DOI: 10.1002/ejic.200700093

Synthesis, Coordination and Catalytic Utility of Novel Phosphanyl–ferrocenecarboxylic Ligands Combining Planar and Central Chirality

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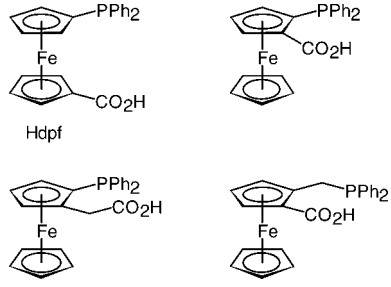
Keywords: Asymmetric catalysis / Ferrocene ligands / Rhodium / Palladium / Allylic alkylation

The chiral ferrocene derivative (R,R_p)-2-[1-(diphenylphosphanyl)ethyl]ferrocenecarboxylic acid (**1**) is prepared together with selected derivatives resulting from modification at the phosphane moiety [*P*-oxide (**5**) and *P*-sulfide (**4**)] and the carboxyl group {amides bearing benzyl (**6**) and (*R*)- or (*S*)-1-phenylethyl substituents [(*R*)-**7** and (*S*)-**7**] at the amide nitrogen atom}. Acid **1** and amide **6** are studied as ligands in rhodium and palladium complexes. Bridge cleavage of the dimer [{Rh(μ-Cl)Cl(η^5-C_5Me_5)}$_2$] with **1** gives [RhCl$_2$(η^5-C_5Me_5)(**1**-κ*P*)] (**9**) containing P-monodentate **1**, which undergoes smooth conversion to the (phosphanylalkyl)ferrocenecarboxylato complex [RhCl(η^5-C_5Me_5){Fe(η^5-C_5H_5)(η^5-C_5H_3-1-CH(Me)PPh$_2$-2-COO-κ^2*O*,*P*}] (**10**) upon treatment with silica gel or alumina. Yet another *O*,*P*-chelate complex, [Rh{Fe(η^5-C_5H_5)(η^5-C_5H_3-1-CH(Me)PPh$_2$-2-COO-κ^2*O*,*P*}(CO)(PCy$_3$)] (**11**; Cy = cyclohexyl) is obtained directly by an acid-base reaction between the acetylacetonato complex [Rh(acac)(CO)(PCy$_3$)] and **1**. Amide **6** reacts with [{Pd(μ-Cl)(η^3-C_3H_5)}$_2$] to give the expected phosphane complex [PdCl(η^3-C_3H_5)(**6**-κ*P*)] (**12**), while the replacement of the cyclooctadiene (cod) ligand in [PdCl(Me)(cod)] affords the chelate complex [PdCl(Me)(**6**-κ^2*O*,*P*)] (**13**). All compounds are characterised by spectroscopic methods and the solid-state structures of **5**, **9**, **11**, **13**, (R,S_p)-2-[1-(diphenylphosphoryl)-ethyl]-1-[*N*-(*R*)-(1-phenylethyl)carbamoyl]ferrocene [(*R*)-**8**; phosphane oxide from (*R*)-**7**], and the synthetic precursors (R,S_p)-1-bromo-2-[1-(diphenylphosphanyl)ethyl]ferrocene (**2**) and (R,S_p)-1-bromo-2-[1-(diphenylthiophosphoryl)ethyl]ferrocene (**3**) determined by single-crystal X-ray diffraction. The catalytic properties of **1** and the amides are probed in enanatioselective rhodium-catalysed hydrogenation and palladium-catalysed asymmetric allylic alkylation.

Introduction

The chemistry of ferrocene has attracted a great deal of attention ever since its discovery in the early 1950s.[1] Ferrocene derivatives have become some of the most frequently studied organometallic compounds, finding applications in organometallic synthesis, materials science, bioorganometallic chemistry and, above all, in catalysis.[2,3] To date an enormous number of chiral and achiral ligands derived from ferrocene have been reported and utilised as donors in the preparation of various coordination compounds[2a] and as catalyst components in transition metal-mediated reactions on both a laboratory and industrial scale.[2a,4]

We have focused our research mainly on phosphanyl–ferrocenecarboxylic donors. The first ligand of this kind, 1′-(diphenylphosphanyl)ferrocenecarboxylic acid (Hdpf), was reported in 1996,[5] and since then we have synthesised several other phosphanyl–ferrocenecarboxylic ligands (see Scheme 1) and studied their structural and coordination properties. More recently, we have extended our interest towards the utilisation of these phosphane–carboxylic acids and their derivatives as organometallic synthons and catalyst components.[6]



Scheme 1.

In this contribution we report the synthesis of a novel phosphanyl–ferrocenecarboxylic ligand combining planar and central chirality, namely (R,R_p)-2-[1-(diphenylphosphanyl)ethyl]ferrocenecarboxylic acid (**1**), which is a homologue of *rac*-2-[(diphenylphosphanyl)methyl]ferrocenecarboxylic acid.[7] We also describe the preparation of selected derivatives of **1** modified at both the phosphanyl and carboxyl groups, and use of the acid and amides thereof as ligands in rhodium and palladium complexes and as catalyst components in enantioselective rhodium-catalysed hydrogenation and palladium-catalysed allylic alkylation reactions.

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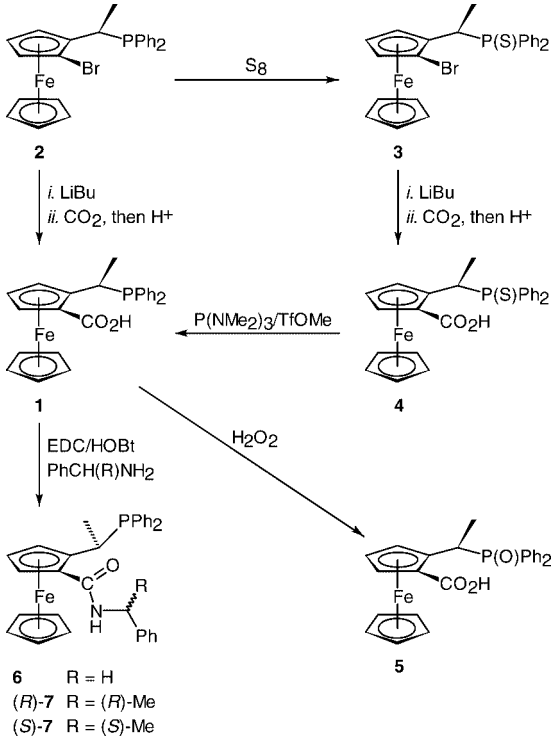
Supporting information for this article is available on the WWW under http://www.eurjic.org or from the author.

Results and Discussion

Preparation and Structural Characterisation of the Ligands

The key compound in this study, (R,R_p)-2-[1-(diphenylphosphanyl)ethyl]ferrocenecarboxylic acid (**1**), was synthesised from the known chiral precursor (R,S_p)-1-bromo-2-[1-(diphenyphosphanyl)ethyl]ferrocene (**2**)[8] by lithiation and subsequent carboxylation with carbon dioxide (Scheme 2). Alternatively, **1** was prepared first in its *P*-protected form **4** according to a similar methodology and the bromo-substituted phosphane sulfide **3** as the precursor. Following desulfurisation of **4** with $P(NMe_2)_3$/methyl triflate[9] afforded acid **1**. The structures of the bromo precursors **2** and **3**, including their absolute configuration, have been determined by X-ray crystallography (see Figure 1, Figure S1 in the Supporting Information and Table 1).



Scheme 2.

Acid **1** was further converted into its corresponding phosphane oxide **5** by treatment with aqueous hydrogen peroxide in acetone. A small amount of crystalline **5** was unintentionally obtained during the attempted crystallisation of **1** from ethyl acetate/hexane and its structure was established by single-crystal X-ray diffraction (see below). All compounds have been characterised by spectroscopic methods and elemental analysis. The ^1H and ^{13}C NMR spectra of **1**, **4** and **5** are in agreement with their formulations and show signals due to phosphorus-coupled ethane-1,1-diyl and phenyl groups and a 1,2-disubstituted ferrocene unit. The ^{31}P NMR chemical shifts follow the expected trend [δ_P = 11.1 (**1**), 36.5 (**5**) and 54.7 ppm (**4**)],[10] with the $^1J_{P,C}$ coupling constants of the C_{ipso} carbon atoms within the cyclopentadienido and phenyl rings increasing in the same order (**1** < **5** < **4**).[11] In addition, the NMR spectra of **2**–**5** indicate the presence of only one diastereoisomeric form for each compound.

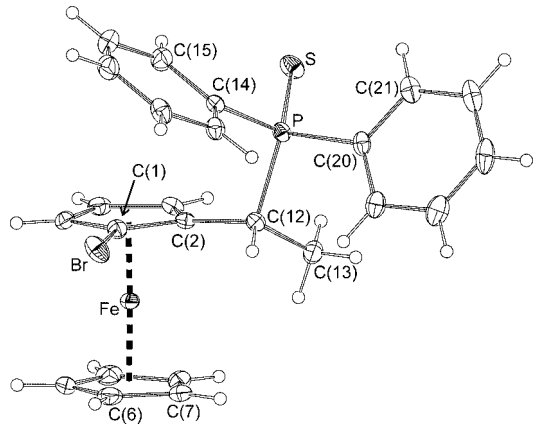


Figure 1. PLATON view of the molecular structure of **3** showing displacement ellipsoids with 30% probability. Note: a structural drawing of the corresponding phosphane **2** is available as Supporting Information (Figure S1).

Table 1. Selected bond lengths [Å] and angles [°] for **2** and **3**.[a]

	2	**3**
Fe–Cg(1)	1.6499(8)	1.6387(1)
Fe–Cg(2)	1.655(1)	1.650(1)
∠Cp(1),Cp(2)	5.6(1)	3.2(2)
C(1)–Br	1.887(2)	1.888(2)
C(2)–C(12)	1.499(3)	1.502(3)
C(12)–C(13)	1.528(3)	1.532(3)
P–C(12)	1.885(2)	1.852(3)
P–C(14)	1.842(2)	1.813(3)
P–C(20)	1.838(2)	1.819(3)
P–S	–	1.957(1)
C(2)–C(12)–P	108.5(1)	110.2(2)
C–P–C[b]	101.3(1)–103.20(9)	104.9(1)–105.9(1)
S–P–C[c]	–	112.73(8)–113.74(8)

[a] The ring planes are defined as follows: Cp(1) = C(1–5); Cp(2) = C(6–10). Cg(1) and Cg(2) denote the respective ring centroids. [b] Range of C(12)–P–C(14,20) and C(14)–P–C(20) angles. [c] Range of S–P–C(12,14,20) angles.

