement of a pfc-κ*O* intermediate is less likely because the bond of ruthenium to the hard oxygen donor is more labile than the bond between soft ruthenium and phosphorus atoms. The position of the isomerization equilibrium and, hence, diastereoselectivity of the reaction obviously reflects steric properties of the (S_p)-pfc$^-$ anion since the diastereomeric ratio in similar reactions varies greatly upon changing the chelate ligand. For example, (*R*)-1-{2-(diphenylphosphino)naphthyl}isoquinoline [(*R*)-Quinap] reacts with [{RuCl(μ-Cl)(η^6-*p*-cymene)}$_2$] and Ag[SbF_6], giving [RuCl-{(*R*)-Quinap-κ^2*N*,*P*}(η^6-*p*-cymene)][SbF_6] as a 5 : 1 mixture of diastereoisomers.[22] Analogous reactions with the phosphine-phosphine oxides (*R*)- and (*S*)-2-diphenylphosphinoyl-2′-diphenylphosphino-1,1′-binaphthyl (BINPO) give only one diastereoisomer[23] and similar reactions of C-chiral but racemic [$RuCl_2${$Ph_2PCH(R)P(O)Ph_2$-κ*P*}(η^6-*p*-cymene)] with Ag[SbF_6] affords uniformly cationic complexes [RuCl{$Ph_2PCH(R)P(O)Ph_2$-κ*P*,*O*}(η^6-*p*-cymene)][SbF_6] (R = Me, Pr, Ph) as single diastereoisomers with the same relative configuration.[24] In the case of related complexes with chiral α-amino acidate ligands, [RuCl($H_2NCHRCO_2$-κ^2*O*,*N*)(η^6-arene)], the ratio of diastereoisomers changes with the steric properties of the ligand and stabilization by hydrogen bonding.[25]

In an attempt to identify steric factors possibly influencing the diastereomeric equilibrium, the structure of (R_{Ru},S_p)-**5** was determined by single-crystal X-ray diffraction. Although no solvent was detected in the bulk sample, the crystal obtained by recrystallization from a dichloromethane–hexane mixture contained loosely bound solvating dichloromethane. The solvating molecules are disordered within channels parallel to the crystallographic C_4 axis in a space defined by the complex molecules (see Experimental).

The molecular structure of (R_{Ru},S_p)-**5** is shown in Fig. 4 and selected geometric parameters are given in Table 3. The molecule shows the anticipated three-legged piano stool structure in which the (S_p)-pfc$^-$ anion chelates the ruthenium centre. The six-membered metallacycle [RuPC(2)C(1)C(11)-O(2)] is almost perfectly planar; the maximum deviation of the defining atoms from their least-squares plane is only 0.070(7) Å for C(11). The arene plane and the plane of the remaining donor atoms [PClO(2)] do not deviate much from a co-planar arrangement, the corresponding dihedral angle being 8.8(3)°. The coordination environment around the ruthenium atom in (R_{Ru},S_p)-**5** is pseudo-octahedral with three sites occupied by the *fac*-coordinated η^6-arene and, hence, a deviation of the donor–Ru–donor angles from a right angle can be regarded as the measure of coordination sphere deformation. The observed values, maximum O(2)–Ru–P = 92.8(1)° and minimum O(2)–Ru–Cl = 82.6(2)°, indicate that chelation does not affect the

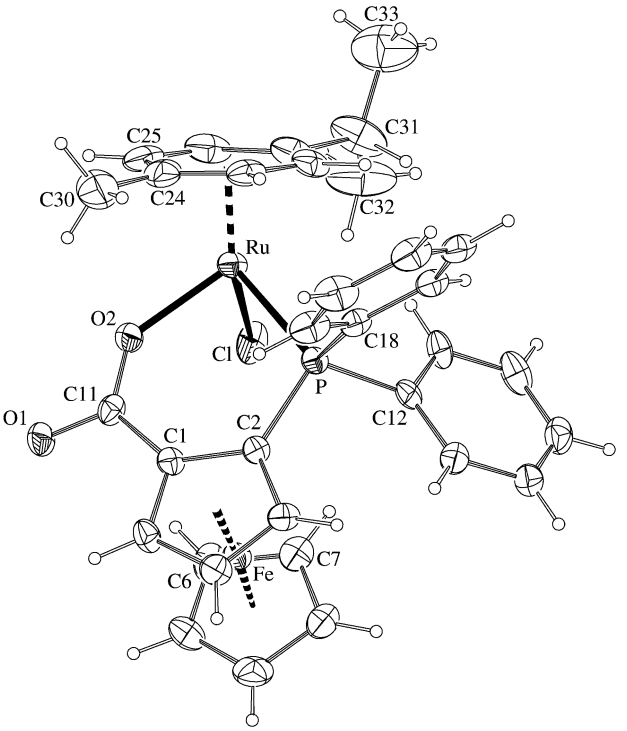


Fig. 4 Structure of (R_{Ru},S_p)-**5**·0.7CH_2Cl_2. Molecules of solvating dichloromethane are not shown. As the atom numbering scheme is similar to that of (S_p)-**4**, only selected atoms are labelled.

