AN ALTERNATIVE APPROACH TO CHIRAL 2-[1′-(DIPHENYLPHOSPHANYL)FERROCENYL]-4,5-DIHYDROOXAZOLES

Dušan DRAHOŇOVSKÝ[a1], Ivana CÍSAŘOVÁ[b1], Petr ŠTĚPNIČKA[b2], Hana DVOŘÁKOVÁ[c], Petr MALOŇ[d] and DALIMIL DVOŘÁK[a2,*]

[a] *Department of Organic Chemistry, Institute of Chemical Technology, Prague, 166 28 Prague 6, Czech Republic; e-mail: [1] drahonod@vscht.cz, [2] dvorakd@vscht.cz*

[b] *Department of Inorganic Chemistry, Charles University, Hlavova 2030, 128 40 Prague 2, Czech Republic; e-mail: [1] cisarova@prfdec.natur.cuni.cz, [2] stepnic@natur.cuni.cz*

[c] *Laboratory of NMR Spectroscopy, Institute of Chemical Technology, Prague, 166 28 Prague 6, Czech Republic; e-mail: hana.dvorakova@vscht.cz*

[d] *Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, 166 10 Prague 6, Czech Republic; e-mail: malon@uochb.cas.cz*

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The reaction of 1′-(diphenylphosphanoyl)ferrocenecarbonyl chloride, generated *in situ* by the reaction of 1′-(diphenylphosphanoyl)ferrocenecarboxylic acid and oxalyl chloride, with chiral aminoalcohols gave amidoalcohols [Fe(η^5-$C_5H_4P(O)Ph_2$)(η^5-$C_5H_4C(O)NHCHRCH_2OH$)] **13**, (R = i-Pr, (*S*); R = i-Pr, (*R*); R = *t*-Bu, (*S*) and R = Ph, (*R*). The amidoalcohols **13** were converted to 2-[1′-(diphenylphosphanoyl)ferrocen-1-yl]-4,5-dihydrooxazoles **14** by ring-closing reaction with a tosyl chloride–triethylamine mixture. Subsequent reduction of **14** with trichlorosilane in the presence of triethylamine afforded the corresponding 2-[1′-(diphenylphosphanyl)ferrocenyl]-4,5-dihydrooxazoles **10**. Compounds **13d**, **14d** and **10d** were subjected to a detailed ^{1}H, ^{13}C and ^{31}P NMR analyses. CD spectra of all **10** were measured. *trans*-Dichlorobis{(*S*)-2-[1′-(diphenylphosphanyl)ferrocenyl]-4-isopropyl-4-5-dihydrooxazole-κ*P*}palladium(II) (**15**) was synthesised and its solid-state structure was determined by single-crystal X-ray diffraction.

Keywords: Ferrocenes; Oxazolines; Phosphines; *P*-Ligands; Palladium; Enantioselective catalysis; Crystal structure.

Enantioselective synthesis using chiral transition-metal-based catalysts is established as an indispensable tool for organic preparative chemistry. However, design of proper chiral ligands is essential to obtain the desired enantiomer in high yield since the degree of asymmetric induction varies greatly with even very minor changes in the ligand structure. Chiral bidentate ligands capable of chelation that contain two different donor centres[1] have gained considerable attention. Particularly phosphinylated oxazolines[2] of the type **1** (Chart 1) were found to be catalyst components of

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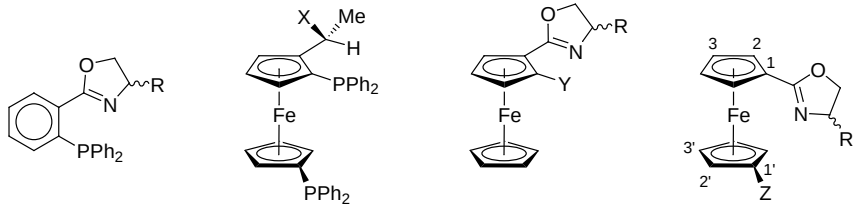
choice for palladium- and molybdenum-mediated allylic substitution, Heck reaction[3], *etc.*

Synthetic versatility, relative inertness, and unique stereoelectronic properties predetermine the ferrocene skeleton to act as a frequently used framework for the design of chiral catalysts. As examples may serve numerous ligands derived from *N*,*N*-dimethyl-1-ferrocenylethylamine by asymmetric *ortho*-lithiation and an amino-group replacement (Chart 1, **2**, X = NR_2, OR, OAc, PR_2, *etc.*) or, more recently, (4-substituted 4,5-dihydrooxazol-2-yl)-ferrocenes (Chart 1, **3**, Y = H) which have proved to be effective catalysts



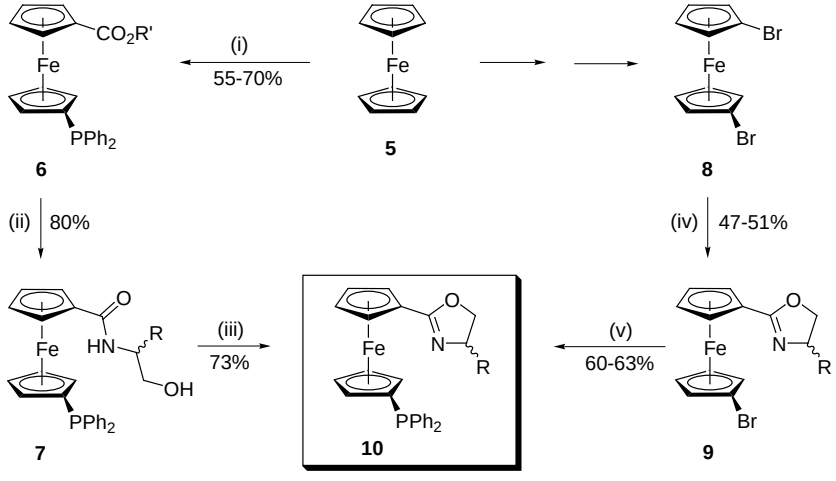
1 **2** **3** **4**

CHART 1

for, *e.g.*, cross-coupling of Grignard reagents with organyl halides, enantioselective allylic substitution, hydrosilylation and hydrogenation of prochiral olefins and ketones[4]. The modification of the ferrocene skeleton by introducing an auxiliary donor group into the position adjacent to the oxazoline moiety (Chart 1, **3**, Y = PPh_2 (ref.[5]), SPh, CHO, CO_2H, $SnBu_3$, $SiMe_3$ (ref.[6]), SePh (ref.[7]), or $CPh_2(OH)$ (ref.[8])) further enhances the selectivity of catalysed reactions by changing electron distribution and by fixing the geometry of catalytically active species *via* chelate formation, hydrogen bonding or by non-bonding interactions such as steric interactions. However, the use of analogous 1,1′- or 1,1′,2-functionalised ferrocenes as ligands is restricted almost exclusively to those derived from 1,1′-bis(diphenylphosphanyl)ferrocene and 1,1′-bis(4,5-dihydrooxazol-2-yl)ferrocenes including bis(*ortho*-phosphanylated) derivatives of the latter[9] (Chart 1, **4**, Z = 4,5-dihydrooxazol-2-yl).

We reasoned that chiral 2-[1′-(diphenylphosphanyl)ferrocenyl]-4,5-dihydrooxazoles **10** may combine high catalytic activity of 1,1′-bis(diphenylphosphanyl)ferrocene and excellent enantioselectivities achieved with chiral (diphenylphosphanyl)oxazoline ligands in Pd-catalysed allylic substitution reactions. In the course of our work on the synthesis of 2-[1′-(diphenylphosphanyl)ferrocenyl]-4,5-dihydrooxazoles **10**, two inde-

pendent syntheses of these compounds appeared. The first started from 1′-(diphenylphosphanyl)ferrocenecarboxylic acid **6** (or its ester) which was converted to the corresponding amidoalcohols **7** and then cyclised with $MeSO_2Cl$–Et_3N. The parent acid **6** was obtained from ferrocene **5** in three steps *via* 1,1′-bis(tributylstannyl)ferrocene[10] (Scheme 1). The key compound of the second reported approach is 1,1′-dibromoferrocene (**8**) which was first converted to 2-(1′-bromoferrocenyl)-4,5-dihydrooxazole **9**, whose bromine atom was subsequently replaced with diphenylphosphanyl group[11] (Scheme 1). When used as ligands in Pd-catalysed allylic substitution reactions, oxazolines **10** gave almost quantitative chemical yields. However, the achieved enantioselectivities were lower compared to the best phosphanyloxazoline ligands, probably because more intermediates (possessing differently twisted cyclopentadienyl rings) are involved in the reaction[10].