Acids **1**, **4** and **5** display characteristic carbonyl stretching bands in their IR spectra, the position of which varies with substitution at the phosphorus atom. Thus, whereas phosphane **1** and phosphane sulfide **4** show similar $\nu_{C=O}$ frequencies (1667 and 1663 cm^{-1}, respectively), the $\nu_{C=O}$ band of phosphane oxide **5** is shifted to higher energy (1685 cm^{-1}). This difference probably reflects different hydrogen-bonding patterns in the solid samples.[6]

The crystal structure of **5** (Figure 2a, Table 2) confirms both the expected connectivity and configuration [i.e., (R,R_p)-**5**]. The geometry of the ferrocene unit is quite regular except for a slight torsion at the substituted cyclopentadienido (Cp) ring, as indicated by the torsion angle C(11)–C(1)–C(2)–C(12) of –11.5(4)°. This can be accounted for by steric interactions between the sterically demanding ferrocene substituents and intermolecular interactions (see below). Nonetheless, the substituents bind symmetrically to

the ferrocene unit, the C(11)–C(1)–C(2/5) and C(12)–C(2)–C(1/3) angles being similar. The carboxyl group [C(11)O(1) O(2)] is rotated from the Cp(1) plane (see Table 2) by 6.4(3)°, while the phosphorus-substituted side arm is oriented above the Cp(1) plane, with an angle between the C(12)–P bond and the Cp(1) plane of 78.0(1)°. The P=O bond is directed outward the carboxyl group [torsion angle C(2)–C(12)–P–O(3) 61.1(2)°], which brings the P=O(3) and C(12)–C(13) bonds into a synclinal orientation [C(13)–C(12)–P–O(3) –63.1(2)°]. Such an arrangement, as well as the individual geometric parameters, compares favourably with those of racemic 2-[(diphenylphosphoryl)methyl]ferrocenecarboxylic acid.[7]

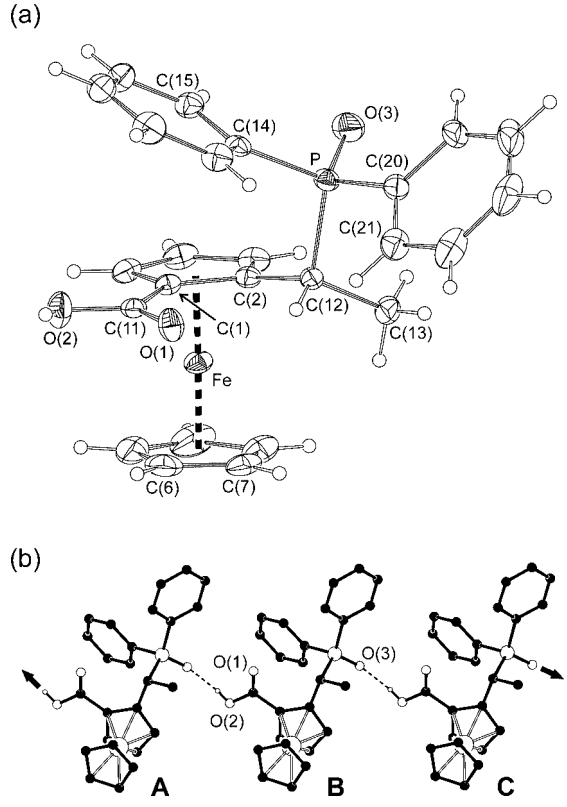


Figure 2. (a) Molecular structure of **5**. Displacement ellipsoids are shown at the 30% probability level. (b) Section of the infinite hydrogen-bonded chain in the structure of **5** showing the hydrogen bonds as dashed lines. Symmetry operations: A (x, 1 + y, z), B (x, y, z), C (x, y – 1, z).

Individual molecules in the crystal of **5** are linked into infinite chains along the crystallographic b axis by means of hydrogen bonds between the carboxylic OH group and the phosphoryl oxygen atom [O(2)–H(90)···O(3^{i}): O(2)···O(3^{i}) 2.517(3) Å (i: x, 1 + y, z); angle at H: 162(4)°; Figure 2b]. Similar hydrogen-bonding patterns have been found in the crystal structures of 1′-(diphenylphosphoryl)-ferrocenecarboxylic acid [O···O 2.588(4) Å][12] and (S_p)-2-(diphenylphosphoryl)ferrocenecarboxylic acid [O···O 2.556(4) Å].[13]

For the purpose of catalytic testing we prepared a series of *N*-benzylamides without (**6**) and with [(*R*)- and (*S*)-**7**] additional asymmetric centres (Scheme 2). The amides were

Table 2. Selected bond lengths [Å] and angles [°] for **5** and (*R*)-**8**.[a]

	5	(*R*)-**8**[d]
E	O(2)	N
Fe–Cg(1)	1.648(1)	1.650(1)
Fe–Cg(2)	1.646(2)	1.654(1)
∠Cp(1),Cp(2)	3.2(2)	2.0(2)
C(1)–C(11)	1.491(4)	1.495(3)
C(11)–O(1)	1.205(3)	1.229(2)
C(11)–E	1.300(4)	1.352(2)
C(2)–C(12)	1.492(3)	1.497(3)
C(12)–C(13)	1.544(4)	1.534(3)
C(12)–P	1.837(2)	1.835(2)
P–C(14)	1.808(2)	1.813(2)
P–C(20)	1.808(3)	1.808(2)
P=O(3 or 2)	1.469(2)	1.471(2)
O(1)–C(11)–E	125.5(3)	122.3(2)
C(2)–C(12)–P	107.3(2)	108.6(2)
C(2)–C(12)–C(13)	114.2(2)	114.0(2)
P–C(12)–C(13)	109.1(2)	107.9(1)
C–P=O[b]	108.1(1)–114.1(1)	112.0(1)–114.4(1)
C–P–C[c]	104.7(1)–108.1(1)	103.0(1)–107.32(9)

[a] The ring planes are defined as for **2** and **3**; see Table 1. [b] Range of O(3)–P–C(12,14,20) (**5**) or O(2)–P–C(12,14,20) [(*R*)-**8**] angles. [c] Range of C(12)–P–C(14,20) and C(14)–P–C(20) angles. [d] Further data: N–C(26) 1.465(3), C(26)–C(27) 1.513(3), C(26)–C(28) 1.526(4) Å; C(11)–N–C(26) 122.4(2), N–C(26)–C(27) 109.1(2), N–C(26)–C(28) 111.0(2)°.

obtained in very good yields by standard amidation of **1** with the appropriate amine in the presence of 1-hydroxybenzotriazole (HOBt) and *N*-[3-(dimethylamino)propyl]-*N*′-ethylcarbodiimide (EDC),[14] and characterised by spectroscopic methods. An independent confirmation of the structures came from the structure determination of the ferrocene amide–phosphane oxide (*R*)-**8** (Figure 3, Table 2), which was obtained in small amounts during prolonged recrystallisation of (*R*)-**7** from ethyl acetate/hexane under aerobic conditions.

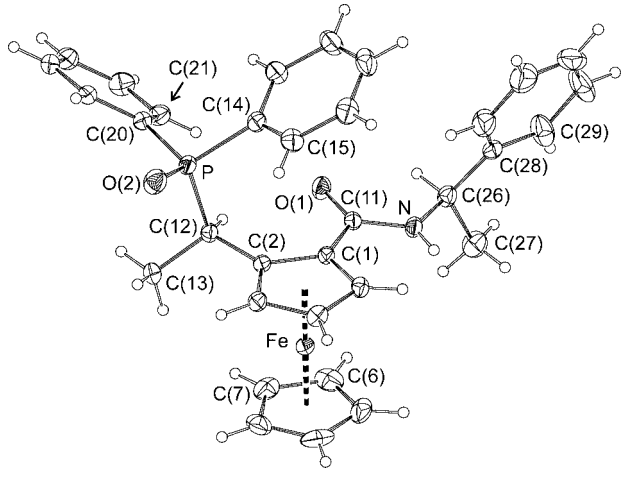
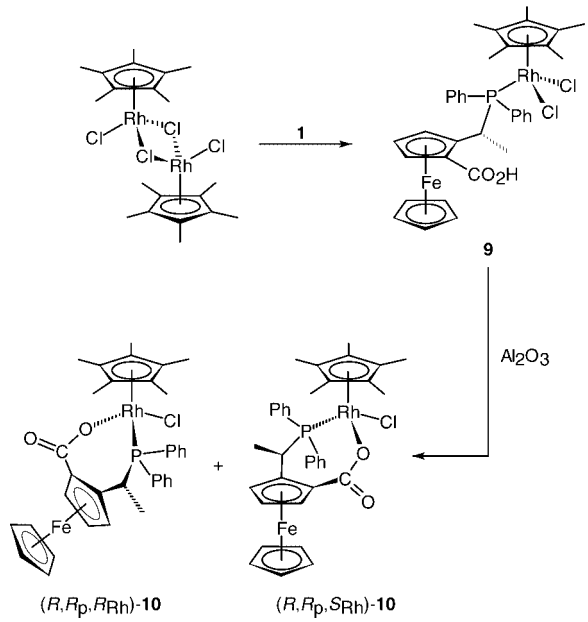


Figure 3. Molecular structure of (*R*)-**8**. Displacement ellipsoids are shown at the 30% probability.

Again, the structure confirms the expected configuration at the stereogenic elements, with the (*R*)-1-phenylethyl group acting as the reference chirality centre. The molecular geometry and conformation, including the mutual orienta-

tion of the functional groups, are similar to those in **5**. The C(12)–P vector points above the Cp(1) plane, intersecting the latter at an angle of 74.8(1)°, whilst the substituents at the P–C(12) bond adopt a conformation similar to **5**, departing slightly from the ideal staggered arrangement [cf. C(2)–C(12)–P–O(2) 74.0(2)° and C(13)–C(12)–P–O(2) –49.9(2)°]. Finally, the amide moiety [C(11)O(1)N] is rotated from the Cp(1) plane by 9.5(2)° and adopts a *syn* geometry [C(26)–N–C(11)–O(1) –1.2(3)°], with the phenyl group oriented away from the ferrocene plane [the dihedral angle between the C(26)–C(28) bond and the C(28–33) ring is 49.0(2)°]. In the crystal, the molecules of (*R*)-**8** associate through N–H(90)···O(2^{ii}) (ii: 1 – *x*, –1/2 + *y*, 1/2 – *z*) hydrogen bonds [N···O(2) 3.066(2) Å; angle at H(90): 158°] to form infinite angular chains parallel to the crystallographic *b* axis. The crystal assembly is further supported by relatively weaker C–H···O(2) interactions.



Scheme 3.

Coordination Studies: Rhodium Complexes

With the aim of using these newly prepared ferrocene-linked phosphane–carboxylate donors in rhodium- and palladium-catalysed reactions, we first tested the coordination ability of acid **1** and amide **6** towards these metal ions. Thus, the reaction between **1** and di-μ-chlorobis[chloro(η^5-pentamethylcyclopentadienido)rhodium(III)] gave the expected product of bridge cleavage (**9**; Scheme 3). When treated with chromatography grade alumina or silica gel (during column chromatography or in a batch mode), complex **9** underwent clean dehydrohalogenation to give phosphane–carboxylato complex **10** as a mixture of diastereoisomers that differ in their configuration at the newly formed stereogenic centre (Rh atom). The diastereoisomeric ratio of about 1:9 determined by NMR spectroscopy clearly indicates that the ferrocene phosphane–carboxylato ligand provides a pronounced steric bias during the chelate formation.

The P-monodentate coordination of **1** in compound **9** is reflected mainly in a low-shift of the ^{31}P NMR signal [cf. the coordination shift, $\Delta_P = \delta_P$(complex) – δ_P(ligand) = 23.2 ppm for **9**] and its splitting into a ^{103}Rh-coupled doublet ($^1J_{Rh,P}$ = 140 Hz). On the contrary, the carboxyl ^{13}C NMR signal and the $\nu_{C=O}$ band of the IR spectrum differ only slightly from those in the free ligand. On going from **9** to **10**, the ^{31}P NMR resonance shifts to even lower fields (Δ_P = 40.9/38.7 ppm for the major/minor diastereoisomer) while coordination of the deprotonated carboxyl group is clearly manifested by characteristic carboxylate bands in the IR spectrum (1581 and 1307 cm^{-1}; cf. 1664 cm^{-1} for **9** and 1321 cm^{-1} for **11**).

It is noteworthy that complex **9** shows markedly broad ^{1}H NMR resonances at +25 °C, particularly those due to the CH*Me* and C_5H_3 protons, which sharpen upon both heating to 50 °C and cooling to 0 °C. Such behaviour is indicative of a hindered intramolecular motion, which most likely results from steric interaction between the bulky (η^5-C_5Me_5)Rh unit and the ligand. The motion apparently becomes slow at low temperature, where the "equilibrium" shifts in favour of the preferred (low-energy) conformer, while higher temperatures result in a fast molecular motion and, hence, signal averaging. The expected nature of the observed dynamic behaviour is supported by the ^{31}P NMR spectra, which show a rather minor shift of the main signal over the whole temperature range monitored (δ_P = 34.9 ppm at 50 °C, and 34.0 ppm at 0 °C; $^1J_{Rh,P} \approx$ 145 Hz in both cases), thus excluding that chemically different forms are involved in the equilibrium.