Table 3 Selected geometric parameters (R_{Ru},S_p)-**5** · 0.7CH_2Cl_2[a]

Fe–Cg^1	1.650(3)	Fe–C(Cp) ave.	2.03(1)
Fe–Cg^2	1.632(4)	C–C(Cp) ave.	1.41(2)
Ru–Cg^3	1.697(4)		
Ru–Cl	2.391(2)	O(2)–Ru–P	92.8(1)
Ru–P	2.325(2)	O(2)–Ru–Cl	82.6(2)
Ru–O(2)	2.066(4)	P–Ru–Cl	87.3(6)
C(2)–P	1.816(6)	Ru–P–C(2,12,18)	114.4(2)–118.8(2)
P–C(12)	1.821(7)	C–P–C[b]	100.6(3)–109.0(3)
P–C(18)	1.831(6)	C(2)–P–Ru	111.4(2)
C(1)–C(11)	1.508(8)	C(1)–C(2)–P	124.8(4)
C(11)–O(1)	1.256(8)	C(3)–C(2)–P	127.4(5)
C(12)–O(2)	1.271(8)	O(1)–C(11)–O(2)	121.4(6)
Ru–C(arene)[c]	2.171(6)–2.269(7)	C(11)–O(2)–Ru	137.7(4)
C–C(arene)[c]	1.42(1)–1.44(1)	C(5)–C(1)–C(11)	122.3(6)
C(24)–C(30)	1.48(1)	C(2)–C(1)–C(11)	130.0(6)
C(27)–C(31)	1.45(2)		
C(31)–C(32)	1.54(2)		
C(31)–C(33)	1.50(1)		
C(11)–C(1)–C(2)–P			−6.1(9)
C(2)–C(1)–C(11)–O(1)			172.5(6)
C(2)–C(1)–C(11)–O(2)			−13(1)
C(1)–C(2)–P–Ru			−0.9(5)
Cp^1,Cp^2	2.9(4)	Cym,Cp^1	51.1(4)
Cp^1,Ph^1	42.6(4)	Cym,Ph^1	45.6(4)
Cp^1,Ph^2	70.5(4)	Cym,Ph^2	34.5(4)
Ph^1,Ph^2	79.8(4)		

[a] Planes are defined as follows: Cp^1, C(1–5); Cp^2, C(6–10); Ph^1, C(12–17); Ph^2, C(18–23), and Cym, C(24–29). Cg^1 and Cg^2 are centroids of the cyclopentadienyl rings Cp^1 and Cp^2, respectively. Cg^3 denotes the centroid of the C(24–29) η^6-arene plane. [b] C(2)–P–C(12,18) and C(12)–P–C(18) angles. [c] η^6-Arene moiety: C(24–29).

metal centre geometry in any significant way. Nevertheless, the ligand bite angle O(2)–Ru–P in (R_{Ru},S_p)-**5** is about 10° larger than the angle in other structurally characterized complexes with six-membered chelate rings.[26] The Ru–donor bond lengths compare well to, for instance, a complex with a chelating 2-acetamidocinnamate ligand, [Ru{OC(O)C(=CHPh)-N(COMe)-κ^2*O*,*N*}(PPh_3)(η^6-*p*-cymene)] [Ru–O 2.073(4), C–O 1.292(8), C=O 1.226(8) and Ru–P 2.356(2) Å][27] the cationic carbene [Ru{=C(CH_2Fc)OMe}(η^6-*p*-cymene)(Hdpf-κ*P*)]PF_6 [Ru–Cl 2.390(3) and Ru–P 2.343(3) Å],[17b] a phosphinophenoxide complex, [RuCl{3-MeO-2-(PPh[2,6-$(MeO)_2C_6H_3$])-1-OC_6H_3-κ^2*O*,*P*}(η^6-*p*-cymene)] [Ru–Cl 2.401(4), Ru–O 2.069(6) and Ru–P 2.342(3) Å][28] and the diruthenium(II) complex [(μ-dppf){$RuCl_2$(η^6-1,2,3,4-$Me_4C_6H_2$)}$_2$]·CH_2Cl_2 [dppf = 1,1′-bis(diphenylphosphino)ferrocene; Ru–P 2.350(4), Ru–Cl 2.404(5) and 2.400(3) Å].[29]

The ferrocene unit in (R_{Ru},S_p)-**5** remains virtually unaffected by coordination. Its cyclopentadienyl rings are perfectly eclipsed {τ[C(1)–Cg^1–Cg^2–C(6)] = −0.1(5)°} and show a tilt of 2.9(4)°. The ferrocene unit is directed away from the Ru(η^6-arene) part so that the dihedral angle between the Cp^1 and arene least-squares planes is 51.1(1)° (see Table 3). The arrangement of the diphenylphosphino moiety is significantly distorted. The phenyl groups show different rotations with respect to the substituted cyclopentadienyl plane Cp^1 [dihedral angles 42.6(4) and 70.5(4)°], likely conforming to steric requirements of the arene ligand, which is rotated so as to bring the bulky *iso*-propyl group to a less hindered position away from the diphenylphosphinyl group. An inverted arrangement of the phosphinocarboxylate ligand with the PPh_2 group directed away from the arene ligand would be unfavourable due to crowding between the arene and the rigid ferrocene unit.