(i) 1. BuLi, TMEDA; 2. Bu_3SnCl; 3. BuLi; 4. Ph_2PCl; 5. BuLi; 6. $ClCO_2Me$ (R' = Me) or CO_2 (R' = H); (ii) aminoalcohol, Na (R' = Me) or 1. DCC, C_6F_5OH; 2. aminoalcohol, Et_3N; (iii) CH_3SO_2Cl, Et_3N; (iv) 1. s-BuLi; 2. CO_2; 3. H^+; 4. PCl_5; 5. aminoalcohol, Et_3N; 6. TsCl, Et_3N; (v) 1. s-BuLi; 2. $ClPPh_2$

SCHEME 1

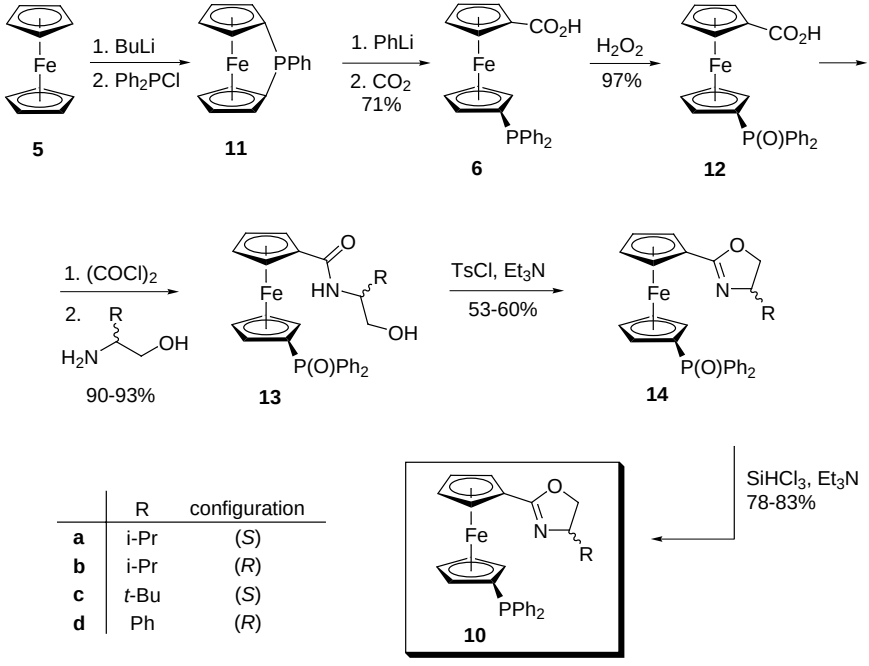
Herein, we wish to report on a novel, alternative synthetic approach to 2-[1′-(diphenylphosphanyl)ferrocenyl]-4,5-dihydrooxazoles **10**. We also present CD spectra of these compounds and single-crystal X-ray structure of a complex, bearing one of the phosphanyloxazolines as the *P*-ligand,

trans-dichlorobis{(*S*)-2-[1′-(diphenylphosphanyl)ferrocenyl]-4-isopropyl-4,5-dihydrooxazole-κ*P*}palladium(II) (**15**).

RESULTS AND DISCUSSION

Synthesis of the Oxazoline Ligands

The synthesis of 2-[1′-(diphenylphosphanyl)ferrocenyl]-4,5-dihydrooxazoles **10a**–**10d** is outlined in Scheme 2. Our approach also starts from 1′-(diphenylphosphanyl)ferrocenecarboxylic acid (**6**), which is readily accessible from ferrocenophane[12] **11**. Acid **6** was converted to the amido-



SCHEME 2

alcohol. However, the following oxazoline ring closure with a tosyl chloride–triethylamine mixture, which is routinely used for the oxazoline ring closure[13], failed to give even acceptable yields of desired product(s). Therefore the diphenylphosphanyl group in acid **6** was first protected as the corresponding phosphane oxide[12]. Thus, 1′-(diphenylphosphanoyl)-ferrocenecarboxylic acid (**12**) was converted *in situ* to its chloride by treat-

ment with oxalyl chloride, which was reacted with the appropriate chiral β-aminoalcohols to give amidoalcohols **13a**–**13d** as yellow-brown foams in high yields. The spectral data of these compounds (NH signal in ^{1}H NMR spectra and typical amide bands in IR spectra) are in full agreement with the features expected for the amides **13a**–**13d**; no *O*-acylation was observed. The amidoalcohols **13a**–**13d** were converted into 2-[1′-(diphenylphosphanoyl)ferrocenyl]-4,5-dihydrooxazoles **14a**–**14d** by the action of a tosyl chloride–triethylamine mixture in dichloromethane solution[12]. As the compounds **14a**–**14d** are rather unstable, they were immediately used in the next reaction step; reduction of diphenylphosphanoyl group with trichlorosilane under standard conditions[14] proceeded smoothly, giving the desired 2-[1′-(diphenylphosphanyl)ferrocenyl]-4,5-dihydrooxazoles **10a**–**10d** in 79–83% yields.

All compounds were fully characterised by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy and one compound from each type (**13d**, **14d** and **10d**) was subjected to a detailed analysis by combination of one- and two-dimensional NMR techniques (*e.g.*, NOE, COSY, ^{13}C HMQC and ^{13}C HMBC). The interpretation of ^{1}H NMR data was not straightforward due to broadened resonances of the cyclopentadienyl (Cp) protons and extensive overlaps in the aromatic region. Moreover, ^{13}C NMR spectra of compounds **13d**, **14d** and **10d** revealed entirely different pattern compared to the parent acid[12] **6**, the assignment of ferrocene carbon-13 resonances being further complicated by scalar ^{31}P–^{13}C interactions and anisochronicity of diastereotopic ferrocene CH groups. Nevertheless, ^{1}H/^{31}P double-decoupled ^{13}C spectra enabled us to assign all cyclopentadienyl carbon resonances (including diastereotopic pairs C-2/C-2′ and C-3/C-3′) and to determine the ^{13}C–^{31}P coupling constants (see Experimental). Non-equivalent cyclopentadienyl proton resonance H-2,2′ and H-3,3′ in the molecule of amidoalcohol **13d** were assigned on the basis of NOE (DPFGSE NOE)[15] measurements. For instance, proton H-2 (δ_H 5.01 ppm) in **13d** showed NOE interaction with H-3 (δ_H 4.26 ppm), H-3′ (δ_H 4.79 ppm) and aromatic protons (δ_H 7.84 ppm). NOE interaction was also observed between H-3′ (δ_H 4.79 ppm) and H-2 (δ_H 5.01 ppm), H-2′ (δ_H 4.05 ppm) and H-3′ (δ_H 4.49 ppm) (Fig. 1). In comparison with compounds **13d** and **14d**, in which the Cp protons are anisochronic, compound **10d** showed non-equivalency to a much lesser extent, probably due to a higher mobility of its cyclopentadienyl rings.

The series of oxazolines **10a**–**10d** was further studied by CD spectra with respect to substituent and configuration at position 4 of the oxazoline ring (Fig. 2). The general pattern of the spectra is analogous to the related systems published in ref.[5b]. There is a broad band with the maximum dichroic

absorption at about 480 nm and at least two other bands at lower wavelengths (311 and 257 nm). The signs of the Cotton effect strictly relate to the configuration of the oxazoline ring substituents; neither bulkiness nor electron-donating properties of the substituent seem to influence CD spectra in any manner. This is in contrast with findings made with analogous systems in ref.[5b], where the opposite conformations were suggested to account for differences in CD spectra even if the configuration at the oxazoline ring remains the same. However, those systems possessed diphenylphosphanyl group on the same Cp ring in a position adjacent to the oxazoline moiety.