The structure of **9** was corroborated by X-ray crystallography. The unit cell of **9** comprises two crystallographically distinct, but structurally very similar, molecules (Figure 4a, Table 3). This multiplication of otherwise almost identical moieties within the asymmetric unit apparently results from the crystal packing. The independent molecules aggregate into familiar dimers through double hydrogen bonds between their carboxyl groups [(C=O···H–O)$_2$ with O···O 2.652(4)/2.541(4) Å; Figure 4b]. However, such a bonding pattern requires two appropriately oriented carboxyl groups which, in a *chiral* space group, necessitates multiplication of the "repeating" units (instead of the crystallographically imposed symmetry typically observed in centrosymmetric space groups). Indeed, the most notable difference between the two independent molecules is the orientation of their carboxyl groups, which are mutually rotated by 180°. The hydrogen-bonded dimers further assemble into columnar stacks through π···π interactions between the non-substituted ferrocene and Rh-bonded cyclopentadienido rings [Cg(12)···Cg(13) 3.455(3) Å, tilt 2.5°; Cg(22)···Cg(23) 3.460(3) Å, tilt 7.5°; see Table 3 for definitions].

The different steric demands of the donors around the rhodium atom in **9** naturally result in angular deformation of the coordination environment (see the interligand angles

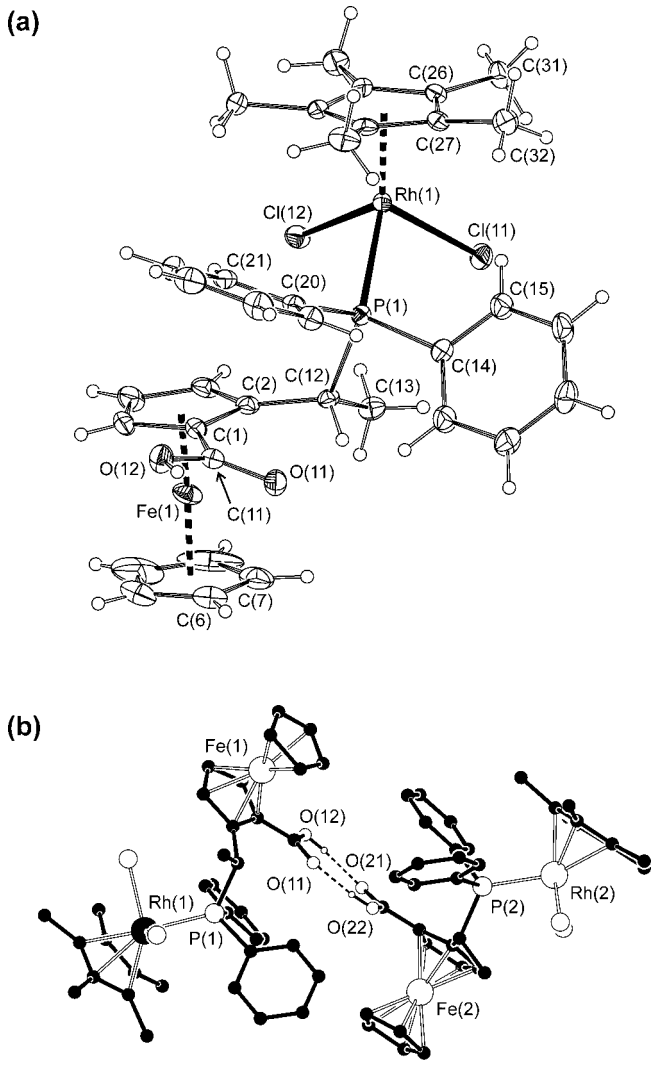


Figure 4. (a) PLATON view of molecule 1 in the crystal structure of complex **9**. Displacement ellipsoids are drawn with 30% probability. Molecule 2 is very similar and its labelling scheme is strictly analogous: On going from molecule 1 to molecule 2, the non-carbon, heavy atoms change the first digit in their atom labels to 2 while the atom labels for the carbon atoms are obtained by adding 40 to the respective atom label in molecule 1. (b) Dimeric motif in the crystal of **9**. Hydrogen bonds are shown as dashed lines.

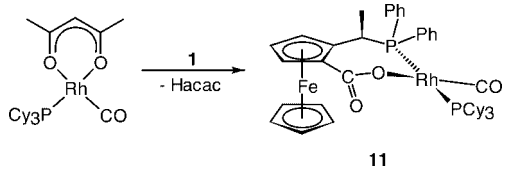
Table 3. Selected bond lengths [Å] and angles [°] for **9**.[a]

	Molecule 1 (n = 1)	Molecule 2 (n = 2)
Rh(n)–Cl(n1/n2)	2.4069(9)/2.392(1)	2.420(1)/2.402(1)
Rh(n)–P(n)	2.3621(9)	2.3558(9)
Rh–Cg(n3)	1.838(2)	1.828(2)
Cl(n1)–Rh(n)–Cl(n2)	91.40(3)	94.12(4)
P(n)–Rh(n)–Cl(n1/n2)	89.77(3)/89.42(3)	88.92(4)/90.62(4)
Cg(n3)-Rh(n)–Cl(n1/n2)	122.26(5)/118.65(6)	119.93(6)/119.38(7)
Cg(n3)-Rh(n)–P(n)	133.97(6)	133.76(7)
Fe–Cg(n1)	1.644(2)	1.653(2)
Fe–Cg(n2)	1.653(2)	1.659(2)
∠Cp(n1),Cp(n2)	2.8(3)	0.8(3)
C=O[b]	1.258(3)	1.262(4)
C–OH[c]	1.277(4)	1.275(4)
O–C=O[d]	123.9(3)	123.1(3)
P–C[e]	1.834(4)–1.893(2)	1.830(3)–1.907(4)
C–P–C[f]	101.2(1)–104.3(2)	100.4(2)–103.4(2)

[a] Definitions: Cp(11) = C(1–5), Cp(12) = C(6–10), Cp(21) = C(41–45), Cp(22) = C(46–50), Cp(13) = C(26–30), and Cp(23) = C(66–70). Cg(n1,n2,n3) represent the respective centroids. For a note on the atom labelling scheme, see Figure 4. [b] C(11)–O(11) (molecule 1) or C(51)–O(21) (molecule 2). [c] C(11)–O(12) (molecule 1) or C(51)–O(22) (molecule 2). [d] O(11)–C(11)–O(12) (molecule 1) or O(21)–C(51)–O(22) (molecule 2). [e] Range of P(1)–C(12,14,20) (molecule 1) or P(2)–C(52,54,60) (molecule 2) distances. [f] Range of C(12)–P(1)–C(14,20) and C(14)–P(1)–C(20) (molecule 1) or C(52)–P(2)–C(54,60) and C(54)–P(2)–C(60) (molecule 2) angles.

in Table 3), albeit without any significant slanting of the three-legged piano-stool geometry, as evidenced by the dihedral angles of the basal [Cl(n1),Cl(n2),P(n)] and Cp(n3) planes of 8.1(2)° and 7.0(2)° for molecules 1 and 2 (≡ n), respectively. The overall molecular geometry is similar to that of the analogous complex with P-monodentate 2-[(diphenylphosphanyl)methyl]ferrocenecarboxylic acid.[7] The P-monodentate phosphane–carboxylic ligand is oriented such that its ferrocene and phenyl groups are kept clear of the (η^5-C_5Me_5)Rh moiety while the methyl group of the ethane-1,1-diyl linker is located approximately below the rhodium atom [cf. Rh(1)–P(1)–C(12)–C(2/13) and Rh(2)–P(2)–C(52)–C(42/53) torsion angles of –85.9(3)/45.6(3)° and –85.4(3)/44.9(3)°, respectively]. The Cp(n1) and Cp(n3) rings are nearly parallel in both molecules, the respective dihedral angles being 7.3(2)° [Cp(11)/Cp(13) in molecule 1] and 8.2(2)° [Cp(21)/Cp(23) in molecule 2]. This arrangement obviously corresponds with the π···π stacking interactions mentioned above.

Similarly to other ferrocene-based phosphane–carboxylic acids,[6,7,15] **1** reacts with [Rh(acac)(CO)(PCy_3)] (Hacac = pentane-2,5-dione, Cy = cyclohexyl) to give a complex with *O*,*P*-chelating phosphane–carboxylate (**11**, Scheme 4) by replacement of the acetylacetonate and concomitant proton transfer. Compound **11** shows characteristic strong bands due to $\nu_{C\equiv O}$ at 1959 cm^{-1} and carboxylate vibrations at 1612 and 1321 cm^{-1} in its IR spectrum. The presence of two different phosphane donors in *trans* positions is best manifested in the ^{31}P NMR spectrum, which shows two doublets of doublets at δ_P = 40.9 and 46.5 ppm with typical coupling constants ($^1J_{Rh,P} \approx 125$, $^2J_{P,P}$ = 319 Hz),[7,15,16] and further by ^{31}P-^{13}C coupling patterns in the ^{13}C NMR spectrum (e.g., by a doublet of triplets at δ_C = 190.20 ppm with $^1J_{Rh,C}$ = 73 and $^2J_{P,C}$ = 16 Hz for Rh-*C*O).



Scheme 4.

As revealed by X-ray diffraction analysis (Figure 5, Table 4), the coordination environment of the rhodium atom in **11** is almost planar with the phosphane moieties in *trans* positions. The maximum deviation of the donor atoms and the metal atom from the mean coordination plane [Rh]

(see Table 4 for definitions) is much less than 0.1 Å. Likewise, the interligand angles differ only marginally from 90° which, together with their sum of 360.4°, rules out any tetrahedral deformation of the coordination polyhedron.

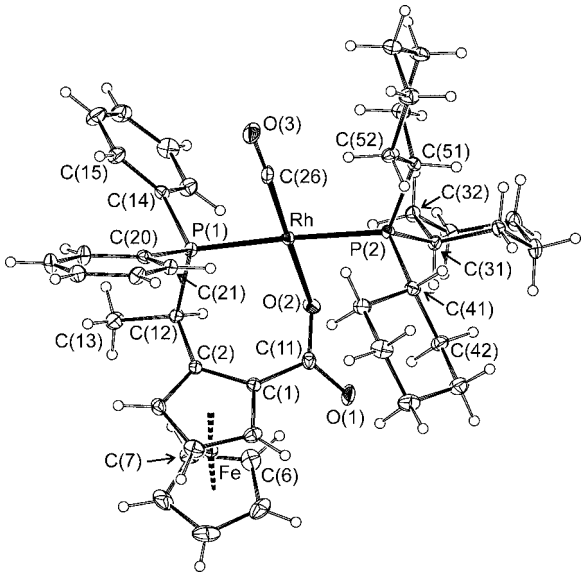


Figure 5. PLATON view of the molecular structure of **11** showing displacement ellipsoids at the 30% probability level.

On the whole, the coordination geometry compares favourably with that in similar complexes featuring 2-[(diphenylphosphanyl)methyl]ferrocenecarboxylate[7] and 1′-(diphenylphosphanyl)ferrocenecarboxylate as the *O*,*P*-chelating ligands.[15a] The pendant phosphane and, consequently, the [Rh] plane in **11** are directed above the ferrocene framework such that the [Rh] and Cp(1) planes subtend a dihedral angle of about 73° (see Table 4 for definition of the ring planes). The methyl and rhodium "substituents" at the P(1)–C(12) bond are arranged in an antiperiplanar manner [C(13)–C(12)–P(1)–Rh 169.3(2)°] whilst the ferrocene unit and the rhodium atom are close to synperiplanar [C(2)–C(12)–P(1)–Rh –62.3(2)°]. In such an arrangement, the formation of the Rh–O(2) bonds leads to a rotation of the carboxyl group from its parent Cp(1) plane by about 33° (note that the carboxyl and [Rh] planes are rotated by about 53°). The overall conformation is similar to the 2-[(diphenylphosphanyl)methyl]ferrocenecarboxylato complex mentioned above from which **11** differs only by substitution at the phosphanyl side chain (methyl vs. H). Similarly to the mentioned complex, the "PC_3" moieties of the phosphane donors in **11** appear staggered when looking in the P(1)–P(2) direction and all cyclohexyl rings adopt a chair conformation,[17] binding the phosphorus atom in equatorial positions.