Concluding remarks

A series of planarly chiral ferrocene derivatives was obtained from ferrocenecarboxylic acid *via* oxazoline (*S*,S_p)-**1** by a combination of oxazoline protecting and chiral *ortho*-directing group approaches. The deprotonation of the key compound, (S_p)-Hpfc, gives the (S_p)-pfc^- anion capable of chelating metal centres. As exemplified by the synthesis of complex (R_{Ru},S_p)-**5**, the steric properties of the phosphinocarboxylate ligand induce highly diastereoselective chelation, yielding a thermodynamically (sterically) preferred isomer after epimerization. The mechanism of epimerization likely involves a reversible Ru–O bond cleavage, a subsequent formal rotation around the Ru–P bond and, finally, closure of the chelate ring. The proposed course of isomerization is in accordance with the expected differences in bond strengths between the soft ruthenium(II) centre and the hard and soft donor atoms of the hybrid ligand. Despite being formed in an equilibrium reaction, the (R_{Ru},S_p)-**5** diastereoisomer is stable to configurational inversion at the metal centre in solution. This fact becomes particularly important in view of the application of chiral metal-based Lewis acids resulting from halogen abstraction in systems similar to **5** as catalysts for asymmetric Diels–Alder reactions[30] or hydrogen transfer reduction of ketones.[31]

Experimental

Materials and methods

All reactions were carried under argon atmosphere. Tetrahydrofuran (THF) was dried by refluxing over potassium–benzophenone under argon. Dichloromethane was stored over potassium carbonate. Methanol, acetic anhydride and pyridine were distilled under argon. Oxazoline (*S*,S_p)-**1**[11e] and [{RuCl(μ-Cl)(η^6-*p*-cymene)}$_2$][32] were prepared by literature procedures. All other chemicals were used as received from commercial suppliers.

NMR spectra were recorded on a Varian UNITY Inova 400 spectrometer (^{1}H, 399.95; ^{13}C, 100.58; ^{31}P, 161.90 MHz) at 298 K. Chemical shifts (δ) are given relative to internal tetramethylsilane (^{1}H and ^{13}C) or external 85% aqueous H_3PO_4 (^{31}P). IR spectra were recorded on an FT IR Nicolet Magna 650 instrument in the range of 400–4000 cm^{-1}. Optical rotations were measured on an automatic polarimeter Autopol III (Rudolph Research, New Jersey; $[\alpha]_D$/deg cm^3 g^{-1} dm^{-1}, *c*/g 10^{-2} cm^{-3}). Fast atom bombardment (FAB) mass spectra were measured on a ZB-SEQ VG Analytical spectrometer (positive ion mode, Xe fast atoms, 8 kV, matrix: thioglycerol–glycerol 3 : 1).

Syntheses

(*S*,S_p)-2-Acetamido-3-methylbutyl 2-(diphenylphosphino)ferrocenecarboxylate, (*S*,S_p)-2. A mixture of water (0.90 cm^3, 50 mmol) and anhydrous sodium sulfate (7.10 g, 50 mmol) was carefully shaken up and suspended in THF (15 cm^3). The suspension was briefly stirred and oxazoline (*S*,S_p)-**1** (0.481 g, 1.00 mmol) was added. When all the oxazoline had dissolved, trifluoroacetic acid (0.39 cm^3, 5.1 mmol) was added, causing the colour of the supernatant to change from orange to red. After stirring overnight in the dark, the mixture, once again orange, was filtered to remove insoluble salts. The solid was washed with THF and the combined THF solutions were evaporated under reduced pressure at a temperature not exceeding 30 °C leaving a dark orange oil. The oil was dissolved in dichloromethane (20 cm^3), the solution cooled in an ice bath and acetic anhydride (3.3 cm^3, 35 mmol) followed by pyridine (6.6 cm^3, 70 mmol) were slowly introduced. After stirring for a

further 18 h at room temperature in the dark, the mixture was carefully washed with 3 M HCl (3×25 cm^3), saturated aqueous sodium hydrogencarbonate (3×25 cm^3) and finally with water (25 cm^3). The organic phase was dried over $MgSO_4$, evaporated and the residue purified by column chromatography (silica gel, acetate–dichloromethane, 1 : 2 v/v). A small amount of unreacted oxazoline eluted first, followed by the major band of the product. Evaporation and drying *in vacuo* (2 Torr, 80 °C, 1 h) afforded pure (S,S_p)-**2** as an orange solid (note: orange glassy material that crystallizes upon standing was obtained in several cases). Yield: 0.381 g, 70%.