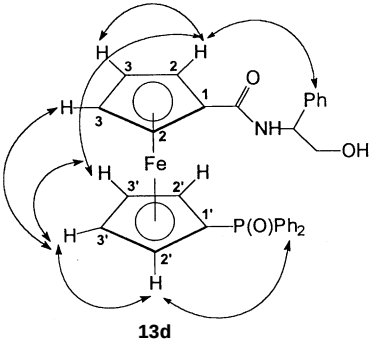


FIG. 1
NOE connectivities observed for **13d**

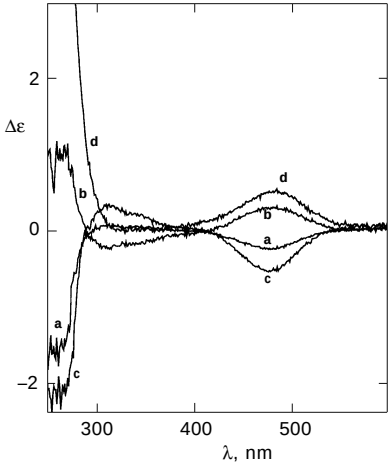
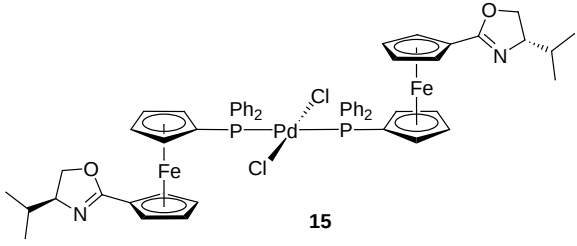


FIG. 2
CD spectra of **10a**–**10d** in methanol

*Synthesis and Crystal Structure of trans-Dichlorobis{(S)-2-[1′-(diphenylphosphanyl)ferrocenyl]-4-isopropyl-4-5-dihydrooxazole-κP}palladium(II) (**15**)*

The displacement of benzonitrile ligands in $[PdCl_2(PhCN)_2]$ or cycloocta-1,5-diene in $[PdCl_2(\eta^4\text{-}C_8H_{12})]$ with two equivalents of oxazoline **10a** gives *trans*-dichlorobis(phosphanylferrocenyloxazoline)palladium(II) complex **15** in which the organometallic ligands acts as *P*-donors. Attempts to isolate a 1 : 1 complex failed. However, ^{31}P NMR spectra showed that a mixture of two compounds (δ_P 15.0, 16.8) is formed for P/Pd ratios lower than 2.



15

Authentication of the structure assigned for **15** is based on elemental analyses, NMR and IR spectra. A strong support for *trans*-bis(*P*-coordination) of the phosphanyloxazoline ligands comes from the $^{31}P\{^1H\}$ NMR spectrum, where the signal at δ_P +15.3 (Δ_P 34.1, coordination shift $\Delta_P = \delta_{complex} - \delta_{ligand}$) is close to that of a related complex *trans*-[Pd(**6**-κ*P*)$_2$Cl$_2$] (δ_P +15.6 in DMSO-d_6; Δ_P 34.0)[16]. Furthermore, the signals of the phenyl groups and the phosphanylated Cp-ring in ^{13}C NMR spectra are observed as apparent triplets due to virtual AA′X spin systems typical of *trans*-bis(phosphane) complexes of platinum metals[17].

More detailed information about the structure of the complex was obtained from single-crystal X-ray analysis. The view of the crystal structure of **15** is presented in Figs 3 and 4 and the important geometric parameters are given in Table I. There are two crystallographically independent molecules in the unit cell (chiral *P1* space group), leaving the channels between them occupied by loosely bonded solvating dichloromethane, which is readily lost under ambient conditions.

All bond distances and angles within the independent molecules are similar. However, the molecules differ in the configuration of the conformationally chiral ferrocene moieties while the configuration at the oxazoline asymmetric carbon atom remains naturally unchanged, thus forming a (*S*, *S*, S_p, S_p) [molecule 1 (ligand 1 + 2)], (*S*, *S*, R_p, R_p) [molecule 2

(ligand 3 + 4)] pair (Fig. 4). This is the consequence of fixing the positions of the substituents on the ferrocene skeleton in the solid state. No such separation of diastereoisomers can be expected in solution because of inter-

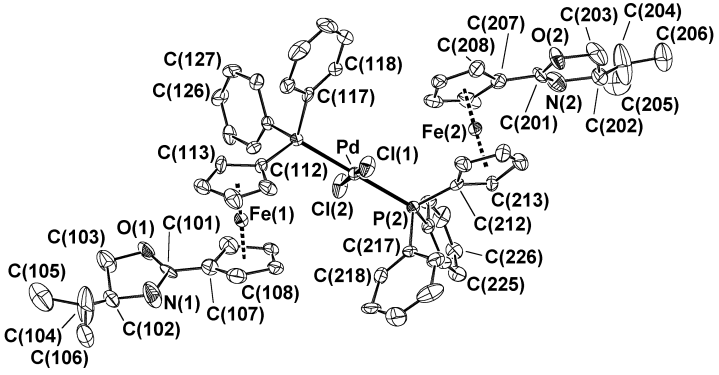


FIG. 3

Perspective view of **15** (molecule 1). Thermal ellipsoids are drawn at the 30% probability level. For clarity, hydrogen atoms are omitted and only two carbon atoms of each ring are labelled. The labelling scheme of molecule 2 is obtained by adding 1 to the first digit of the corresponding atom label in molecule 1

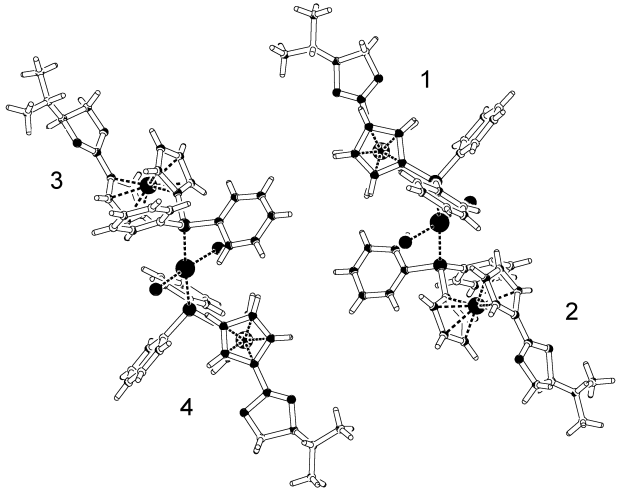


FIG. 4

View of the two crystallographically independent molecules of **15** along the crystallographic *a* axis. Solvating dichloromethane was omitted; the four ligand moieties are labelled by Arabic numerals

TABLE I
Selected bond lengths (in Å), bond angles, dihedral angles[a] and torsion angles (in °) for complex **4**

Bonds, angles	*n*			
	1	2	3	4
Pd–Cl(*n*)	2.295(4)	2.273(4)	2.288(4)	2.292(4)
Pd–P(*n*)	2.357(4)	2.345(4)	2.356(4)	2.360(4)
P(*n*)–P(*n*12)	1.81(1)	1.80(1)	1.80(2)	1.80(2)
P(*n*)–P(*n*17)	1.83(1)	1.85(1)	1.80(2)	1.83(2)
P(*n*)–P(*n*23)	1.80(2)	1.83(1)	1.81(2)	1.84(2)
N(*n*)–C(*n*01)	1.23(2)	1.30(2)	1.26(2)	1.21(3)
N(*n*)–C(*n*02)	1.49(2)	1.57(2)	1.46(2)	1.51(2)
O(*n*)–C(*n*01)	1.30(2)	1.34(2)	1.38(2)	1.45(2)
O(*n*)–C(*n*03)	1.43(2)	1.48(2)	1.43(2)	1.46(2)
C(*n*01)–C(*n*07)	1.43(2)	1.46(2)	1.40(3)	1.51(3)
C(*n*02)–C(*n*03)	1.58(2)	1.52(2)	1.55(2)	1.59(3)
C(*n*02)–C(*n*04)	1.32(2)	1.29(3)	1.36(3)	1.36(3)
C(*n*04)–C(*n*05)	1.59(4)	1.58(5)	1.56(3)	1.55(4)
C(*n*04)–C(*n*06)	1.43(3)	1.42(3)	1.48(3)	1.52(3)
Cl(*n*)–Pd–P(*n*)	87.1(2)	91.7(1)	91.6(2)	87.3(1)
Cl(*n*)–Pd–P(*n*+1)	87.5(1)		93.7(1)	
P(*n*)–Pd–Cl(*n*+1)	93.6(1)		93.7(1)	
C(*n*12)–P–C(*n*17)	107.9(7)	103.5(6)	105.9(8)	103.2(7)
C(*n*12)–P–C(*n*23)	101.5(6)	102.0(6)	100.6(7)	99.9(8)
C(*n*17)–P–C(*n*23)	102.9(7)	102.7(6)	104.6(6)	104.2(4)
C(*n*01)–N(*n*)–C(*n*02)	108(2)	99(1)	113(1)	106(2)
N(*n*)–C(*n*02)–C(*n*03)	102(1)	103(2)	98(1)	98(1)
N(*n*)–C(*n*02)–C(*n*04)	116(2)	117(2)	118(2)	115(1)
C(*n*03)–C(*n*02)–C(*n*04)	118(2)	119(2)	120(2)	118(2)
C(*n*02)–C(*n*04)–C(*n*05)	118(2)	116(3)	115(2)	112(2)
C(*n*02)–C(*n*04)–C(*n*06)	129(3)	126(3)	122(2)	120(2)
C(*n*05)–C(*n*04)–C(*n*06)	105(2)	107(3)	114(2)	123(2)
C(*n*02)–C(*n*03)–O(*n*)	99(1)	107(1)	102(1)	109(1)
C(*n*03)–O(*n*)–C(*n*01)	112(1)	101(1)	110(2)	97(1)
O(*n*)–C(*n*01)–N(*n*)	116(2)	126(1)	109(2)	124(2)
τ_{Fc}[b]	–138.8(3)	–146.8(3)	146.8(4)	141.6(6)
<CpP, Ph^A	79.9(6)	70.3(6)	75.1(5)	79.0(7)
<CpP,Ph^B	78.6(6)	87.6(6)	88.6(6)	79.6(7)
<Ph^A,Ph^B	78.5(4)	80.0(5)	78.6(5)	77.1(5)
<CpP,CpOx	4.9(1)	2(1)	3(1)	2.8(1)
<CpOx,Ox	17.8(6)	7(2)	5(2)	10.9(4)
<Ox,iPr	5(2)	7(5)	14(5)	0(2)
τ_{Ox}[c]	1(3)	4(2)	0(2)	5(3)
C(*n*02) *vs* Ox[d]	0.30(4)	0.31(3)	0.46(3)	0.41(3)
Q_{Ox}[e], Å	0.16(2)	0.19(2)	0.28(2)	0.25(2)
φ_{Ox}[e], °	108(6)	103(5)	110(4)	105(4)