Palladium Complexes

When studying palladium(II) complexes we focused on amide **6** due to its expected ability to ligate metal centres in different ways. First, we turned to (allyl)palladium species as they are relevant to palladium-mediated allylic alkylation reactions (see below). The reaction of [{Pd(μ-Cl)(η^3-C_3H_5)}$_2$] with **6** in a 1:2 molar ratio was monitored in situ. A single "product" **12** was detected in the ^{1}H NMR spectrum, which shows two sets of broad signals at room temperature (25 °C). Heating to 50 °C resulted in the coalescence of most signals (see Experimental Section). On the other hand, cooling to 0 °C and below caused the broad resonances to sharpen and split into two distinct sets of signals attributable to isomers due to a fluxional η^3-allyl moiety.[18] The ^{31}P NMR spectra are in agreement with these observations, showing two narrow-spaced signals (δ_P = 34.8 and 34.6 ppm at 0 °C), which collapse into a sharp singlet at higher temperature (δ_P = 35.3 ppm at 50 °C). The ^{31}P NMR shift and unaffected $\nu_{C=O}$ band in the IR spectrum allowed us to formulate **12** as a fluxional complex with P-monodentate **6**, i.e. [PdCl(η^3-C_3H_5)(**6**-κ*P*)], which results from a simple bridge-cleavage reaction. Support for this formulation was obtained from the ESI mass spectrum, which shows a peak at *m*/*z* = 678 attributable to [(η^3-C_3H_5)-Pd(**6**)]$^+$.

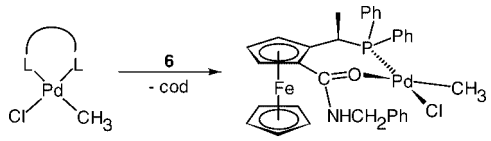
The chelating, non-fluxional palladium(II) complex **13** was obtained from the reaction of **6** with [PdCl(Me)(cod)] (cod = η^2:η^2-cycloocta-1,5,-diene; Scheme 5). The spectro-

Table 4. Selected bond lengths [Å] and angles [°] for **11**.[a]

Rh–P(1)	2.3041(9)	P(1)–Rh–O(2)	93.12(6)
Rh–P(2)	2.3692(8)	P(1)–Rh–C(26)	86.5(1)
Rh–O(2)	2.064(2)	P(2)–Rh–O(2)	85.24(6)
Rh–C(26)	1.793(3)	P(2)–Rh–C(26)	95.5(1)
C(26)–O(3)	1.155(4)	Rh–C(26)–O(3)	175.8(3)
Fe–Cg(1)	1.643(2)	∠Cp(1),Cp(2)	5.9(2)
Fe–Cg(2)	1.652(2)	∠Cp(1),[COO]	33.3(4)
C(1)–C(11)	1.506(4)	∠[Rh],[COO]	53.3(4)
C(11)–O(1)	1.229(4)	∠[Rh],Cp(1)	73.3(1)
C(11)–O(2)	1.288(4)	O(1)–C(11)–O(2)	124.1(3)
C(2)–C(12)	1.500(4)	C(2)–C(12)–P	107.8(2)
C(12)–C(13)	1.537(5)	C(2)–C(12)–C(13)	113.9(3)
P(1)–C[b]	1.815(3)–1.867(3)	C–P(1)–C[c]	102.0(1)–108.6(2)
P(2)–C[d]	1.855(3)–1.875(3)	C–P(2)–C[e]	102.6(1)–105.5(1)

[a] Definitions: Ring planes: Cp(1) = C(1–5), Cp(2) = C(6–10); Cg(1,2) denote the respective ring centroids. [Rh] = {Rh, P(1), P(2), O(2), C(26)}, [COO] = {C(11), O(1), O(2)}. [b] Range of P–C(12,14,20) distances. [c] Range of C(12)–P–C(14,20) and C(14)–P(1)–C(20) angles. [d] Range of P–C(31,41,51) distances. [e] Range of C(31)–P–C(41,51) and C(41)–P(2)–C(51)angles.

scopic data of **13** clearly indicate the formation of only one of all possible isomers that differ in the coordination mode of the amide ligand (*P,O* vs. *P,N*) *and* configuration (*trans*-P,Cl and *trans*-P,C) in solution. Whereas the P-coordination was clearly inferred from the shift of the ^{31}P NMR resonance to lower fields (Δ_P = 44.0 ppm), the shift of the $\nu_{C=O}$ (amide I) band to lower energies and a low-field shift of the C=O resonance in the ^{13}C NMR spectrum (Δ_C = 5.3 ppm) suggested coordination through the amide oxygen atom. A *trans*-P,Cl configuration was proposed on the basis of a comparison of $^3J_{P,H}$ values for the palladium-bonded methyl group obtained from the ^1H NMR spectrum with literature data.[19,20]



13

Scheme 5. Preparation of complex **13** (L–L is cycloocta-1,5-diene).

The crystal structure of **13** (Figure 6, Table 5) confirmed both the anticipated coordination mode of **6** and the *trans*-P,Cl disposition of the donors. The palladium atom and its four donor atoms are coplanar within 0.1 Å; the sum of the interligand angles is 360.15°. The Pd–donor distances are rather unexceptional, comparing well with those in [PdCl(C_6F_5){2-$Ph_2PC_6H_4CONHCHMe_2$-κ^2*O,P*}] [Pd–Cl 2.3691(4), Pd–P 2.2114(4), Pd–O 2.098(1) Å],[21] [PdCl(Me)(L-κ^2*P,P′*)] (L = various chiral ferrocene-derived diphosphanes of the type [Fe{η^5-C_5H_3(PR_2-1)[CH(Me)-PR'_2-2]}(η^5-C_5H_5)]; Pd–C 2.081–2.141 Å)[20a,22] and bis{μ-[2-(diphenylphosphanyl)ferrocenyl]carboxylato-*O,O′,P*}bis-{methylpalladium(II)}] [Pd–C 2.013(3) Å], for example.[23]

The structural data of the related amido phosphane oxide (*R*)-**8** enable an inspection of the changes in the amide group geometry upon coordination. On going from (*R*)-**8** to **13**, for example, the C=O bond elongates by about 0.03 Å while the C(11)–N/C(1) bond lengths decrease by about 0.02 Å. This is consistent with donation from the amide oxygen atom and a corresponding electron density shift towards C11. As usual, the amide moiety is almost

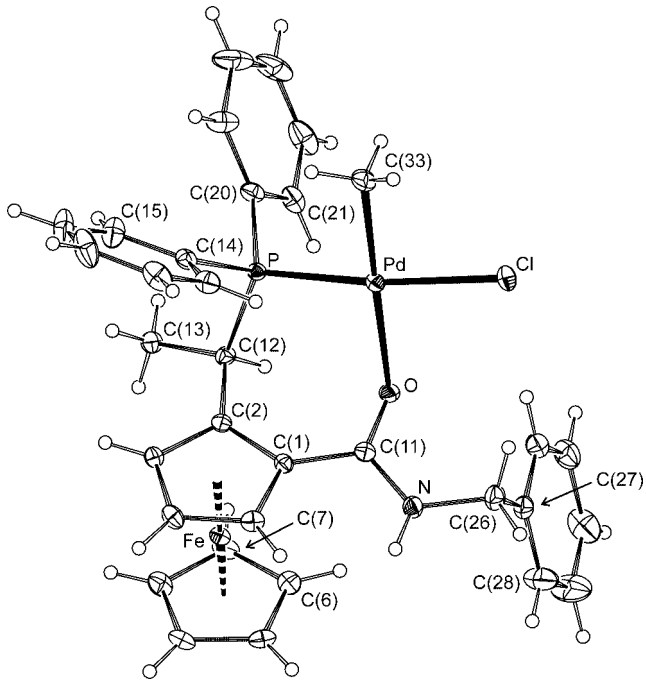


Figure 6. PLATON view of the molecular structure of **13** showing 30% probability displacement ellipsoids.

planar [τ(O–C(11)–N–C(26) 7.0(4)°] but is rotated from the Cp1 plane by 16.8(3)° along the C1–C11 bond, which brings the O atom above the ferrocene unit and in the vicinity of the palladium atom. The geometry of the ferrocene unit remains practically unaffected: the Fe–Cg distances are nearly the same as in (*R*)-**8** and the cyclopentadienido ligands show a tilt of 3.7(2)°. However, a minor deformation, not detectable in (*R*)-**8**, can be found at the amide-linking bond C(1)–C(11), which is bent away from the phosphanylalkyl chain. The C(11)–C(1)–C(2/5) angles differ by as much as 18° [125.9(2)/107.9(2)°] whereas the difference between the C(12)–C(2)–C(1/3) angles is only 2.5°. Such a distortion of the valence angles can be attributed to *O,P*-chelate coordination, making the donor sites more distant.

In the solid state, the molecules of **13** interact predominantly through N–H(90)···Cl^{iii} bonds [N–H(90)···Cl^{iii} (iii: 1 – *x*, 1/2 + *y*, 2 – *z*) 3.281(2) Å; angle at H(90) 160°], which

Table 5. Selected bond lengths [Å] and angles [°] for **13**.[a]

Pd–Cl	2.3781(8)	Cl–Pd–O	89.97(6)
Pd–P	2.2028(6)	Cl–Pd–C(33)	88.92(9)
Pd–O	2.171(2)	P–Pd–O	93.76(6)
Pd–C(33)	2.029(3)	P–Pd–C(33)	87.50(8)
Fe–Cg(1)	1.647(1)	∠Cp(1),Cp(2)	3.7(2)
Fe–Cg(2)	1.657(1)	∠[Pd],[CON]	55.8(3)
C(1)–C(11)	1.478(4)	∠[Pd],Cp(1)	67.2(1)
C(11)–O	1.257(4)	O–C(11)–N	119.7(3)
C(11)–N	1.334(4)	C(11)–N–C(26)	121.6(2)
N–C(26)	1.468(4)	C(2)–C(12)–P	108.6(2)
C(26)–C(27)	1.506(5)	C(2)–C(12)–C(13)	112.9(2)
P–C[b]	1.815(3)–1.865(3)	C–P–C[c]	105.5(1)–109.4(1)

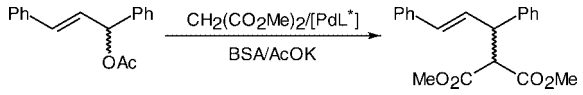
[a] Definitions: Ring planes are defined as follows: Cp(1) = C(1–5), Cp(2) = C(6–10); Cg(1,2) are the respective ring centroids. [Pd] = {Pd,Cl,P,O,C(33)}, [CON] = {C(11),O,N}. [b] Range of P–C(12,14,20) distances. [c] Range of C(12)–P–C(14,20) and C(14)–P(1)–C(20) angles.

gives rise to infinite helical chains running along the crystallographic 2_1 screw axis.

Catalytic Tests

In order to probe the catalytic performance of this newly synthesised family of ligands derived from **1**, we first chose the rhodium-catalysed hydrogenation of methyl β-acetamidocinnamate.[24] Somewhat unexpectedly, the reductions performed under standard conditions (see Experimental Section) did not proceed at all. As the next step, we turned to palladium-mediated asymmetric allylic alkylation,[25] which is a widely used benchmark test that often allows a direct comparison with other chiral ferrocene-based ligands.

When performing allylic substitutions (Scheme 6) we used 1,3-diphenylprop-2-en-1-yl acetate as the substrate, dimethyl malonate/*N*,*O*-bis(trimethylsilyl)acetamide/potassium acetate as the nucleophile source, and pre-catalysts formed in situ from [{Pd(μ-Cl)(η^3-C_3H_5)}$_2$] and a slight excess of the appropriate ligand. All reactions were carried out in dichloromethane at room temperature. The results are summarised in Table 6.