^{1}H NMR ($CDCl_3$): δ 0.97 (d, $^3J_{HH} = 6.7$ Hz, 3 H, CH*Me*$_2$), 1.06 (d, $^3J_{HH} = 6.6$ Hz, 3 H, CH*Me*$_2$), 1.72 (s, 3 H, *Me*CO), 2.03–2.18 (m, 1 H, C*H*Me$_2$), 3.71 (ddd, $J \approx 2.6$, 1.5, 1.0 Hz, 1 H, C_5H_3, *H*-3), 3.83 (dd, $^3J_{HH} = 3.0$, $^2J_{HH} = 11.2$ Hz, 1 H, C*H*$_2$O), 3.88 [dddd, $^3J_{HH} \approx {}^3J_{HH} \approx 8$ (N*H*, C*H*Me$_2$), $^3J_{HH} \approx {}^3J_{HH} \approx 3$ Hz (C*H*$_2$), 1 H, C*H*NH], 4.18 (s, 5 H, C_5H_5), 4.51 (ddd, $J \approx 2.6$, 2.6, 0.6 Hz, 1 H, C_5H_3, *H*-4), 4.62 (dd, $^3J_{HH} = 3.0$, $^2J_{HH} = 11.3$ Hz, 1 H, C*H*$_2$O), 5.19 (ddd, $J \approx 2.6$, 1.5, 1.3 Hz, 1 H, C_5H_3, *H*-5), 5.66 (br d, 1 H, N*H*), 7.11–7.52 (m, 10 H, P*Ph*$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 19.52, 19.61 (CH*Me*$_2$), 23.24 (*Me*CO), 29.34 (d, $J = 4.9$ Hz, *C*HMe$_2$), 53.70 (*C*HNH), 64.89 (*C*H$_2$O), 71.05 (C_5H_5), 72.53 (C_5H_3, *C*-4), 75.15 (d, $^3J_{PC} = 1.8$ Hz, C_5H_3, *C*-5), 75.28 (d, $^1J_{PC} = 17.4$ Hz, C_5H_3, *C*-2), 75.64 (d, $^2J_{PC} = 4.3$ Hz, C_5H_3, *C*-3), 77.55 (d, $^2J_{PC} = 14.0$ Hz, C_5H_3, *C*-1), 128.23 (PPh$_2$, *C*H$_p$), 128.35 (d, $^3J_{PC} = 7.3$ Hz, PPh$_2$, *C*H$_m$), 128.39 (d, $^3J_{PC} = 6.1$ Hz, PPh$_2$, *C*H$_m$), 129.53 (PPh$_2$, *C*H$_p$), 131.77 (d, $^2J_{PC} = 17.7$ Hz, PPh$_2$, *C*H$_o$), 135.29 (d, $^2J_{PC} = 22.0$ Hz, PPh$_2$, *C*H$_o$), 137.46 (d, $^1J_{PC} = 11.0$ Hz, PPh$_2$, C_{ipso}), 139.59 (d, $^1J_{PC} = 12.2$ Hz, PPh$_2$, C_{ipso}), 169.73 (Me*C*O), 171.62 (d, $^3J_{PC} = 2.8$ Hz, *C*O$_2$). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −14.9 (s). IR (Nujol): $\tilde{\nu}$/cm^{-1} ν_{NH} 3240 (br m), ester $\nu_{C=O}$ 1710 (vs), amide I 1639 (vs), amide II $\approx$1560 (composite br m). $[\alpha]_D^{22} = -149.5°$ ($c = 1.0$, $CHCl_3$). Anal. calcd. for $C_{30}H_{32}FeNO_3P$: C, 66.55; H, 5.96; N, 2.59%. Found: C, 66.17; H, 6.06; N, 2.57%.

(S,S_p)-2-Acetamido-3-methylbutyl 2-(diphenylphosphinoyl)ferrocenecarboxylate, (S,S_p)-3. Ester amide (S,S_p)-**2** (108.8 mg, 0.20 mmol) was dissolved in acetone (5 cm^3), the solution was cooled in an ice bath and treated with excess 30% aqueous hydrogen peroxide (0.5 cm^3) for 1 h. Unreacted hydrogen peroxide was destroyed by addition of 10% aqueous sodium thiosulfate (1 cm^3) and stirring for another 30 min; acetone was evaporated under reduced pressure and the residue extracted with CH_2Cl_2. The combined organic extracts were dried with magnesium sulfate and evaporated. The residue was dissolved in a little hot ethyl acetate and the solution was allowed to crystallize by hexane diffusion over several days to give (S,S_p)-**3** as fine yellow needles (84.2 mg, 76%).