[a] Mean values: Fe–C 2.04(4), C–C(Cp) 1.42(5), C–C(Ph) 1.38(6) Å. The planes are defined as follows; CpP: C(*n*12)–C(*n*16); PhA: C(*n*17)–C(*n*22); PhB: C(*n*23)–C(*n*28); CpOx: C(*n*12)–C(*n*16); Ox: N(*n*), C(*n*01), O(*n*) and C(*n*03); i-Pr: C(*n*04)–C(*n*06). [b] P(*n*)–Centroid–Centroid–C(*n*01) torsion angle. [c] N(*n*)–C(*n*01)–O(*n*)–C(*n*03) torsion angle. [d] Perpendicular distance of C(*n*02) to the Ox plane (in Å). [e] Ring puckering coordinates for the oxazoline ring: N(*n*), O(*n*) and C(*n*01)–C(*n*03).

conversion of the conformers due to only a low rotation barrier of the Cp rings around the ferrocene D_5 axis.

The donor atoms around the palladium centre form an almost perfect *trans*-square planar coordination environment typical of *trans*-[$PdCl_2(PR_3)_2$] complexes with monodentate phosphanes. The Cl–Pd–Cl angle of 174.8(2)° for Pd(1) [174.9(2)° for Pd(2)], P–Pd–P angle of 174.6(1)° [174.7(1)°] as well as the fact that the sum of the four P–Pd–Cl angles differs from 360° by less than 0.1° indicate that no tetrahedral distortion of the coordination sphere occurs (*cf.* the perpendicular displacement of the central Pd atom from the four-atom ligand plane of maximum 0.06 Å). In both independent molecules, the Pd–P/Pd–Cl distances of 2.273(4)/2.345(4) and 2.295(4)/2.360(4) Å (for molecules 1 and 2, respectively) correspond well to those reported for an analogous centrosymmetric complex *trans*-[$PdCl_2$(**6**-κ*P*)$_2$]·$2CH_3CO_2H$ (2.296(1)/2.363(1) Å)[16] and a palladium(II) complex of an *ortho*-functionalised ferrocenyloxazoline, [$PdCl_2$\{1-(diphenylphosphanyl)-2-((*S*,*R*)-4-isopropyl-4,5-dihydrooxazol-2-yl)ferrocene)-κ^2-*P*,*N*\}] (Pd–Cl 2.279(2) and 2.370(2); Pd–P 2.230(2) Å)[5c].

The phenyl and Cp groups subtend dihedral angles of their least-squares planes varying from 75 to 89°; the longest perpendicular distance of a phosphorus atom from the ring plane was observed between P(1) and the C(112)–C(116) phenyl ring plane (0.16(2) Å). The ferrocene moieties itself show no significant deformation of bond lengths and angles when compared to the parent phosphinocarboxylic acid[12] **6**. In all four ferrocene moieties in the unit cell, the Cp rings are only slightly tilted (maximum dihedral angle of their least-squares planes is 4.9(1)° for molecule 1) and adopt an almost exact eclipsed conformation with anti arranged substituents as can be demonstrated by the torsion angles phosphorus–centroid–centroid–oxazolinyl pivotal carbon atom, τ, close to the ideal value of 144°. However, as mentioned above, two of the them are (*S*)-*anti*-eclipsed (τ ≈ –144°; Fig. 4, ligands 1 and 2) whereas the remaining two are (*R*)-*anti*-eclipsed (τ ≈ +144°, Fig. 4, ligands 3 and 4). The bond lengths and angles within the oxazoline rings (C=N 1.23–1.30, C–N 1.49–1.57, O–CN 1.30–1.45, O–CC 1.43–1.46 and C–C 1.52–1.59 Å) are similar to those in, *e.g.*, (*S*)-2-((*S*)-2-(diphenylphosphanyl)ferrocenyl)-4-isopropyl-4,5-dihydrooxazole and (*S*)-2-((*S*)-4-isopropyl-2-(phenylselenyl)ferrocenyl)-4,5-dihydrooxazole[7]. The ring puckering coordinates[18] Q < 0.3 Å and φ = 103–110° together with the N(n)–C(n01)–O(n)–C(n03) torsion angles, $\tau_{Ox}(n)$, n = 1–4, of nearly 0° imply that the oxazoline rings possess a perfect envelope conformation with the C(n02) atom disposed out of the plane of the four remaining ring atoms by 0.30(4)–0.46(3) Å (Table I).

CONCLUSIONS

In conclusion, we have demonstrated, that 2-[1′-(diphenylphosphanyl)-ferrocenyl]-4,5-dihydrooxazoles **10a**–**10d** can be easily prepared from 1′-(diphenylphosphanyl)ferrocenecarboxylic acid (**6**), which is obtained from ferrocene in two steps *via* ferrocenophane[12] **11**. However, the use of tosyl chloride for the cyclisation of the corresponding amidoalcohols requires protection of the phosphane group as phosphane oxide. Therefore a combination of the recently described cyclisation using mesyl chloride[10] with the above mentioned preparation of **6** from ferrocenophane **11** seems to be the most straightforward access to the phosphinooxazolines **10**. The phosphine protection we worked out may become useful, when other synthetic transformations incompatible with the phosphine group (such as oxidation and halogenation) are required. Moreover, the method used for the preparation of acid **6** makes it possible to synthesise analogous 1,1′-disubstituted ferrocene derivatives bearing two different substituents at the phosphorus atom. This possibility is currently under study in our laboratory.

EXPERIMENTAL

Unless stated otherwise, all manipulations were carried out in an argon atmosphere using Schlenk techniques. The solvents were dried and degassed by standard procedures. Radial-layer chromatography on silica gel (Chromatotron Model 8924, 2 mm plate) was used for purification of crude products; silica gel (Merck, 70–230 mesh) was used for column chromatography. NMR spectra were measured on a Varian UNITY Inova 400 spectrometer (^{1}H, 399.95 MHz; ^{13}C, 100.58 MHz; ^{31}P, 161.90 MHz), Varian Gemini 300 (^{1}H, 300.07 MHz; ^{13}C, 75.46 MHz), a Bruker AMX3 400 (^{1}H, 400.13 MHz; ^{13}C, 100.62 MHz; ^{31}P, 161.98 MHz) or a Bruker DRX 500 Avance (^{1}H, 500.13 MHz; ^{13}C, 125.77 MHz; ^{31}P, 202.46 MHz) spectrometer at 298 K. Chemical shifts (δ-scale, ppm) are given relative to internal Me_4Si (^{1}H, ^{13}C) or external 85% aqueous H_3PO_4 (^{31}P). Unambiguous assignment of the NMR signals is based on ^{13}C{^{1}H}, ^{13}C{^{1}H, ^{31}P}, ^{13}C APT, COSY, ^{13}C HMQC, ^{13}C HMBC and DPFGSE NOE spectra. Signals of the ferrocenyl resonances are distinguished using the labelling scheme given in Fig. 1 and Chart 1; "fc" in NMR spectra denotes signals due to ferrocene-1,1′-diyl group. IR spectra in Nujol mulls were recorded on an FT-IR Mattson Genesis or Nicolet 750 FT-IR spectrometer in the range 400–4 000 cm^{-1}. Fast atom bombardment (FAB) mass spectra were measured on ZAB-SEQ (VG Analytical) spectrometer using Xe fast atoms (8 kV) and the thioglycerol–glycerol (3 : 1) matrix unless noted otherwise. Optical rotations were measured on an automatic polarimeter Autopol III (Rudolph Reseach, New Jersey) and are given in deg cm^3 g^{-1} dm^{-1}. CD spectra were recorded at room temperature on Jobin Yvon Mark VI dichrograph for methanol solutions (*ca* $1 \cdot 10^{-3}$ mol l^{-1}) in a quartz cell with the optical path 0.1 cm. The spectra were recorded as averages of two subsequent scans (no time dependence was observed) and further replotted using Spectracalc and Gramms (Galactic Industries) software for spectral analysis.