Scheme 6.

Table 6. Application of **1** and its amides in palladium-catalysed enantioselective allylic alkylation.[a]

Entry	Ligand	Conv. (isolated yield) [%][b]	*ee* [%] (config.)[c]
1	**1**	100 (94)	10 (*S*)
2	**6**	55	41 (*R*)
3	(*R*)-**7**	42	43 (*R*)
4	(*S*)-**7**	22	35 (*R*)

[a] See Experimental Section for conditions. [b] Conversion determined by ^{1}H NMR spectroscopy. [c] Absolute configuration assigned by comparison of the sign of the optical rotation with the literature data.

The reaction in the presence of the catalyst obtained from **1** proceeded with the highest rate (conversion) but with disappointingly low enantioselectivity (Table 6, Entry 1). Replacement of the carboxy group with a carbamoyl moiety resulted in lower chemical yields and higher *ee* values, although with an *opposite* configuration of the major product (Table 6, Entries 2–4). This change of configuration of the preferred alkylated product can be attributed to a changed donor ability of the ligands (P,O for **1** vs. P,N or P,O for the amides) or to a changed access for the nucleophile towards the η^3-allyl intermediate. A comparison of the results obtained with amides that differ only in their *N*-substituents (type and chirality) indicates that the nature of the benzylic group has only a small influence on the course of the catalytic reaction in terms of enantioselectivity while changing the reaction rate. Our observations correspond with previous attempts to clarify the role of individual chirality elements in ferrocene-based donors possessing both central and planar chirality, which clearly showed that the reaction course is governed not only by both chirality elements but also by their *mutual* matching.[26]

Despite the numerous reports concerning the use of ferrocene-based donors in allylic alkylations, there seems to be no example available in the literature relating directly to the compounds under study (same reaction, similar ligands). Most reports involving phosphanyl–ferrocenecarboxylic acids and their amides deal, with varying success, with reactions involving *cyclic* allylic acetates.[27,28] Nonetheless, acid **1** and its amides show *ee* values inferior to those reported for the chemically related (phosphanylferrocenyl)oxazolines[4b,26d,29] and for *meso*-1,1′-bis(diphenylphosphanyl)-2,2′-bis{*N*-(ω-hydroxyalkyl)carbamoyl}ferrocenes, which combine *two* phosphane and amide moieties.[30] Even so, the catalytic performance observed for **1** and the related amido phosphanes is lower than that of Josiphos-type ligands[31] where, however, a stronger ligand–palladium interaction can be expected due to the presence of two phosphane moieties.

Conclusions

We have reported the preparation of a novel, enantiopure phosphanyl–ferrocenecarboxylic ligand combining planar and central chirality elements, namely (*R*,*R*$_p$)-2-[1-(diphenylphosphanyl)ethyl]ferrocenecarboxylic acid (**1**), and its derivatives modified at both the phosphorus (**4** and **5**) and carboxyl groups [amides **6**, (*S*)-**7** and (*R*)-**7**]. A study of the representative phosphanes as ligands for rhodium (**1**→**9**, **10**, **11**) and palladium(II) (**6**→**12** and **13**) clearly has shown their coordination versatility and the potentially multidentate nature of these phosphanyl–ferrocenecarboxylic donors. Based on these results, we have also investigated the catalytic performance of the modified phosphanes in enantioselective rhodium-catalysed hydrogenation and asymmetric palladium-catalysed allylic alkylation. Whereas the former reaction gave disappointing results, not proceeding with any of the ligands tested [**1**, **6**, (*R*)-**7**, and (*S*)-**7**], the latter proved more successful, thereby providing an insight into the role of the individual molecular parts on the reaction rate and stereodiscrimination.

Experimental Section

Materials and Methods: All syntheses were performed under argon with exclusion of direct daylight. Tetrahydrofuran was dried by refluxing with potassium/benzophenone ketyl and distilled. Toluene was dried with sodium metal and distilled. Dichloromethane and chloroform were predried by standing over anhydrous potassium carbonate and then distilled from calcium hydride. Butan-2-one was dried with phosphorus pentaoxide and distilled prior to use. (*R*,*S*$_p$)-1-Bromo-2-[1-(diphenylphosphanyl)ethyl]ferrocene (**2**), [{(μ-Cl)RhCl(η^5-C_5Me_5)}$_2$],[32] [Rh(acac)(CO)(PCy$_3$)][15c] and [PdCl(Me)(cod)][33] were prepared according to the literature procedures. Other chemicals (Lachema, Fluka) and solvents used for crystallisations (Lach-Ner) were used without further purification. NMR

spectra were recorded with a Varian Unity Inova spectrometer (^{1}H: 399.95; ^{13}C: 100.58; ^{31}P: 161.90 MHz) at 25 °C unless indicated otherwise. Chemical shifts (δ) are given relative to internal tetramethylsilane (^{13}C and ^{1}H) or to external 85% aqueous H_3PO_4 (^{31}P). IR spectra were recorded with an FT IR Nicolet Magna 650 spectrometer. Positive ion electron impact (EI) and fast atom bombardment (FAB) mass spectra [including high resolution (HR) measurements] were obtained with a ZAB SEQ spectrometer. Electrospray (ESI) mass spectra were recorded with a Micromass Q-TOF spectrometer (acetonitrile solvent). Optical rotations were measured with an automatic polarimeter Autopol III (Rudolph Research) at room temperature.

Preparation of (R,R_p)-2-[1-(Diphenylphosphanyl)ethyl]ferrocenecarboxylic Acid (1): Butyllithium (2.1 mL, 2.5 M in hexanes, 5.3 mmol) was added dropwise to a stirred solution of **2** (1.91 g, 4.0 mmol) in thf (50 mL) at –78 °C. After stirring at –78 °C for 1 h, the reaction solution was poured onto crushed solid CO_2 (approx. 50 g) and allowed to stand at room temperature overnight. The mixture was then diluted with water and diethyl ether (approx. 30 mL each), and washed with saturated aqueous NaCl solution (2 × 30 mL). The organic phase was dried with anhydrous $MgSO_4$ and the solvents were evaporated under vacuum. The residue was purified by chromatography on silica gel, eluting with dichloromethane/methanol (20:1). A minor band of (*R*)-[1-(diphenylphosphanyl)ethyl]ferrocene eluted first, followed by the band of the product, which, after evaporation of the solvent, afforded **1** as an orange solid foam. Yield: 1.482 g (84%). ^{1}H NMR ($CDCl_3$): δ = 1.55 (dd, $^3J_{H,H}$ = 7.1, $^3J_{P,H}$ = 13.9 Hz, 3 H, CHC*H*$_3$), 4.21 (s, 5 H, C_5H_5), 4.28 (qd, $^3J_{H,H}$ = 7.1, $^2J_{P,H}$ = 5.7 Hz, 1 H, C*H*CH$_3$), 4.36 (m, 1 H, C_5H_3), 4.40 (apparent t, $J \approx$ 2.7 Hz, 1 H, C_5H_3), 4.68 (m, 1 H, C_5H_3), 7.01–7.64 (m, 10 H, P*Ph*$_2$) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 18.49 (d, $^2J_{P,C}$ = 19 Hz, CH*C*H$_3$), 28.90 (d, $^1J_{P,C}$ = 15 Hz, *C*HCH$_3$), 67.44 (d, $^3J_{P,C}$ = 2 Hz, C_5H_3 *C*-CO$_2$H), 69.95 (C_5H_3 *C*H), 69.97 (C_5H_3 *C*H), 70.32 (C_5H_5), 70.85 (d, $J_{P,C}$ = 5 Hz, C_5H_3 *C*H), 95.82 (d, $^2J_{P,C}$ = 16 Hz, C_5H_3 *C*-CH), 127.48 (d, $^3J_{P,C}$ = 6 Hz, PPh$_2$ *C*H$_m$), 128.07 (PPh$_2$ *C*H$_p$), 128.31 (d, $^3J_{P,C}$ = 6 Hz, PPh$_2$ *C*H$_m$), 129.09 (PPh$_2$ *C*H$_p$), 133.23 (d, $^2J_{P,C}$ = 18 Hz, PPh$_2$ *C*H$_o$), 134.40 (d, $^2J_{P,C}$ = 20 Hz, PPh$_2$ *C*H$_o$), 135.78, 136.69 (2 × d, $^1J_{P,C}$ = 16 Hz, PPh$_2$ *C*$_{ipso}$), 178.06 (*C*O$_2$H) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 11.1 (s) ppm. IR (Nujol): $\tilde{\nu}$ = 1667 (s), 1303 (m), 1227 (m), 1157 (w), 1088 (w), 1000 (vw), 958 (vw), 821 (w), 742 (m), 697 (m), 496 (w), 479 (w) cm^{-1}. MS (EI+): *m*/*z* (%) = 442 (13) [M]$^{+\cdot}$, 257 (59) [M – PPh$_2$]$^+$, 239 (6), 213 (8), 186 (51), 183 (34) [PPh$_2$ – 2 H]$^+$, 152 (12), 138 (22), 121 (27) [C_5H_5Fe]$^+$, 119 (63), 108 (100). HR MS calcd. for $C_{25}H_{23}{}^{56}FeO_2P$ [M]$^{+\cdot}$ 442.0785; found 442.0782. [a]$_D$ = –56.5 (c = 1.0, $CHCl_3$).

Preparation of (R,R_p)-2-[1-(Diphenylthiophosphoryl)ethyl]ferrocenecarboxylic Acid (4): A solution of **1** (115 mg, 0.26 mmol) and sulfur (13 mg, 0.41 mmol) in toluene (10 mL) was heated at reflux for 1.5 h. After cooling to room temperature, the reaction solution was concentrated to dryness and the residue purified by column chromatography (silica gel, dichloromethane/methanol, 10:1). Subsequent evaporation of the solvent gave **4** as an orange solid foam. Yield: 111 mg (90%). ^{1}H NMR ($CDCl_3$): δ = 1.67 (dd, $^3J_{H,H}$ = 7.0, $^3J_{P,H}$ = 18.6 Hz, 3 H, CHC*H*$_3$), 4.24 (s, 5 H, C_5H_5), 4.52 (apparent t, $J \approx$ 2.7 Hz, 1 H, C_5H_3), 4.61 (m, 1 H, C_5H_3), 4.80 (dq, $^3J_{H,H}$ = 7.0, $^2J_{P,H}$ = 8.3 Hz, 1 H, C*H*CH$_3$), 4.92 (m, 1 H, C_5H_3), 7.08–8.22 (m, 10 H, P*Ph*$_2$) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 16.43 (CH*C*H$_3$), 32.61 (d, $^1J_{P,C}$ = 48 Hz, *C*HCH$_3$), 67.34 (d, $^2J_{P,C}$ = 2 Hz, C_5H_3 *C*-CO$_2$H), 70.01 (C_5H_3 *C*H), 70.57 (C_5H_5), 70.67 (C_5H_3 *C*H), 72.82 (d, $^3J_{P,C}$ = 2.5 Hz, C_5H_3 *C*H), 90.07 (C_5H_3 *C*-CH), 127.23, 128.66 (2 × d, $^3J_{P,C}$ = 12 Hz, PPh$_2$ *C*H$_m$), 130.23 (d, $^1J_{P,C}$ = 75 Hz, PPh$_2$ *C*$_{ipso}$), 130.77 (d, $^4J_{P,C}$ = 3 Hz, PPh$_2$ *C*H$_p$), 131.60 (d, $^1J_{P,C}$ = 79 Hz, PPh$_2$ *C*$_{ipso}$), 131.68 (d, $^4J_{P,C}$ = 3 Hz, PPh$_2$ *C*H$_p$), 131.95, 132.31 (2 × d, $^2J_{P,C}$ = 9 Hz, PPh$_2$ *C*H$_o$), 177.10 (*C*O$_2$H) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 54.7 (s) ppm. IR (Nujol): $\tilde{\nu}$ = 1663 (s), 1437 (sh), 1300 (m), 1227 (m), 1158 (w), 1100 (m), 1028 (w), 999 (w), 824 (w), 752 (m), 729 (s), 708 (m), 690 (m), 651 (m), 588 (w), 511 (w), 486 (m) cm^{-1}. MS (EI+): *m*/*z* (%) = 474 (39) [M]$^+$, 442 (4) [M – S]$^{+\cdot}$, 338 (8), 275 (100) [M – Ph$_2$PS]$^+$, 218 (25), 186 (16), 183 (18), 138 (12), 119 (39), 108 (28). HR MS calcd. for $C_{25}H_{23}{}^{56}FeO_2PS$ [M]$^{+\cdot}$ 474.0506; found 474.0518. [a]$_D$ = 39 (c = 1.0, $CHCl_3$).