^{1}H NMR ($CDCl_3$): δ 1.03, 1.08 ($2 \times$ d, $^3J_{HH} = 6.7$ Hz, 3 H, CH*Me*$_2$); 1.88 (d of septets, $^3J_{HH} = 10.4$, 6.7 Hz, 3 H, C*H*Me$_2$), 2.13 (s, 3 H, *Me*CO), 2.94 (dd, $^2J_{HH} = 11.2$, $^3J_{HH} = 2.6$ Hz, 1 H, C*H*$_2$O), 3.75 (br dddd, $J \approx 1.6$, 2.6, 10, 10 Hz, 1 H, C*H*Me$_2$), 3.79 (ddd, $J \approx 2.6$, 1.3, 1.0 Hz, C_5H_3, *H*-3), 4.49 (s, 5 H, C_5H_5), 4.58 (ddd, $J \approx 2.6$, 2.6, 0.8 Hz, 1 H, C_5H_3, *H*-4), 5.09 (dd, $^2J_{HH} = 11.2$, $^3J_{HH} = 1.6$ Hz, 1 H, C*H*$_2$O), 5.30 (ddd, $J \approx 2.6$, 1.3, 1.3 Hz, 1 H, C_5H_3, *H*-5), 7.30–7.72 (m, 10 H, PPh$_2$), 9.11 (d, $J = 9.6$ Hz, 1 H, N*H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 19.91, 19.96 (CH*Me*$_2$), 23.32 (*Me*CO), 29.14 (*C*HMe$_2$), 54.17 (*C*HNH), 64.41 (*C*H$_2$O), 71.45 (C_5H_5), 72.98 (d, $^3J_{PC} = 12$ Hz, C_5H_3, *C*-4), 73.94 (d, $^1J_{PC} = 81$ Hz, C_5H_3, *C*-2), 74.53 (d, $^2J_{PC} = 23$ Hz, C_5H_3, *C*-1), 76.28 (d, $^3J_{PC} = 8$ Hz, C_5H_3, *C*-5), 80.21 (d, $^2J_{PC} = 15$ Hz, C_5H_3, *C*-3), 128.19, 128.31 ($2 \times$ d, $^3J_{PC} = 9$ Hz, PPh$_2$, *C*H$_m$), 131.15 (d, $^2J_{PC} = 10$ Hz, PPh$_2$, *C*H$_o$), 131.70, 131.76 ($2 \times$ d, $^4J_{PC} = 2$ Hz, PPh$_2$, *C*H$_p$), 131.80 (d, $^2J_{PC} = 10$ Hz, PPh$_2$, *C*H$_o$), 133.61 (d, $^1J_{PC} = 110$ Hz, PPh$_2$, C_{ipso}), 133.63 (d, $^1J_{PC} = 110$ Hz, PPh$_2$, C_{ipso}), 169.95, 170.11 (*C*O). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 31.8 (s). IR (Nujol): $\tilde{\nu}$/cm^{-1} ν_{NH} 3244 (m), 3214 (m); ester $\nu_{C=O}$ 1710 (vs), amide I 1674 (vs), amide II 1558 (br, m). $[\alpha]_D^{20} = -96.1°$ ($c = 1.0$, $CHCl_3$). Anal. calcd. for $C_{30}H_{32}FeNO_4P$: C, 64.64; H, 5.79; N, 2.51%. Found: C, 64.88; H, 5.68; N, 2.55%.

(S_p)-2-(Diphenylphosphino)ferrocenecarboxylic acid, (S_p)-Hpfc. Ester amide (S,S_p)-**2** (271 mg, 0.50 mmol) was dissolved in a mixture of THF (5 cm^3) and methanol (5 cm^3). An aqueous 3 M sodium hydroxide solution (5 cm^3, 15 mmol) was added and the resulting orange solution was stirred at 50 °C overnight. The organic solvents were removed under reduced pressure, the residue was acidified with aqueous 3 M HCl and extracted with dichloromethane (3×10 cm^3). The combined organic extracts were washed with water (2×25 ml), dried ($MgSO_4$) and evaporated. The residue was purified by chromatography on silica gel using a dichloromethane-methanol (20 : 1, v/v) mixture as the eluent. A small amount of methyl (S_p)-2-(diphenylphosphino)ferrocenecarboxylate is eluted first (*ca.* 7 mg, 3%; identified by NMR), followed by the product, which was obtained after evaporation and drying *in vacuo* (1 Torr, 60 °C, 1 h) as a bright orange solid (192 mg, 93%).

^{1}H NMR ($CDCl_3$): δ 3.79 (ddd, $J \approx 2.6$, 1.4, 0.9 Hz, 1 H, C_5H_3, *H*-3), 4.24 (s, 5 H, C_5H_5), 4.49 (ddd, $J \approx 2.6$, 2.6, 0.6 Hz, 1 H, C_5H_3, *H*-4), 5.09 (ddd, $J \approx 2.6$, 1.5, 1.4 Hz, 1 H, C_5H_3, *H*-5), 7.19–7.54 (m, 10 H, P*Ph*$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 71.27 (d, $J = 1.2$ Hz, C_5H_5), 72.44 (C_5H_3, *C*-4), 74.06 (d, $^1J_{PC} = 15.9$ Hz, C_5H_3, *C*-2), 74.8 (C_5H_3, *C*-5), 75.82 (d, $^2J_{PC} = 4.9$ Hz, C_5H_3, *C*-3), 76.99 (d, $^2J_{PC} = 15.9$ Hz, C_5H_3, *C*-1), 128.02 (PPh$_2$, *C*H$_p$), 128.11 (d, $^3J_{PC} = 12.2$ Hz, PPh$_2$, *C*H$_m$), 128.18 (d, $^3J_{PC} = 12.8$ Hz, PPh$_2$, *C*H$_m$), 129.13 (PPh$_2$, *C*H$_p$), 132.20 (d, $^2J_{PC} = 19.5$ Hz, PPh$_2$, *C*H$_o$), 135.04 (d, $^2J_{PC} = 21.4$ Hz, PPh$_2$, *C*H$_o$), 137.91 (d, $^1J_{PC} = 12.2$ Hz, PPh$_2$, C_{ipso}), 139.14 (d, $^1J_{PC} = 11.6$ Hz, PPh$_2$, C_{ipso}), 177.12 (d, $^2J_{PC} = 2.4$ Hz, *C*O$_2$H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −17.4 (s). IR (Nujol): $\tilde{\nu}$/cm^{-1} $\nu_{C=O}$ 1712 (m), 1664 (vs). $[\alpha]_D^{20} = -257.6°$ ($c = 0.99$, $CHCl_3$). Anal. calcd. for $C_{23}H_{19}FeO_2P$: C, 66.69; H, 4.62%. Found: C, 66.15; H, 4.71%.