Acid[13] **6**, $[PdCl_2(\eta^4\text{-}C_8H_{12})]$ (ref.[19]) and $[PdCl_2(PhCN)_2]$ (ref.[20]) were prepared by literature procedures. Optically active aminoalcohols were prepared by reduction of the corresponding amino acids with $LiAlH_4$ (ref.[21]).

1′-(Diphenylphosphanoyl)ferrocenecarboxylic Acid (**12**)

Acid **6** (2.49 g, 6.0 mmol) was dissolved in hot acetone (100 ml). The solution was cooled in ice bath, hydrogen peroxide (2.5 ml 30%, *ca* 24 mmol) was added and the mixture was stirred for 15 min at 0 °C while precipitation of an orange solid started. After destroying an excess of H_2O_2 by addition of 10% aqueous sodium thiosulfate (50 ml) and stirring for 15 min at 0 °C, acetone was removed in vacuum. The resulting orange suspension was diluted with water (50 ml), acidified (1 ml 6 M HCl) and extracted with dichloromethane. Combined organic phases were washed with water, dried with anhydrous $MgSO_4$ and evaporated. The residue was dried over KOH overnight to afford **12** (2.51 g, 97%) as an yellow-orange solid. All spectral characteristics (NMR, IR) of the product were identical to those reported previously[13], but the yield increased more than twice using this improved procedure.

Synthesis of Amidoalcohols **13a**–**13d**. General Procedure

Oxalyl chloride (0.5 ml, 5.7 mmol) was added to an ice-cool stirred suspension of phosphine oxide **12** (0.50 g, 1.16 mmol) in dichloromethane (10 ml) and the mixture was allowed to warm to room temperature. During 15 min all solid dissolved forming a dark red solution, which was stirred for another 20 min. The volatiles were then removed in vacuum, the resulting dark red oil was dissolved in dichloromethane (10 ml) and slowly, without cooling, added to a solution of the corresponding β-aminoalcohol (2.32 mmol) and triethylamine (0.5 ml, 3.48 mmol) in dichloromethane (10 ml). The resulting reaction mixture was stirred overnight, washed with water, dried over anhydrous $MgSO_4$ and concentrated in vacuum. The crude product was purified by chromatography (dichloromethane–ethyl acetate 1 : 2, v/v).

N-((S)-2-Hydroxy-1-isopropylethyl)-1′-(diphenylphosphanoyl)ferrocenecarboxamide (**13a**): Brown-yellow foam, yield 90%. ^{1}H NMR (500.13 MHz, $CDCl_3$): 1.04 (d, $^3J_{HH}$ = 6.9, 3 H, CH_3); 1.06 (d, $^3J_{HH}$ = 6.9, 3 H, CH_3); 2.16 (m, 1 H, C**H**$(CH_3)_2$); 3.78 (bd, 1 H, C**H**$_2$OH); 3.87 (m, 2 H, C**H**CH_2); 4.03 (bs, 2 H, fc); 4.27 (bs, 1 H, fc); 4.37 (bs, 1 H, fc); 4.47 (bs, 1 H, fc); 4.81 (bs, 1 H, fc); 4.96 (bd, 1 H, OH); 4.99 (bs, 1 H, fc); 5.10 (bs, 1 H, fc); 7.32–7.65 (m, 8 H, Ph); 7.78–7.84 (m, 2 H, Ph); 8.24 (bd, 1 H, $^3J_{HH}$ = 8, NH). ^{13}C{^{1}H} NMR (125.77 MHz, $CDCl_3$): 19.5 (CH_3); 19.9 (CH_3); 29.2 ($CH(CH_3)_2$); 57.4 ($CHCH_2$); 63.6 ($CHCH_2$); 70.2 (fc, C-2); 70.4 (fc, C-3); 70.8 (fc, C-2 and C-3); 71.6 (d, $^3J_{PC}$ = 10.4, fc, C-3′); 73.1 (d, $^1J_{PC}$ = 115.4, fc, C-1′); 73.6–73.9 (m, fc, C-2′ and C-3′); 76.0 (d, $^2J_{PC}$ = 12.0, fc, C-2′); 78.8 (fc, C-1); 128.6 (apparent t, J' = 12.5, Ph, CH); 131.3 (m, Ph, CH); 131.4 (d, $^1J_{PC}$ = 108.5, Ph, C_{ipso}); 132.2 (Ph, CH); 132.9 (d, $^1J_{PC}$ = 108.3, Ph, C_{ipso}); 169.1 (C=O). ^{31}P{^{1}H} NMR (161.98 MHz, $CDCl_3$): 31.5. IR (CCl_4): 3 354 m (NH); 1 641 vs (amide I); 1 547 s (amide II). $[\alpha]_D^{22}$ +124.1 (*c* 1.02, $CHCl_3$). For $C_{28}H_{30}FeNO_3P$ (515.4) calculated: 65.26% C, 5.87% H, 2.72% N; found: 64.92% C, 6.12% H, 2.65% N.

N-((R)-2-Hydroxy-1-isopropylethyl)-1′-(diphenylphosphanoyl)ferrocenecarboxamide (**13b**): Brown- yellow foam, yield 85%. ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and IR spectra were identical with those of **13a**. FAB MS, *m/z*: 516 $[M + 1]^+$. $[\alpha]_D^{22}$ –158.6 (*c* 1.11, $CHCl_3$). For $C_{28}H_{30}FeNO_3P$ (515.4) calculated: 65.26% C, 5.87% H, 2.72% N; found: 64.97% C, 5.93% H, 2.61% N.

N-((S)-1-tert-Butyl-2-hydroxyethyl)-1′-(diphenylphosphanoyl)ferrocenecarboxamide (**13c**): Brown-yellow foam, yield 90%. ^{1}H NMR (500.13 MHz, $CDCl_3$): 1.07 (s, 9 H, $C(CH_3)_3$); 3.77–3.82 (m, 1 H, CHC**H**$_2$); 3.88–3.94 (m, 1 H, CHC**H**$_2$); 3.96–4.00 (m, 1 H, C**H**CH_2); 4.01 (m, 2 H, fc, H-3 and H-2′); 4.26 (m, 1 H, fc, H-3); 4.43 (m, 2 H, fc, H-3′ and H-2′); 4.79 (m, 1 H, fc, H-3′); 4.86 (br dd, $^3J_{HH}$ = 4.4, 7.9, 1 H, OH); 4.98 (m, 1 H, fc, H-2); 5.10 (m, 1 H, fc, H-2); 7.39–7.44 (m, 2 H, Ph); 7.48–7.63 (m, 6 H, Ph); 7.77–7.82 (m, 2 H, Ph); 8.01 (d, $^3J_{HH}$ = 9.3, NH). ^{13}C{^{1}H} NMR (125.77 MHz, $CDCl_3$): 27.6 ($C(CH_3)_3$); 34.8 ($C(CH_3)_3$); 58.8 ($CHCH_2$); 63.3 ($CHCH_2$); 70.4 (fc, C-2); 70.5 (fc, C-3); 70.7 (fc, C-3); 70.9 (fc, C-2); 71.7 (d, $^3J_{PC}$ = 10.6, fc, C-3′); 73.3 (d, $^1J_{PC}$ = 115.0, fc, C-1′); 73.5 (d, $^3J_{CP}$ = 14.6, fc, C-3′); 73.9 (d, $^2J_{PC}$ = 10.5, fc, C-2′); 76.1 (d, $^2J_{PC}$ = 11.8, fc, C-2′); 78.5 (fc, C-1); 128.5 (m, PPh_2, CH); 131.3 (m, PPh_2, CH); 131.5 (d, $^1J_{PC}$ = 108.3, PPh_2, C_{ipso}); 132.1 (m, PPh_2, CH); 133.1 (d, $^1J_{PC}$ = 108.1, PPh_2, C_{ipso}); 169.4 (C=O). ^{31}P{^{1}H} NMR (161.98 MHz, $CDCl_3$): 33.4. IR ($CHCl_3$): 3 354 m (NH); 1 642 vs (amide I); 1 542 s (amide II). $[\alpha]_D^{22}$ +183.4 (*c* 1.12, $CHCl_3$). For $C_{29}H_{32}FeNO_3P$ (529.4) calculated: 65.80% C, 6.09% H, 2.65% N; found: 65.37% C, 5.94% H, 2.415 N.