Preparation of (R,R_p)-2-[1-(Diphenylphosphoryl)ethyl]ferrocenecarboxylic Acid (5): In air, hydrogen peroxide (0.3 mL 30%, 2.5 mmol) was added to a solution of acid **1** (93 mg, 0.21 mmol) in acetone (5 mL) whilst stirring and cooling in an ice bath. The cooling bath was removed after 5 min and stirring was continued at room temperature for 30 min. A saturated aqueous solution of $Na_2S_2O_3$ (5 mL) was added to remove the excess of H_2O_2 and, after an additional 10 min, acetone was removed under reduced pressure, the residue diluted with water (10 mL) and extracted with dichloromethane (3 × 10 mL). The combined extracts were washed with saturated aqueous NaCl solution (20 mL), dried with $MgSO_4$, and the solvents were evaporated under vacuum. The residue was immediately purified by column chromatography (silica gel, dichloromethane/methanol mixture, 10:1) to yield **4** as a yellow solid foam after solvent evaporation. Yield: 48 mg (50%); the reaction is accompanied by decomposition, which results in the formation of a dark material that remains adsorbed at the top of the chromatographic column. ^{1}H NMR ($CDCl_3$): δ = 1.71 (dd, $^3J_{H,H}$ = 7.3, $^3J_{P,H}$ = 15.7 Hz, 3 H, CHC*H*$_3$), 4.23 (s, 5 H, C_5H_5), 4.43 (apparent t, $J \approx$ 2.7 Hz, 1 H, C_5H_3), 4.46 (dq, $^3J_{H,H} \approx {}^2J_{P,H} \approx$ 7.5 Hz, 1 H, C*H*CH$_3$), 4.66 (m, 2 H, 2 × C_5H_3), 7.12–8.02 (m, 10 H, P*Ph*$_2$) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 15.21 (d, $^2J_{P,C}$ = 2 Hz, CH*C*H$_3$), 31.91 (d, $^1J_{P,C}$ = 65 Hz, *C*HCH$_3$), 68.67 (C_5H_3 *C*-CO$_2$H), 70.31 (C_5H_3 *C*H), 70.49 (C_5H_5), 70.51 (C_5H_3 *C*H), 71.84 (d, $J_{P,C}$ = 2 Hz, C_5H_3 *C*H), 89.79 (C_5H_3 *C*-CH), 127.58, 128.59 (2 × d, $^3J_{P,C}$ = 12 Hz, PPh$_2$ *C*H$_m$), 130.32, (d, $^1J_{P,C}$ = 52 Hz, PPh$_2$ *C*$_{ipso}$), 131.27 (d, $^1J_{P,C}$ = 57 Hz, PPh$_2$ *C*$_{ipso}$), 131.29 (d, $^4J_{P,C}$ = 2.5 Hz, PPh$_2$ *C*H$_p$), 131.41, 131.68 (2 × d, $^2J_{P,C}$ = 9 Hz, PPh$_2$ *C*H$_o$), 131.89 (d, $^4J_{P,C}$ = 2 Hz, PPh$_2$ *C*H$_p$), 175.99 (*C*O$_2$H) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 36.5 (s) ppm. IR (Nujol): $\tilde{\nu}$ = 1685 (s), 1281 (m), 1215 (m), 1153 (s), 1118 (m), 1105 (m), 1083 (m), 1027 (w), 1000 (w), 820 (w), 742 (m), 723 (s), 696 (m), 541 (m), 497 (m), 472 (w) cm^{-1}. MS (EI+): *m*/*z* (%) = 458 (7) [M]$^{+\cdot}$, 393 (2) [M – C_5H_5]$^+$, 368 (5), 322 (4). HR MS calcd. for $C_{25}H_{23}{}^{56}FeO_3P$ [M]$^{+\cdot}$ 458.0734; found 458.0750. [a]$_D$ = 30.5 (c = 1.0, $CHCl_3$).

Preparation of (R,S_p)-1-bromo-2-[1-(diphenylthiophosphoryl)ethyl]ferrocene (3): A solution of **2** (382 mg, 0.80 mmol) and sulfur (32 mg, 1.0 mmol) in toluene (10 mL) was heated at reflux for 1 h and then stirred at room temperature overnight. The solvent was evaporated under vacuum, and the residue was purified by column chromatography (silica gel; diethyl ether/hexane, 1:1). Subsequent concentration afforded the product as an orange solid. Yield: 359 mg (88%). ^{1}H NMR ($CDCl_3$): δ = 1.66 (dd, $^3J_{H,H}$ = 7.1, $^3J_{P,H}$ = 18.4 Hz, 3 H, CHC*H*$_3$), 3.80 (dq, $^3J_{H,H} \approx {}^2J_{P,H} \approx$ 7.5 Hz, 1 H, C*H*CH$_3$), 4.19 (s, 5 H, C_5H_5), 4.22 (apparent t, $J \approx$ 2.6 Hz, 1 H, C_5H_3), 4.26 (m, 1 H, C_5H_3), 4.68 (m, 1 H, C_5H_3), 7.10–8.16 (m, 10 H, P*Ph*$_2$) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 17.01 (CH*C*H$_3$), 33.72 (d, $^1J_{P,C}$ = 49 Hz, *C*HCH$_3$), 66.38 (s, 2 C, 2 × C_5H_3 *C*H), 68.76 (C_5H_3 *C*H), 71.00 (C_5H_5), 80.93 (d, $^3J_{P,C}$ = 2 Hz, C_5H_3 *C*-Br), 86.04 (C_5H_3 *C*-CH), 127.54, 128.67 (2 × d, $^3J_{P,C}$ = 12 Hz, PPh$_2$ *C*H$_m$), 129.79 (d, $^1J_{P,C}$ = 74 Hz, PPh$_2$ *C*$_{ipso}$), 131.03, 131.78 (2 × d, $^4J_{P,C}$ = 3 Hz, PPh$_2$ *C*H$_p$), 131.91 (d, $^1J_{P,C}$ = 80 Hz, PPh$_2$ *C*$_{ipso}$), 132.00, 132.36 (2 × d, $^2J_{P,C}$ = 9 Hz, PPh$_2$ *C*H$_o$) ppm. ^{31}P{^{1}H} NMR

($CDCl_3$): δ = 53.5 (s) ppm. MS (EI+): *m*/*z* (%) = 510 (40)/508 (40) $[M]^+$, 445 (3)/443 (3) $[M - C_5H_5]^+$, 363 (9), 338 (8), 308 (67), 293 (97)/291 (100) $[M - Ph_2PS]^+$, 260 (13), 217 (18) $[Ph_2PPS]^+$, 196 (14), 185 (16), 183 (30) $[Ph_2P - 2\ H]^+$, 155 (25), 153 (18), 139 (26), 121 (21) $[C_5H_5Fe]^+$. HR MS calcd. for $C_{24}H_{22}{}^{56}FePS^{79}Br$ $[M]^{+\cdot}$ 507.9713; found 507.9703. $C_{24}H_{22}Br^{56}FePS$ (509.2): calcd. C 56.61, H 4.35; found C 56.29, H 4.34. $[\alpha]_D$ = 55.5 (*c* = 1.0, $CHCl_3$).

Alternative Preparation of 1: The reaction was performed as described above for the preparation of **1**, starting from bromide **3** (280 mg, 0.55 mmol in 10 mL of thf) and butyllithium (0.3 mL, 2.5 M in hexanes, 0.75 mmol). Purification of the crude product by column chromatography (silica gel; dichloromethane/methanol, 10:1) afforded **4** as an orange glassy solid. Yield: 138 mg (53%). In the next step, phosphane sulfide **4** (58 mg, 0.12 mmol) was dissolved in dichloromethane (5 mL) and MeOTf (0.05 mL, 0.44 mmol) was added. The mixture was stirred at room temperature for 3 h. The solvent was removed under reduced pressure, the residue immediately dissolved in dichloromethane (5 mL), and treated with $P(NMe_2)_3$ (0.06 mL, 0.33 mmol). After stirring the resulting mixture at room temperature overnight, the volatiles were removed under vacuum and the residue was purified by column chromatography (silica gel, dichloromethane/methanol, 20:1). Concentration of the appropriate fraction gave acid **1** as an orange glassy solid. Yield: 23 mg (43%).

General Procedure for the Preparation of Amides: 1-Hydroxybenzotriazole (HOBt) was added to a solution of acid **1** in dichloromethane (15 mL) and the reaction mixture was stirred at 0 °C for 5 min (some HOBt, which is used in excess, remained undissolved). *N*-(3-Dimethylaminopropyl)-*N*′-ethylcarbodiimide (EDC) was then added dropwise and the formed solution was stirred at 0 °C for another 30 min, during which time the colour of the solution turned from orange to red. Finally, the appropriate amine (neat) was added and stirring was continued at room temperature for an additional 20 h. The mixture was then extracted with 3 M HCl (10 mL), twice with saturated aqueous $NaHCO_3$ (10 mL), and brine (10 mL). The organic phase was dried with $MgSO_4$, and the solvents were evaporated under vacuum. The residual orange oil was purified by column chromatography on silica gel, eluting with dichloromethane/methanol (20:1).