(S_p)-2-(Diphenylphosphinoyl)ferrocenecarboxylic acid, (S_p)-4. Aqueous hydrogen peroxide (5 drops of 30% solution) was added to an ice-cooled solution of (S_p)-Hpfc (42 mg, 0.10 mmol) in acetone (2 cm^3) with stirring. After stirring for another 30 min at 0 °C, excess hydrogen peroxide was destroyed with 10% aqueous sodium thiosulfate (10 drops) and stirring for 30 min at room temperature. Acetone was removed under reduced pressure, and the residue was diluted with water, acidified with 3 drops of 6 M HCl and extracted into dichloromethane. The extract was dried over magnesium sulfate and evaporated to give the phosphine oxide as an orange yellow solid in quantitative yield (43 mg).

^{1}H NMR ($CDCl_3$): δ 4.21 (ddd, $J \approx 2.6$, 2.6, 1.6 Hz, 1 H, C_5H_3, *H*-3), 4.26 (s, 5 H, C_5H_5), 4.71 (ddd, $J \approx 2.6$, 2.6, 1.8 Hz, 1 H, C_5H_3, *H*-4), 5.39 (ddd, $J \approx 2.6$, 1.4, 1.4 Hz, 1 H, C_5H_3, *H*-5), 7.38–7.92 (m, 10 H, P*Ph*$_2$), 14.07 (s, 1 H, CO$_2$*H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 70.78 (d, $^1J_{PC} = 112$ Hz, C_5H_3, *C*-2), 71.51 (d, $^2J_{PC} = 13$ Hz, C_5H_3, *C*-1), 71.87 (C_5H_5), 74.18 (d, $^3J_{PC} = 11$ Hz, C_5H_3, *C*-4), 76.37 (d, $^2J_{PC} = 13$ Hz, C_5H_3, *C*-3), 76.84 (d, $^3J_{PC} = 8$ Hz, C_5H_3, *C*-5), 128.73, 128.73 ($2 \times$ d, $^3J_{PC} = 13$ Hz, PPh$_2$, *C*H$_m$); 129.71 (d, $^1J_{PC} = 111$ Hz, PPh$_2$, C_{ipso}), 131.38, 131.85 ($2 \times$ d, $^2J_{PC} = 10$ Hz, PPh$_2$, *C*H$_o$); 132.21 (d, $^1J_{PC} = 107$ Hz, PPh$_2$, C_{ipso}), 132.66 (d, $^4J_{PC} = 2$ Hz, PPh$_2$, *C*H$_p$), 133.07 (d, $^4J_{PC} = 3$ Hz, PPh$_2$, *C*H$_p$), 170.27 (*C*O$_2$H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 38.3 (s). IR (Nujol): $\tilde{\nu}$/cm^{-1} $\nu_{C=O}$ 1692 (vs). $[\alpha]_D^{20} = -37.3°$ ($c = 0.7$, $CHCl_3$). Anal. calcd. for $C_{23}H_{19}FeO_3P$: C, 64.21; H, 4.45%. Found: C, 63.61; H, 4.38%.

(R_{Ru},S_p)-Chloro[2-(diphenylphosphino)ferrocenecarboxylato-κ^2O,P]{η^6-1-methyl-4-(1-methylethyl)benzene}ruthenium(II), (R_{Ru},S_p)-5. (S_p)-Hpfc (44.2 mg, 0.11 mmol) and potassium

tert-butoxide (12.2 mg, 0.11 mmol) were dissolved in methanol (2 cm^3) and stirred for 30 min at room temperature. Then, a solution of di-μ-chloro-bis{chloro(η^6-*p*-cymene)ruthenium(II)} (30.6 mg, 50 μmol) in dichloromethane (2 cm^3) was added to the resulting solution of (S_p)-Kpfc. A fine precipitate formed immediately. After the mixture had been stirred for 3 h, the solvents were evaporated under reduced pressure and the solid residue extracted with dichloromethane (2×1 cm^3). The extract was filtered through a Celite pad to remove precipitated KCl and the clear filtrate was allowed to crystallize by liquid-phase diffusion of excess hexane over several days at −18 °C in the dark to give (R_{Ru},S_p)-**5** as a greenish brown solid (55.8 mg, 82%).