N-(S)-2-Hydroxy-1-phenylethyl)-1′-(diphenylphosphanoyl)ferrocenecarboxamide (**13d**): Brown-yellow foam, yield 87%. ^{1}H NMR (500.13 MHz, $CDCl_3$): 3.91 (dd, $^3J_{HH}$ = 3.4, 12.3, 1 H, CHC**H**$_2$); 3.99 (dd, $^3J_{HH}$ = 7.7, 12.3, 1 H, CHC**H**$_2$); 4.05 (m, 2 H, fc, H-3 and H-2′); 4.26 (s, 1 H, fc, H-3); 4.43 (s, 1 H, fc, H-2′); 4.49 (s, 1 H, fc, H-3′); 4.78 (s, 1 H, fc, H-3′); 5.02 (s, 1 H, fc, H-2); 5.18 (s, 2 H, fc, H-2 and C**H**CH_2); 5.29 (bs, 1 H, OH); 7.20–7.86 (m, 15 H, Ph); 8.88 (d, $^3J_{HH}$ = 5.9, 1 H, NH). ^{13}C{^{1}H} NMR (125.76 MHz, $CDCl_3$): 57.0 ($CHCH_2$); 66.2 ($CHCH_2$); 70.3 (fc, C-2); 70.5 (fc, C-3); 70.8 (fc, C-3); 71.0 (fc, C-2); 72.1 (d, $^3J_{PC}$ = 10.7, fc, C-3′); 73.0 (d, $^1J_{PC}$ = 115.2, fc, C-1′); 73.6 (d, $^3J_{PC}$ = 10.6, fc, C-3′); 73.8 (d, $^2J_{PC}$ = 14.3, fc, C-2′); 76.0 (d, $^2J_{PC}$ = 12.1, fc, C-2′); 78.5 (fc, C-1); 126.9 (Ph_{amide}, CH); 127.0 (Ph_{amide}, CH); 128.2 (Ph_{amide}, CH); 128.4–128.7 (m, PPh_2, CH); 131.3–131.4 (m, PPh_2, CH); 131.4 (d, $^1J_{CP}$ = 108.7, PPh_2, C_{ipso}); 132.2 (m, PPh_2, CH); 132.7 (d, $^1J_{PC} \approx$ 108, PPh_2, C_{ipso}); 140.5 (Ph_{amide}, C_{ipso}); 169.3 (C=O). ^{31}P{^{1}H} NMR (202.46 MHz, $CDCl_3$): 34.9. IR ($CHCl_3$): 3 348 m (NH); 1 650 vs (amide I); 1 545 s (amide II). $[\alpha]_D^{22}$ –94.2 (*c* 1.04, $CHCl_3$). For $C_{31}H_{28}FeNO_3P$ (549.4) calculated: 67.77% C, 5.14% H, 2.55% N; found: 67.31% C, 5.53% H, 2.21% N.

Synthesis of (Phosphanoylferrocenyl)oxazolines **14a**–**14d**. General Procedure

Triethylamine (0.7 ml, 5.28 mmol) and tosyl chloride (0.25 g, 1.32 mmol) were successively added to an ice-cool solution of the corresponding amidoalcohol **13** (0.66 mmol) in dichloromethane (5 ml). The reaction mixture was allowed to warm to room temperature, stirred overnight and then partitioned between dichloromethane and saturated aqueous ammonium chloride. The organic phase was dried over anhydrous $MgSO_4$, filtered and the solvent was evaporated in vacuum. Crude product was purified by chromatography (ethyl acetate–dichloromethane–methanol 8 : 1 : 1, v/v).

(S)-2-[1′-(Diphenylphosphanoyl)ferrocenyl]-4-isopropyl-4,5-dihydrooxazole (**14a**): Yellow-brown oil, yield 60%. ^{1}H NMR (500.13 MHz, $CDCl_3$): 0.91 (d, $^3J_{HH}$ = 7, 3 H, CH_3); 0.99 (d, $^3J_{HH}$ = 7, 3 H, CH_3); 1.81 (m, 1 H, C**H**$(CH_3)_2$); 3.92–3.98 (m, 1 H, C**H**CH_2); 4.00 (t, $^3J_{HH}$ = 8, 1 H, CHC**H**$_2$); 4.24 (t, $^3J_{HH}$ = 8.7, 1 H, CHC**H**$_2$); 4.42–4.51 (m, 6 H, fc); 4.75 (bs, 1 H, fc); 4.76 (bs, 1 H, fcH); 7.42–7.55 (m, 6 H, Ph); 7.65–7.73 (m, 4 H, Ph). ^{13}C{^{1}H} and ^{13}C APT NMR (75.46 MHz, $CDCl_3$); CH, CH_3: 18.4 (CH_3); 19.4 (CH_3); 32.9 ($CH(CH_3)_2$); 70.9, 72.76, 72.81, 73.8, 74.0, 74.2, 74.4, 74.6 ($CHCH_2$ and CH of fc; one signal was not identified due to extensive overlapping); 128.8, 129.0, 131.9, 132.0, 132.2 (CH of Ph); C, CH_2: 70.1 ($CHCH_2$); 70.1, 72.6

(fc, C_{ipso}); 133.9, 135.3 (Ph, C_{ipso}); 165.5 (C=N). $^{31}P\{^1H\}$ NMR (161.99 MHz, $CDCl_3$): 32.4. IR (CCl_4): 1 651 s (C=N).

(R)-2-[1′-(Diphenylphosphanoyl)ferrocenyl]-4-isopropyl-4,5-dihydrooxazole (**14b**): Yellow-brown oil, yield 60%. ^1H NMR, ^{13}C NMR, ^{31}P NMR and IR spectra were identical to those of **14a**. FAB MS, *m/z*: 498 $[M + 1]^+$.

(S)-4-tert-Butyl-2-[1′-(diphenylphosphanoyl)ferrocenyl]-4,5-dihydrooxazole (**14c**): Yellow-brown oil, yield 53%. ^1H NMR (400.13 MHz, $CDCl_3$): 0.90 (s, 9 H, $C(CH_3)_3$); 3.87 (dd, $^3J_{HH}$ = 7.5, 10, 1 H, C**H**CH_2); 4.08 (t, $^3J_{HH}$ = 8, 1 H, CHC**H**$_2$); 4.18 (t, $^3J_{HH}$ = 9.2, 1 H, CHC**H**$_2$); 4.40–4.51 (m, 6 H, fc); 4.74 (bs, 2 H, fc); 7.40–7.54 (m, 6 H, Ph); 7.63–7.73 (m, 4 H, Ph). $^{13}C\{^1H\}$ and ^{13}C APT NMR (100.62 MHz, $CDCl_3$); CH, CH_3: 26.6 ($C(CH_3)_3$); 71.1, 71.2, 73.0, 74.0, 74.1, 74.3, 74.5, 74.6, 76.4 ($CHCH_2$ and CH of fc); 128.9, 129.0, 132.1, 132.2, 132.4, (Ph, CH); C, CH_2: 34.24 ($C(CH_3)_3$); 69.3 ($CHCH_2$); 75.2 (fc, C_{ipso}; the second ferrocene C_{ipso} signal was not found); 134.1, 135.2 (PPh_2, C_{ipso}); 165.76 (C=N). $^{31}P\{^1H\}$ NMR (202.46 MHz, $CDCl_3$): 30.7. IR ($CHCl_3$): 1 656 s (C=N). FAB MS, *m/z*: 512 $[M + 1]^+$.