***N*-Benzyl-(*R*,*R*$_p$)-2-[1-(diphenylphosphanyl)ethyl]ferrocenecarboxamide (6):** Starting from **1** (221 mg, 0.50 mmol), HOBt (78 mg, 0.56 mmol), EDC (0.1 mL, 0.6 mmol) and benzylamine (57 mg, 0.53 mmol), the above procedure gave **6** as an orange solid foam. Yield: 195 mg (73%). ^1H NMR ($CDCl_3$): δ = 1.55 (dd, $^3J_{H,H}$ = 7.1, $^3J_{P,H}$ = 14.9 Hz, 3 H, CHC*H*$_3$), 3.99 (dd, *J* = 5.0, *J* = 14.9 Hz, 1 H, NHC*H*$_2$Ph), 4.18 (s, 5 H, C_5H_5), 4.19 (m, 1 H, C_5H_3), 4.22 (apparent t, *J* ≈ 2.6 Hz, 1 H, C_5H_3), 4.26 (m, 1 H, C_5H_3), 4.47 (dq, $^3J_{H,H} \approx {}^2J_{P,H} \approx 7$ Hz, 1 H, C*H*CH$_3$), 4.48 (dd, $^3J_{H,H}$ = 5.0, $^2J_{H,H}$ = 14.9 Hz, 1 H, NHC*H*$_2$Ph), 5.38 (t, $^3J_{H,H}$ = 5.5 Hz, 1 H, CON*H*), 6.85–7.65 (m, 15 H, P*Ph*$_2$ and CH$_2$*Ph*) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 18.62 (d, $^2J_{P,C}$ = 20 Hz, CH*C*H$_3$), 28.47 (d, $^1J_{P,C}$ = 13 Hz, *C*HCH$_3$), 43.33 (NH*C*H$_2$Ph), 65.41 (C_5H_3 *C*H), 67.81 (C_5H_3 *C*H), 69.13 (d, $J_{P,C}$ = 6 Hz, C_5H_3 *C*H), 70.04 (C_5H_5), 75.65 (C_5H_3 *C*-CONH), 95.06 (d, $^2J_{P,C}$ = 18 Hz, C_5H_3 *C*-CH), 127.30 (d, $^3J_{P,C}$ = 6 Hz, PPh$_2$ *C*H$_m$), 127.30 (CH$_2$Ph *C*H$_p$), 127.68 (br. s, PPh$_2$ *C*H$_p$), 127.69 (CH$_2$Ph *C*H$_o$), 128.33 (d, $^3J_{P,C}$ = 6 Hz, PPh$_2$ *C*H$_m$), 128.60 (CH$_2$Ph *C*H$_m$), 129.14 (br. s, PPh$_2$ *C*H$_p$), 133.50 (d, $^2J_{P,C}$ = 18 Hz, PPh$_2$ *C*H$_o$), 134.45 (d, $^2J_{P,C}$ = 20 Hz, PPh$_2$ *C*H$_o$), 138.72 (CH$_2$Ph C_{ipso}), 170.11 (*C*ONH) ppm; (PPh$_2$ C_{ipso}) signals not observed. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 10.3 (s) ppm. IR (Nujol): $\tilde{\nu}$ = 1635 (s), 1520 (s), 1303 (w), 1266 (w), 1232 (w), 1106 (w), 1027 (w), 1001 (w), 819 (w), 742 (m), 697 (m), 480 (w) cm^{-1}. MS (EI+): *m*/*z* (%) = 531 (58) $[M]^{+\cdot}$, 440 (4) $[M - C_7H_7]^+$, 374 (3), 346 (56) $[M - PPh_2]^+$, 255 (12) $[M - C_7H_7 - PPh_2]^+$, 238 (32), 212 (43), 183 (37) $[PPh_2 - 2\ H]^+$, 121 (40) $[C_5H_5Fe]^+$, 91 (100) $[C_7H_7]^+$. HR MS calcd. for $C_{32}H_{30}{}^{56}FeNOP$ $[M]^{+\cdot}$ 531.1414; found 531.1430. $[\alpha]_D$ = –156.5 (*c* = 1.0, $CHCl_3$).

(*R*,*R*$_p$)-2-[1-(Diphenylphosphanyl)ethyl]-*N*-[(*R*)-1-(phenylethyl)]ferrocenecarboxamide [(*R*)-7]: According to the general procedure with **1** (221 mg, 0.50 mmol), HOBt (78 mg, 0.56 mmol), EDC (0.1 mL, 0.6 mmol) and (*R*)-(1-phenylethyl)amine (64 mg, 0.53 mmol) gave amide (*R*)-**7** as an orange solid foam. Yield: 218 mg (80%). ^1H NMR ($CDCl_3$): δ = 1.49 [d, $^3J_{H,H}$ = 6.8 Hz, NHCH(C*H*$_3$)Ph], 1.53 (dd, $^3J_{H,H}$ = 7.2, $^3J_{P,H}$ = 14.0 Hz, 3 H, PCHC*H*$_3$), 4.18 (s, 5 H, C_5H_5), 4.19 (m, 1 H, C_5H_3), 4.21 (apparent t, *J* ≈ 2.6 Hz, 1 H, C_5H_3), 4.27 (m, 1 H, C_5H_3), 4.39 (dq, $^3J_{H,H}$ = 7.2, $^2J_{P,H}$ = 5.2 Hz, 1 H, PC*H*CH$_3$), 5.00 [dq, $^3J_{H,H} \approx {}^3J_{H,H} \approx 7$ Hz, 1 H, NHC*H*(CH$_3$)Ph], 5.60 (d, $^3J_{H,H}$ = 7.1 Hz, 1 H, CON*H*), 6.90–7.58 [m, 15 H, P*Ph*$_2$ and CH(CH$_3$)*Ph*] ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 18.57 (d, $^2J_{P,C}$ = 19 Hz, PCH*C*H$_3$), 21.87 [NHCH(*C*H$_3$)Ph], 28.58 (d, $^1J_{P,C}$ = 12 Hz, P*C*HCH$_3$), 48.76 [NH*C*H(CH$_3$)Ph], 66.44 (C_5H_3 *C*H), 67.95 (C_5H_3 *C*H), 69.44 (d, $J_{P,C}$ = 5 Hz, C_5H_3 *C*H), 70.12 (C_5H_5), 75.04 (C_5H_3 *C*-CONH), 94.52 (d, $^2J_{P,C}$ = 16 Hz, C_5H_3 *C*-CH), 126.52 (CHPh *C*H$_o$), 127.34 (CHPh *C*H$_p$), 127.45 (d, $^3J_{P,C}$ = 7 Hz, PPh$_2$ *C*H$_m$), 127.88 (PPh$_2$ *C*H$_p$), 128.31 (d, $^3J_{P,C}$ = 7 Hz, PPh$_2$ *C*H$_m$), 128.60 (CHPh *C*H$_m$), 129.25 (PPh$_2$ *C*H$_p$), 133.11 (d, $^2J_{P,C}$ = 17 Hz, PPh$_2$ *C*H$_o$), 134.56 (d, $^2J_{P,C}$ = 20 Hz, PPh$_2$ *C*H$_o$), 143.12 (CHPh C_{ipso}), 169.41 (*C*ONH) ppm; (PPh$_2$ C_{ipso}) signals not observed. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 10.1 (s) ppm. IR (Nujol): $\tilde{\nu}$ = 1632 (s), 1493 (s), 1305 (w), 1262 (w), 1225 (w), 1105 (w), 1000 (w), 820 (m), 742 (s), 697 (s), 480 (m) cm^{-1}. MS (EI+): *m*/*z* (%) = 545 (33) $[M]^{+\cdot}$, 440 (3) $[M - PhCHMe]^+$, 398 (4), 360 (24) $[M - PPh_2]^+$, 255 (11) $[M - PhCHMe - PPh_2]^+$, 238 (10), 213 (40), 186 (19), 183 (17) $[PPh_2 - 2\ H]^+$, 121 (19) $[C_5H_5Fe]^+$, 108 (32), 105 (34) $[C_8H_9]^+$, 85 (67), 83 (100). HR MS calcd. for $C_{33}H_{32}{}^{56}FeNOP$ $[M]^{+\cdot}$ 545.1571; found 545.1557. $[\alpha]_D$ = –69 (*c* = 1.0, $CHCl_3$).

(*R*,*R*$_p$)-2-[1-(Diphenylphosphanyl)ethyl]-*N*-[(*S*)-1-(phenylethyl)]ferrocenecarboxamide [(*S*)-7]: According to the general procedure with **1** (221 mg, 0.50 mmol), HOBt (78 mg, 0.56 mmol), EDC (0.1 mL, 0.6 mmol) and (*S*)-(1-phenylethyl)amine (64 mg, 0.53 mmol) gave (*S*)-**7** as an orange solid foam. Yield: 200 mg (73%). ^1H NMR ($CDCl_3$): δ = 1.34 [d, $^3J_{H,H}$ = 7.1 Hz, NHCH(C*H*$_3$)Ph], 1.52 (dd, $^3J_{H,H}$ = 7.2, $^3J_{P,H}$ = 15.0 Hz, 3 H, PCHC*H*$_3$), 4.07 (s, 5 H, C_5H_5), 4.20–4.22 (2 × m, 2 H, C_5H_3), 4.26 (m, 1 H, C_5H_3), 4.52 (dq, $^3J_{H,H} \approx {}^2J_{P,H} \approx 7$ Hz, 1 H, PC*H*CH$_3$), 4.89 [dq, $^3J_{H,H} \approx {}^3J_{H,H} \approx 7$ Hz, 1 H, NHC*H*(CH$_3$)Ph], 5.40 (d, $^3J_{H,H}$ = 7.1 Hz, 1 H, CON*H*), 6.99–7.65 [m, 15 H, P*Ph*$_2$, and CH(CH$_3$)*Ph*] ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 18.53 (d, $^2J_{P,C}$ = 21 Hz, PCH*C*H$_3$), 22.20 [NHCH(*C*H$_3$)Ph], 28.30 (d, $^1J_{P,C}$ = 12 Hz, P*C*HCH$_3$), 48.48 [NH*C*H(CH$_3$)Ph], 65.32 (C_5H_3 *C*H), 67.79 (C_5H_3 *C*H), 69.33 (d, $J_{P,C}$ = 6 Hz, C_5H_3 *C*H), 69.98 (C_5H_5), 75.11 (C_5H_3 *C*-CONH), 95.24 (d, $^2J_{P,C}$ = 16 Hz, C_5H_3 *C*-CH), 125.80 (CHPh *C*H$_o$), 127.08 (CHPh *C*H$_p$), 127.36 (d, $^3J_{P,C}$ = 7 Hz, PPh$_2$ *C*H$_m$), 127.80 (PPh$_2$ *C*H$_p$), 128.35 (d, $^3J_{P,C}$ = 7 Hz, PPh$_2$ *C*H$_m$), 128.58 (CHPh *C*H$_m$), 129.18 (PPh$_2$ *C*H$_p$), 133.63 (d, $^2J_{P,C}$ = 18 Hz, PPh$_2$ *C*H$_o$), 134.49 (d, $^2J_{P,C}$ = 20 Hz, PPh$_2$ *C*H$_o$), 144.27 (CHPh C_{ipso}), 169.32 (*C*ONH) ppm; (PPh$_2$ C_{ipso}) signals not observed. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 10.4 (s) ppm. IR (Nujol): $\tilde{\nu}$ = 1631 (s), 1495 (s), 1308 (w), 1262 (w), 1228 (w), 1105 (w), 1000 (w), 820 (w), 742 (s), 697 (s), 485 (br. m) cm^{-1}. MS (EI+): *m*/*z* (%) = 545 (100) $[M]^+$, 480 (5) $[M - C_5H_5]^+$, 440 (9) $[M - PhCHMe]^+$, 360 (66) $[M - PPh_2]^+$, 333 (6), 255 (28) $[M - PhCHMe - PPh_2]^+$, 238 (26), 212 (43), 186 (36), 183 (19) $[PPh_2 - 2\ H]^+$, 121 (25) $[C_5H_5Fe]^+$, 108 (54), 105 (50) $[C_8H_9]^+$. HR MS calcd. for $C_{33}H_{32}{}^{56}FeNOP$ $[M]^{+\cdot}$ 545.1571; found 545.1579. $[\alpha]_D$ = –173 (*c* = 1.0, $CHCl_3$).

Preparation of Dichlorido{(*R*,R_p)-2-[1-(diphenylphosphanyl-κ*P*)ethyl]ferrocenecarboxylic acid}(η^5-pentamethylcyclopentadienido)rhodium(III) (9): A solution of acid **1** (90 mg, 0.20 mmol) in chloroform (5 mL) was added to a solution of [{(μ-Cl)RhCl(η^5-C_5Me_5)}$_2$] (62 mg, 0.10 mmol) in the same solvent (5 mL) and the resulting clear mixture was stirred at room temperature overnight. The solution was filtered through a PTFE syringe filter (0.45 μm pore size) and the solvents were evaporated to dryness under vacuum to give the product as a red glassy solid in practically quantitative yield (150 mg) according to NMR spectroscopy. ^{1}H NMR ($CDCl_3$): δ = 1.18 (br. s, 15 H, C_5Me_5), 1.89 (br. dd, $^3J_{H,H}$ = 7.5, $^3J_{P,H}$ = 18.6 Hz, 3 H, CHCH_3), 4.08 (br. s, 1 H, C_5H_3), 4.13 (s, 5 H, C_5H_5), 4.24 (apparent t, $J \approx 2.7$ Hz, 1 H, C_5H_3), 4.58 (m, 1 H, C_5H_3), 4.86 (dq, $^3J_{H,H} \approx {}^2J_{P,H} \approx 7.5$ Hz, 1 H, C*H*CH$_3$), 7.28–8.12 (m, 10 H, P*Ph*$_2$) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 8.43 (C_5Me_5), 20.30 (br. s, CH*C*H$_3$), 37.28 (br. s, *C*HCH$_3$), 67.81 (C_5H_3 *C*-COOH), 69.40 (C_5H_3 *C*H), 69.60 (C_5H_3 *C*H), 71.06 (C_5H_5), 74.81 (C_5H_3 *C*H), 94.19 (br. s, C_5H_3 *C*-CH), 98.77 (dd, $^1J_{Rh,C}$ = 7, $^2J_{P,C}$ = 2 Hz, *C*$_5$Me$_5$), 127.00, 127.81 (2 × d, $^3J_{P,C}$ = 10 Hz, PPh$_2$ *C*H$_m$), 130.43, 130.71 (2 × s, PPh$_2$ *C*H$_p$), 134.22, 136.84 (2 × d, $^2J_{P,C}$ = 9 Hz, PPh$_2$ *C*H$_o$), 176.96 (br. s, *C*OOH) ppm; (PPh$_2$ C_{ipso}) signals not observed. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 34.3 (br. d, $^1J_{Rh,P}$ = 140 Hz) ppm. IR (Nujol): ν̃ = 1664 (composite s), 1299 (m), 1216 (m), 1157 (m), 1095 (m), 1021 (w), 1000 (w), 823 (w), 747 (s), 699 (m), 610 (w), 491 (m) cm^{-1}. HR MS (ESI–): calcd. for $C_{35}H_{37}{}^{35}Cl_2{}^{56}Fe^{103}RhO_2P$ [M – H$^+$]$^-$ 749.0313; found 749.0402; the observed isotopic distribution matched the calculated one.