^{1}H NMR ($CDCl_3$): δ 0.89 (d, $^3J_{HH} = 6.8$ Hz, 3 H, CHMe_2), 1.13 (d, $^3J_{HH} = 7.1$ Hz, 3 H, CHMe_2), 2.03 (s, 3 H, *Me*), 2.62 (sept, $^3J_{HH} = 6.9$ Hz, 1 H, C*H*Me$_2$), 3.99 (s, 5 H, C_5H_5), 4.21 (dt, $J \approx 2.6$, 1.4, 1.4 Hz, 1 H, C_5H_3, *H*-5), 4.33 (br dt, $J = 5.7$ Hz, 1 H, C_6H_4, *H*-3), 4.44 (t, $J \approx 2.6$ Hz, 1 H, C_5H_3, *H*-4), 5.18 (br dd, $J = 5.5$, 1.9 Hz, 1 H, C_6H_4, *H*-2), 5.32 (br d, $J = 6.3$ Hz, 1 H, C_6H_4, *H*-6), 5.35 (dt, $J \approx 1.4$, 1.4, 2.5 Hz, 1 H, C_5H_3, *H*-3), 5.69 (br d, $J = 6.4$ Hz, 1 H, C_6H_4, *H*-5), 7.10–8.30 (m, 10 H, P*Ph*$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 18.01 (*Me*), 21.07, 22.75 (CH*Me*$_2$), 29.86 (*C*HMe$_2$), 69.32 (d, $^1J_{PC} = 51$ Hz, C_5H_3, *C*-2), 71.73 (C_5H_5), 72.42 (d, $^3J_{PC} = 6$ Hz, C_5H_3, *C*-4), 72.44 (C_5H_3, *C*-5), 75.81 (d, $^2J_{PC} = 8$ Hz, C_5H_3, *C*-3), 83.83 (d, $^2J_{PC} = 16$ Hz, C_5H_3, *C*-2), 85.09 (d, $J_{PC} = 2$ Hz, C_6H_4, *C*-2), 86.81 (d, $J_{PC} = 2$ Hz, C_6H_4, *C*-3), 90.54 (d, $J_{PC} = 8$ Hz, C_6H_4, *C*-5), 93.89 (C_6H_4, *C*-1), 98.17 (d, $J_{PC} = 7$ Hz, C_6H_4, *C*-6), 107.46 (C_6H_4, *C*-4), 128.03, 128.22 ($2 \times$ d, $^3J_{PC} = 11$ Hz, PPh_2, *C*H$_m$); 129.84 (d, $^4J_{PC} =$ Hz, PPh_2, *C*H$_p$), 131.14 (d, $^2J_{PC} = 9$ Hz, PPh_2, *C*H$_o$), 131.55 (d, $^4J_{PC} = 2$ Hz, PPh_2, *C*H$_p$), 131.68 (d, $^1J_{PC} = 53$ Hz, PPh_2, C_{ipso}), 135.57 (d, $^2J_{PC} = 11$ Hz, PPh_2, *C*H$_o$), 141.95 (d, $^1J_{PC} = 51$ Hz, PPh_2, C_{ipso}), 174.19 (*C*O). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 22.1 (pfc$^-$). FAB$^+$: *m*/*z* 685.3 ([M + H]$^+$, $C_{33}H_{33}ClFeO_2PRu$).

In situ NMR study. Preparation of (S_p)-Kpfc and complex 5

(S_p)-Hpfc (11.5 mg, 28 μmol) and *tert*-BuOK (3.5 mg, 31 μmol) were dissolved in CD_2Cl_2 and allowed to stand for 30 min at room temperature. NMR spectroscopy of the mixture indicated a complete conversion of (S_p)-Hpfc to (S_p)-Kpfc. Then, [{RuCl(μ-Cl)(η^6-*p*-cymene)}$_2$] (9.5 mg, 15 μmol) was added and the mixture was analyzed by NMR spectroscopy. The ^{31}P{^{1}H} NMR spectra of a freshly prepared sample showed two signals at δ_P 22.3 and 28.8 in a *ca.* 1 : 1 ratio. Upon standing, the ratio changes in favour of the former resonance (see Fig. 3). NMR data for CD_2Cl_2 solutions, (S_p)-Hpfc: δ_H 3.80, 4.53, 5.10 ($3 \times$ m, 2 H, C_5H_3), 4.24 (s, 5 H, C_5H_5), 7.13–7.54 (m, 10 H, P*Ph*$_2$), δ_P −17.7 (s); (S_p)-Kpfc: δ_H 3.57, 4.35, 5.01 ($3 \times$ m, 2 H, C_5H_3), 4.22 (s, 5 H, C_5H_5), 6.98–7.52 (m, 10 H, P*Ph*$_2$); δ_P −16.2 (s).

To prepare complex **5** (S_p)-Hpfc (20.7 mg, 50 μmol) and *tert*-BuOK (6.5 mg, 58 μmol) were dissolved in methanol (1 cm^3). After stirring for 30 min at room temperature, a solution of [{RuCl(μ-Cl)(η^6-*p*-cymene)}$_2$] (15.3 mg, 25 μmol) in dichloromethane (1 cm^3) was added and stirring was continued for another for 3 h. Then, all volatiles were removed in vacuum, the brown residue was extracted with CD_2Cl_2 (0.7 cm^3) and the extract was analyzed by NMR spectroscopy after standing overnight. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ_P 22.3 (s, ≈82%), 28.8 (s, ≈17%).

X-Ray Crystallography

Diffraction data for compound (S,S_p)-**3** (Table 4) were collected on a Nonius KappaCCD image plate diffractometer using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å): 277 frames were measured (1.8° ω oscillation and 81 s counting time each, 40181 integrated diffractions) and analyzed with HKL program package.[33] Cell parameters were determined by least-squares fitting from 30385 partial diffractions with $1.0 \leqslant \theta \leqslant 27.1°$. The structure was solved by direct methods (SIR92[34]) and refined by full-matrix least-squares on F^2 (SHELXL97[35]). Non-hydrogen atoms were refined anisotropically. All hydrogen atoms were identified on difference electron density maps and refined with isotropic displacement parameters.