(R)-2-[1′-(Diphenylphosphanoyl)ferrocenyl]-4-phenyl-4,5-dihydrooxazole (**14d**): Brown-yellow foam, yield 58%. ^1H NMR (500.13 MHz, $CDCl_3$): 4.15 (dd, $^3J_{HH}$ = 8.1, 8.2, 1 H, CHC**H**$_2$); 4.49 (m, 2 H, fc); 4.52 (m, 2 H, fc); 4.55 (m, 2 H, fc); 4.65 (dd, $^3J_{HH}$ = 8.2, 9.7, 1 H, CHC**H**$_2$); 4.85 (m, 2 H, fc); 5.20 (dd, $^3J_{HH}$ = 9.7, 8.1, 1 H, CHPh); 7.26–7.32 (m, 3 H, Ph); 7.34–7.38 (m, 2 H, Ph); 7.44–7.50 (m, 4 H, Ph); 7.51–7.56 (m, 2 H, Ph); 7.67–7.74 (m, 4 H, Ph). $^{13}C\{^1H\}$ NMR (125.76 MHz, $CDCl_3$): 69.9 ($CHCH_2$); 70.4 (fc, C-2); 70.5 (fc, C-2); 71.3 (fc, C-1); 72.4 (fc, 2 × C-3); 73.3 (d, $^2J_{PC}$ = 12.6, fc, C-2′); 73.5 (d, $^2J_{PC}$ = 12.5, fc, C-2′); 73.8 (d, $^3J_{PC}$ = 10.2, fc, 2 × C-3′); 74.3 (d, $^1J_{PC}$ = 112.4, fc, C-1′); 74.5 (CH**C**H_2); 126.6 (Ph_{oxaz}, CH); 127.5 (Ph_{oxaz}, CH); 128.2 (d, J_{PC} = 12.2, PPh_2, CH); 128.7 (Ph_{oxaz}, CH); 131.4 (d, J_{PC} = 9.9, PPh_2, CH); 131.6 (PPh_2, CH); 134.0 (d, $^1J_{PC}$ = 106.6, PPh_2, C_{ipso}); 134.05 (d, $^1J_{PC}$ = 106.6, PPh_2, C_{ipso}); 142.4 (Ph_{oxaz}, C_{ipso}); 166.4 (C=N). $^{31}P\{^1H\}$ NMR (202.46 MHz, $CDCl_3$): 31.3. IR ($CHCl_3$): 1 654 s (C=N). FAB MS, *m/z*: 532 $[M + 1]^+$.

Reduction of (Phosphanylferrocenyl)oxazolines **10a**–**10d**. General Procedure

Triethylamine (0.15 ml, 1.1 mmol) and trichlorosilane (0.1 ml, 0.92 mmol) were successively added to a solution of (phosphanoylferrocenyl)oxazoline **14** (0.46 mmol) in benzene (15 ml) and the resulting mixture was stirred at 75 °C overnight. After cooling, the reaction mixture was washed with ice-cold 30% aqueous NaOH, diluted with water water, and the aqueous phase was extracted with dichloromethane. Combined organic phases were dried over anhydrous $MgSO_4$, the solvents were evaporated in vacuum and the crude product was purified by chromatography under argon (dichloromethane–ethyl acetate 9 : 1, v/v).

(S)-2-[1′-(Diphenylphosphanyl)ferrocenyl]-4-isopropyl-4,5-dihydrooxazole (**10a**): Yellow-orange solid, yield 78%. ^1H NMR (500.13 MHz, $CDCl_3$): 0.90 (d, $^3J_{HH}$ = 6.6, 3 H, CH_3); 0.98 (d, $^3J_{HH}$ = 6.6, 3 H, CH_3); 1.83 (m, 1 H, C**H**$(CH_3)_2$); 3.91–4.07 (m, 2 H, C**H**C**H**$_2$); 4.12 (m, 2 H, fc); 4.17–4.30 (m, 3 H, CHC**H**$_2$ + 2 CH of fc); 4.38 (m, 2 H, fc); 4.69 (bs, 2 H, fc); 7.32–7.45 (m, 10 H, Ph). $^{13}C\{^1H\}$ and ^{13}C APT NMR (125.77 MHz, $CDCl_3$); CH, CH_3: 18.5 (CH_3); 19.6 (CH_3); 33.0 ($CH(CH_3)_2$); 70.52, 70.55, 72.3, 72.9, 73.42, 73.45, 74.57, 74.7, 74.8 ($CHCH_2$ and CH of fc); 128.8 (d, J_{PC} = 6.5, PPh_2, CH); 129.2 (d, J_{PC} = 6.4, PPh_2, CH); 134.1 (d, J_{PC} = 19.2, PPh_2, CH); C, CH_2: 70.1 ($CHCH_2$); 71.9 (fc, C-1); 78.3 (d, $^1J_{CP}$ = 8.0, fc, C-1′); 139.4 (d, $^1J_{CP}$ = 9.8, PPh_2, C_{ipso}); 165.8 (C=N). $^{31}P\{^1H\}$ NMR (202.46 MHz, $CDCl_3$): –17.1. IR ($CHCl_3$): 1 654 s (C=N).

(R)-2-[1′-(Diphenylphosphanyl)ferrocenyl]-4-isopropyl-4,5-dihydrooxazole (**10b**): Yellow-orange solid, yield 76%. M.p. 62–64 °C (pentane).^{1}H NMR, ^{13}C NMR, ^{31}P NMR and IR spectra were identical with those of **10a**. FAB MS, *m/z*: 482 [M + 1]$^+$. $[\alpha]_D^{22}$ +80.7 (*c* 0.68, $CHCl_3$) (ref.[10] $[\alpha]_D^{22}$ –85 (*c* 0.46, $CHCl_3$) for (*S*)-enantiomer; ref.[11] $[\alpha]_D^{22}$ –84.0 (*c* 1.87, $CHCl_3$) for (*S*)-isomer). For $C_{28}H_{28}FeNOP$ (481.4) calculated: 69.87% C, 5.86% H, 2.91% N; found: 70.15% C, 6.18% H, 2.88% N.

(S)-2-[1′-(Diphenylphosphanyl)ferrocenyl]-4-tert-butyl-4,5-dihydrooxazole (**10c**): Yellow-orange solid, yield 78%. M.p. 112–114 °C (heptane); (ref.[11] 115–116 °C (heptane)). ^{1}H NMR (300.07 MHz, $CDCl_3$): 0.93 (s, 9 H, $C(CH_3)_3$); 3.87 (dd, J_{HH} = 7.5, 10, 1 H, C**H**CH_2); 4.08–4.27 (m, 6 H, CHC**H**$_2$ + 4 CH of fc); 4.40 (m, 2 H, fc); 4.69 (m, 2 H, fc); 7.26–7.33 (m, 10 H, Ph). ^{13}C{^{1}H} and ^{13}C APT NMR (100.62 MHz, $CDCl_3$); CH, CH_3: 26.7 ($C(CH_3)_3$); 70.7, 70.7, 72.3, 73.4, 74.5, 74.7, 74.8, 74.9, 76.8 ($CHCH_2$ and CH of fc); 128.9 (d, J_{PC} = 5.8, PPh_2, CH); 129.3 (d, J_{PC} = 10.9, PPh_2, CH); 134.1–134.4 (2 × d, PPh_2, CH); C, CH_2: 34.3 (**C**$(CH_3)_3$); 69.1 ($CHCH_2$); 78.3 (d, $^1J_{CP}$ = 8.2, fc, C-1′; signal due to the second C_{ipso} was not found); 139.4, 139.7 (2 × d, PPh_2, C_{ipso}); 165.8 (C=N). ^{31}P{^{1}H} NMR (202.46 MHz, $CDCl_3$): –17.0. IR ($CHCl_3$): 1 655 s (C=N). FAB MS, *m/z*: 496 [M + 1]$^+$. $[\alpha]_D^{22}$ –120.0 (*c* 0.65, $CHCl_3$) (ref.[10] $[\alpha]_D^{22}$ –131.8 (*c* 0.30, $CHCl_3$); ref.[11] $[\alpha]_D^{22}$ –134.3 (*c* 0.48, $CHCl_3$)).