Diffraction data for compound (S_p)-**4** (Table 4) were collected as for (S,S_p)-**3** except that 102 frames were measured (2.0° ω oscillation and 180 s counting time, 11 558 integrated diffractions) and the cell parameters were determined from

Table 4 Crystallographic data, data collection and structure refinement for compounds (S,S_p)-**3**, (S_p)-**4**, and (R_{Ru},S_p)-**5**·0.7CH_2Cl_2

	(S,S_p)-**3**	(S_p)-**4**	(R_{Ru},S_p)-**5**·0.7CH_2Cl_2
Formula	$C_{30}H_{32}FeNO_4P$	$C_{23}H_{19}FeO_3P$	$C_{33.7}H_{33.4}Cl_{2.4}FeO_2PRu$[e]
Formula wt	557.39	430.20	743.37
T/K	150	150	150
Crystal system	Orthorhombic	Orthorhombic	Tetragonal
Space group	$P2_12_12_1$ (No. 19)	$P2_12_12_1$ (No. 19)	$P4_12_12$ (No. 92)
a/Å	8.5942(1)	8.7508(3)	23.9653(2)
b/Å	16.0218(3)	14.1915(6)	23.9653(2)
c/Å	19.5448(3)	15.6483(8)	11.3015(1)
$\alpha = \beta = \gamma$/°	90	90	90
U/Å^3	2691.21(7)	1943.3(2)	6490.9(1)
Z	4	4	8
μ(Mo-Kα)/mm^{-1}	0.656	0.880	1.188
No. unique diffractions	5920	3383	5727
No. observed diffractions[a]	5314	3101	5328
hkl range	0/10, 0/20, −24/25	0/10, 0/16, −18/18	−26/28, −28/28, −13/12
θ range/°	3.2–27.1	3.0–25.0	3.0–25.0
w_1, w_2[b]	0.0309, 1.3860	0.0311, 1.4405	0.0930, 6.5210
Flack's enantiomorph parameter	−0.02(1)	−0.05(2)	0.01(4)
R for obsd diffractions[c] (%)	3.33	3.63	4.95
wR for obsd diffractions[c] (%)	7.02	7.85	14.3
R for all data[c] (%)	4.25	4.46	5.39
wR for all data[c] (%)	7.41	8.28	14.6
R_{int}[d]	4.7	4.8	5.8
Residual electron density/e Å^{-3}	0.21, −0.36	0.21, −0.38	0.64, −0.74

[a] Diffractions with $I_o > 2\sigma(I_o)$. [b] Weighting scheme: $w = [\sigma^2(F_o^2) + (w_1P)^2 + w_2P]^{-1}$, where $P = 1/3[\max(F_o^2) + 2F_c^2]$. [c] $R(F) = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$, $wR(F^2) = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\{\Sigma w(F_o^2)^2\}]^{1/2}$. [d] $R_{int} = \Sigma|F_o^2 - F_{o,mean}^2|/\Sigma F_o^2$. [e] $C_{33}H_{32}ClFeO_2PRu \cdot 0.70CH_2Cl_2$.

10 490 partial diffractions with $1.0 \leqslant \theta \leqslant 25.0°$. The structure was solved and refined as given above. All non-hydrogen atoms were refined anisotropically. Aromatic hydrogen atoms were fixed in calculated positions with C–H 0.93 Å and $U_{iso}(H) = 1.2\ U_{eq}(C)$. The carboxylic hydrogen atom was identified on a difference electron density map and refined isotropically.

Diffraction data for complex (R_{Ru},S_p)-**5** (Table 4) were collected similarly to those of (S,S_p)-**3**: 340 frames (1.4° ω oscillation and 210 s counting time each, 90 565 integrated diffractions). Cell parameters were determined by least-squares refinement from 115 407 partial diffractions with $1.0 \leqslant \theta \leqslant 25.0°$. The diffraction data were corrected for absorption ($T_{min} = 0.609$, $T_{max} = 0.800$; numerical method, SORTAV routine incorporated in the program package by Nonius BV). The structure was solved and refined as described above. The non-hydrogen atoms of the complex molecule were refined anisotropically whilst all hydrogen atoms were included in calculated positions with fixed C–H bond lengths (methyl 0.96, methine 0.98 and aromatic 0.93 Å) and assigned $U_{iso}(H) = 1.2\ U_{eq}(C)$.

Difference electron density maps revealed a partial inclusion of solvent molecules. The disordered solvate was modelled as if consisting of three rigid CH_2Cl_2 moieties with constrained geometry and ocuppancies set to 0.40, 0.15 and 0.15, respectively, to give reasonable isotropic thermal motion parameters and low R values (two molecules are found in a special position with the ideal occupancy of 0.50). Although the model fits well the diffraction data, the extremes on the residual electron density map that are located in the space accommodating the solvate molecules indicate the real situation to be even more complicated than the model.

CCDC reference numbers 167918–167920. See http://www.rsc.org/suppdata/nj/b1/b109495p/ for crystallographic data in CIF or other electronic format.

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