(R)-2-[1′-(Diphenylphosphanyl)ferrocenyl]-4-phenyl-4,5-dihydrooxazole (**10d**): Yellow-orange solid, yield 76%. M.p. 86–88 °C (heptane). ^{1}H NMR (500.13 MHz, $CDCl_3$): 4.12–4.18 (m, 3 H, CHC**H**$_2$ + 2 CH of fc); 4.24 (m, 2 H, fc); 4.43 (m, 2 H, fc); 4.65 (dd, J_{HH} = 8.4, 9.9, 1 H, CHC**H**$_2$); 4.74–4.79 (m, 2 H, fc); 5.20 (dd, J_{HH} = 8.0, 9.9, C**H**CH_2); 7.23–7.40 (m, 15 H, Ph). ^{13}C{^{1}H} NMR (125.76 MHz, $CDCl_3$): 69.9 ($CHCH_2$); 70.11 (fc, C-2); 70.15 (fc, C-2); 70.6 (fc, C-1); 71.9 (fc, 2 × C-3); 72.7 (m, fc, 2 × C-3′); 74.0 (d, $^2J_{CP}$ = 14.0, fc, C-2′); 74.1 (d, $^2J_{PC}$ = 14.0, fc, C-2′); 74.6 ($CHCH_2$); 77.9 (d, $^1J_{PC}$ = 8.3, fc, C-1′); 126.7 (Ph_{oxaz}, CH); 127.5 (Ph_{oxaz}, CH); 128.16 (Ph, CH); 128.22 (Ph, CH); 128.6 (Ph, CH); 128.7 (Ph, CH); 133.38 (PPh_2, CH); 133.41 (PPh_2, CH); 133.53 (PPh_2, CH); 133.57 (PPh_2, CH); 138.5–138.7 (PPh_2, 2 × C_{ipso}); 142.5 (Ph_{oxaz}, C_{ipso}). ^{31}P{^{1}H} NMR (202.46 MHz, $CDCl_3$): –17.3. IR ($CHCl_3$): 1 649 s (C=N). FAB MS, *m/z*: 516 [M + 1]$^+$. $[\alpha]_D^{22}$ +96.70 (*c* 0.60, $CHCl_3$); (ref.[10] $[\alpha]_D^{22}$ –97.4 (*c* 0.80, $CHCl_3$) for (*S*)-isomer; ref.[11] $[\alpha]_D^{22}$ –104.8 (*c* 0.50, $CHCl_3$) for (*S*)-isomer). For $C_{31}H_{26}FeNOP$ (515.4) calculated: 72.25% C, 5.08% H, 2.72% N; found: 71.95% C, 5.38% H, 2.69% N.

trans-Dichlorobis{(*S*)-2-[1′-(diphenylphosphanyl)ferrocenyl]-4-isopropyl-4,5-dihydrooxazole-κ*P*}palladium(II) (**15**)

Compound $[PdCl_2(PhCN)_2]$ (19 mg, 0.05 mmol) was added to a solution of **10a** (48 mg, 0.10 mmol) in dichloromethane (2 ml). Hexane (5 ml) was carefully added to the resulting clear orange solution as the top layer and the mixture was allowed to stand at –18 °C. The crystals formed after several days were separated, washed with little hexane and dried in air to afford **15** (42 mg, 74%) as rusty orange crystals. Due to the loss of weakly bonded solvating dichloromethane, freshly prepared crystals of **15** disintegrate slowly in air but a minor part of CH_2Cl_2 is retained even after prolonged standing (confirmed by NMR). ^{1}H NMR (399.95 MHz, $CDCl_3$): 0.89 and 0.97 (2 × d, $^3J_{HH}$ = 6.8, 3 H, $CH(CH_3)_2$); 1.82 (octet, $^3J_{HH}$ = 6.8, C**H**$(CH_3)_2$); 3.93–4.00 (m, 1 H, C**H**CH_2); 4.02 (dd, $J_1 \approx J_2 \approx 8$, 1 H, CHC**H**$_2$); 4.25 (dd, J_1 = 8.0, $J_2 \approx$ 9.3, 1 H, CHC**H**$_2$); 4.41 (apparent t, 2 H, fc, H-3′); 4.61 and 4.66 (2 × m, 1 H, fc, H-2′); 4.77 (m, 2 H, fc, H-2); 4.89 (m, 2 H, fc, H-3); 7.30–7.46 (m, 6 H, PPh_2); 7.57–7.68 (m, 6 H, PPh_2). ^{13}C{^{1}H} NMR (100.58 MHz, $CDCl_3$): 17.84 (CH_3); 18.95 (CH_3); 32.31 ($CH(CH_3)_2$); 69.48 ($CHCH_2$); 70.44 (fc, C-3); 70.46 (fc, C-3); 71.79 (fc, C-1); 72.30

($CHCH_2$); 72.30 (apparent t, fc, C-1′); 73.65 (fc, C-2); 73.69 (fc, C-2); 73.90 (apparent t, fc, C-3′); 73.95 (apparent t, fc, C-3′); 76.34 (apparent t, fc, C-2′; 4.66); 76.54 (apparent t, fc, C-2′; 4.61); 127.78, 127.82 (2 × apparent t, PPh_2, CH); 130.33, 130.38 (PPh_2, CH); 130.90, 130.98 (2 × apparent t, PPh_2, C_{ipso}) 134.12, 134.17 (2 × apparent t, PPh_2, CH); 164.97 (s, C=N). $^{31}P\{^1H\}$ NMR (161.90 MHz, $CDCl_3$): +15.3. IR (Nujol): 1 656 s (C=N); 1 300 m; 1 165 m; 1 113 m; 1 097 m; 1 093 m; 1 027 m; 974 m; 833 m; 750 m; 695 m; 537 m; 509 m; 473 m. FAB MS (bis(2-hydroxyethyl) sulfide), *m/z*: 1 140 (M^+).

An analogous reaction of $[PdCl_2(\eta^4\text{-}C_8H_{12})]$ (C_8H_{12} = cycloocta-1,5-diene) with two equivalents of **10a** in dichloromethane gave the same product according to NMR spectra.

X-Ray Crystallographic Study

An orange prism of **15** with dimensions of 0.12 × 0.48 × 0.55 mm^3 was selected directly from the reaction batch. The diffraction data were measured on a four-circle CAD4 diffractometer at 296(1) K using graphite monochromatised MoKα radiation (λ = 0.710 73 Å) and θ–2θ scan. Due to the loss of solvating dichloromethane, the diffraction power decayed to 57% of its initial intensity during the data collection. Fortunately, the intensity decay was strictly linear with time (proved by following the intensities of three standard diffractions measured every 1 h). Of 10 470 diffractions measured ($2\theta \le 48°$; $-11 \le h \le 12$, $-9 \le k \le 13$, $-27 \le l \le 27$) and used in all calculations, 9 289 were regarded as observed according to $F_o > 4\sigma(F_o)$ criterion. The data were corrected for Lorentz-polarisation effects, linear decay and absorption (JANA98, ref.[22]; T_{min} = 0.610, T_{max} = 0.895).

Crystal data for **15**: $[C_{57.8}H_{56}Cl_{11.2}Fe_2N_2O_2P_2Pd]$, M_r = 1 289.21, triclinic, space group *P1* (No. 1), *a* = 11.283(2), *b* = 12.052(2), *c* = 24.196(3) Å; α = 83.08(1), β = 84.50(1), γ = 67.43(1)° (from 25 automatically centered diffractions with $14 \le \theta \le 15°$); *V* = 3 011.7(8) $Å^3$, *Z* = 2, D_c = 1.422 g ml^{-1}, μ(MoKα) = 1.11 mm^{-1}, *F*(000) = 1 312.

The structure was solved by direct methods (SIR92)[23]. Difference electron-density maps revealed features due to the presence of solvating dichloromethane. The solvating molecules were anisotropically refined as "CCl_2" moieties with fractional occupancy (6 molecules per unit cell with the sum of occupancies 3.6). Other non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed in idealised positions (riding model) and assigned temperature factors $U_{iso}(H) = 1.2\ U_{eq}(C)$. Full-matrix least-squares refinement of 1 342 parameters by minimisation of the $\Sigma w(|F_o| - |F_c|)^2$ function, where $w = [\sigma^2(F_o^2) + (0.0944P)^2 + 6.3859P]^{-1}$ and $P = (F_o^2 + 2F_c^2)/3$ converged to *R* = 0.046, *wR* = 0.135, *S* = 1.03 for the observed diffractions (for all data: *R* = 0.055, *wR* = 0.151; SHELXL97, ref.[24]). Refinement of Flack's enantiomorph parametr has confirmed the absolute structure (*x* = 0.00(4) for *ca* 1 500 Friedel opposites with $15 \le \theta \le 17°$ monitored). The maximum and minimum residual electron densities of 1.11 and –0.73 e $Å^{-3}$, respectively, remained within the channels occupied by the solvating dichloromethane.

Crystallographic data (excluding structure factors) for the complex **15** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC-141905. Copies of the data can be obtained free of charge on application to CCDC, e-mail: deposit@ccdc.cam.ac.uk.

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