Preparation of Chlorido{(*R*,R_p)-2-[1-(diphenylphosphanyl)ethyl]-ferrocenecarboxylato-κ^2*O*,*P*}(η^5-pentamethylcyclopentadienido)rhodium(III) (10): Chloroform solutions (5 mL each) of **1** (90 mg, 0.20 mmol) and [{(μ-Cl)RhCl(η^5-C_5Me_5)}$_2$] (62 mg, 0.10 mmol) were mixed and the mixture was stirred at room temperature for 2 h. Neutral chromatography grade alumina (ca. 2 g) was added to the solution and stirring was continued overnight. The alumina was then filtered off and washed thoroughly with chloroform. The liquid phase was concentrated under vacuum to give the product as a red glassy solid. Yield: 134 mg (94%). According to the NMR spectra, the product was an approximately 9:1 mixture of diastereoisomers. Note: An identical product mixture was formed when the solution containing in situ generated **9** was filtered through a short silica gel column. IR (Nujol): ν̃ = 1581 (s), 1307 (s), 1234 (w), 1171 (w), 1095 (m), 1044 (vw), 1025 (w), 999 (w), 816 (m), 746 (vs), 699 (s), 662 (w), 526 (s), 496 (m), 460 (m) cm^{-1}. HR MS (ESI+): calcd. for $C_{35}H_{38}{}^{35}Cl^{56}Fe^{103}RhO_2P$ [M + H]$^+$ 715.0702; found 715.0713. Major isomer: ^{1}H NMR ($CDCl_3$): δ = 1.46 (d, $^2J_{Rh,H}$ = 3.3 Hz, 15 H, C_5Me_5), 1.52 (dd, $^3J_{H,H}$ = 7.3, $^3J_{P,H}$ = 13.9 Hz, 3 H, CHCH_3), 3.22 (m, 1 H, C_5H_3), 3.72 (apparent t, $J \approx 2.6$ Hz, 1 H, C_5H_3), 4.07 (s, 5 H, C_5H_5), 4.67 (dq, $^3J_{H,H} \approx {}^2J_{P,H} \approx 7.5$ Hz, 1 H, C*H*CH$_3$), 4.76 (m, 1 H, C_5H_3), 7.16–7.98 (m, 10 H, P*Ph*$_2$) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 9.02 (d, $^2J_{Rh,C} \approx 1$ Hz, C_5Me_5), 14.16 (d, $^2J_{P,C}$ = 7 Hz, CH*C*H$_3$), 33.90 (d, $^1J_{P,C}$ = 18 Hz, *C*HCH$_3$), 67.89 (d, $J \approx$ 1 Hz, C_5H_3, *C*H), 68.18 (C_5H_3 *C*H), 70.17 (C_5H_5), 72.09 (C_5H_3 *C*H), 77.61 (d, $^3J_{P,C}$ = 2.5 Hz, C_5H_3 *C*-COO), 88.18 (d, $^2J_{P,C}$ = 5 Hz, C_5H_3 *C*-CH), 98.25 (dd, $^1J_{Rh,C}$ = 7, $^2J_{P,C}$ = 3 Hz, *C*$_5$Me$_5$), 125.20 (d, $^1J_{P,C}$ = 41 Hz, PPh$_2$ C_{ipso}), 127.14, 127.48 (2 × d, $^3J_{P,C}$ = 10 Hz, PPh$_2$ *C*H$_m$), 130.22 (d, $^4J_{P,C}$ = 2 Hz, PPh$_2$ *C*H$_p$), 130.84 (d, $^1J_{P,C}$ = 38 Hz, PPh$_2$ C_{ipso}), 131.04 (d, $^4J_{P,C}$ = 2 Hz, PPh$_2$ *C*H$_p$), 133.93, 135.30 (2 × d, $^2J_{P,C}$ = 9 Hz, PPh$_2$ *C*H$_o$), 180.14 (*C*OO) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 52.0 (d, $^1J_{Rh,P}$ = 148 Hz) ppm. Minor isomer: ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 49.8 (d, $^1J_{Rh,P}$ = 146 Hz) ppm.

Preparation of (*SP*-4-2)-Carbonyl{(*R*,R_p)-2-[1-(diphenylphosphanyl)ethyl]ferrocenecarboxylato-κ^2*O*,*P*}(tricyclohexylphosphane)rhodium(I) (11): A solution of acid **1** (45 mg, 0.10 mmol) in butan-2-one (3 mL) was added to a solution of [Rh(acac)(CO)(PCy$_3$)] (51 mg, 0.10 mmol) in butan-2-one (5 mL) and the mixture was heated at reflux for 5 min. The reaction solution was cooled to room temperature and volatiles were removed under vacuum to afford **11** as a yellow solid in quantitative yield (85 mg). ^{1}H NMR ($CDCl_3$): δ = 1.12–2.24 (m, 34 H, P*Cy*$_3$ and CHCH_3), 3.31 (m, 1 H, C_5H_3), 3.96 (apparent t, $J \approx 2.5$ Hz, 1 H, C_5H_3), 4.16 (s, 5 H, C_5H_5), 4.20 (dq, $^3J_{H,H} \approx {}^2J_{P,H} \approx 7$ Hz, 1 H, C*H*CH$_3$), 4.72 (m, 1 H, C_5H_3), 7.31–7.69 (m, 10 H, P*Ph*$_2$) ppm; the CHCH_3 signal is obscured by those of P*Cy*$_3$. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 13.91 (dd, $^2J_{P,C}$ = 2, $^3J_{Rh,C}$ = 6 Hz, CH*C*H$_3$), 26.57 (s, PCy$_3$ γ-*C*H$_2$), 27.56 (dd, $^2J_{P,C}$ = 2, $^3J_{Rh,C}$ = 10 Hz, PCy$_3$ α-*C*H$_2$), 29.12 (dd, $^1J_{P,C}$ = 14, $^2J_{Rh,C}$ = 3 Hz, *C*HCH$_3$), 30.18 (d, $^3J_{P,C}$ = 37 Hz, PCy$_3$ β-*C*H$_2$), 33.36 (d, $^1J_{P,C}$ = 19 Hz, PCy$_3$ *C*H), 66.01 (C_5H_3 *C*H), 66.72 (d, $J_{P,C} \approx 1$ Hz, C_5H_3 *C*H), 70.44 (C_5H_5), 71.71 (C_5H_3 *C*H), 84.27 (d, $^3J_{P,C}$ = 9 Hz, C_5H_3 *C*-COO), 85.90 (d, $^2J_{P,C}$ = 2 Hz, C_5H_3 *C*-CH), 127.43, 128.75 (2 × d, $^3J_{P,C}$ = 9 Hz, PPh$_2$ *C*H$_m$), 128.92 (ddd, $^1J_{P,C}$ = 38, $^2J_{Rh,C} = {}^3J_{P,C} \approx 3$ Hz, PPh$_2$ C_{ipso}), 129.45, 130.75 (2 × d, $^4J_{P,C}$ = 2 Hz, PPh$_2$ *C*H$_p$), 131.53 (d, $^2J_{P,C}$ = 10 Hz, PPh$_2$ *C*H$_o$), 132.67 (dd, $^1J_{P,C}$ = 32, J = 2 Hz, PPh$_2$ C_{ipso}), 135.76 (d, $^2J_{P,C}$ = 12 Hz, PPh$_2$ *C*H$_o$), 175.14 (*C*OO), 190.20 (dt, $^1J_{Rh,C}$ = 73, $^2J_{P,C}$ = 16 Hz, *C*≡O) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 40.9 (dd, $^1J_{Rh,P}$ = 125, $^2J_{P,P}$ = 319 Hz, *P*Ph$_2$), 46.5 (dd, $^1J_{Rh,P}$ = 127, $^2J_{P,P}$ = 319 Hz, *P*Cy$_3$) ppm. IR (Nujol): ν̃ = 1959 (vs), 1612 (s), 1321 (s), 1244 (w), 1174 (w), 1101 (w), 997 (w), 815 (w), 785 (w), 745 (m), 721 (m), 708 (m), 694 (w), 593 (w), 532 (m) cm^{-1}. MS (FAB+): *m*/*z* = 853 [M + H]$^+$, 824 [M – CO]$^+$. HR MS calcd. for $C_{44}H_{56}{}^{56}Fe^{103}RhO_3P_2$ [M + H]$^+$ 853.2109; found 853.2079.

(η^3-Allyl)palladium Complexes with 6. An in situ NMR Study: Amide **6** (11 mg, 0.02 mmol) was added to a solution of [{Pd(μ-Cl)(η^3-C_3H_5)}$_2$] (3.7 mg, 0.01 mmol) in $CDCl_3$ (1 mL). The mixture was stirred in the dark for 1 h, then filtered through a PTFE syringe filter (0.45 μm) and the filtrate used directly for NMR measurements. The sample used for IR measurements was obtained by concentrating the reaction mixture under vacuum. ^{1}H NMR ($CDCl_3$, 50 °C): δ = 1.83 (dd, $^3J_{P,H}$ = 18.0, $^3J_{H,H}$ = 7.2 Hz, 3 H, CHCH_3), 4.00 (dd, $^2J_{H,H}$ = 14.8, $^3J_{H,H}$ = 4.9 Hz, 1 H, CH_2Ph), 4.16 (s, 5 H, C_5H_5), 4.21 (m, 1 H, C_5H_3), 4.31 (m, 1 H, C_5H_3), 4.46 (dd, $^2J_{H,H}$ = 14.8, $^3J_{H,H}$ = 6.6 Hz, 1 H, CH_2Ph), 5.01 (dq, $^3J_{H,H} \approx {}^2J_{P,H} \approx 7$ Hz, 1 H, C*H*CH$_3$), 5.47 (br. t, $^3J_{H,H} \approx 6$ Hz, 1 H, N*H*), 7.06–7.94 (m, 15 H, P*Ph*$_2$ and CH$_2$*Ph*) ppm; the remaining three signals of the allyl moiety and one C_5H_3 resonance are observed as broad bands between δ = 2.1 and 3.1 ppm and at δ ≈ 4.93 and 5.40 ppm. ^{31}P{^{1}H} NMR ($CDCl_3$, 50 °C): δ = 35.3 (s) ppm. IR (Nujol): ν̃ = 3314 (m br.), 1639 (s), 1522 (s), 1302 (m), 1266 (m), 1234 (m), 1104 (m), 1099 (m), 1003 (m), 821 (m), 746 (m), 697 (vs), 609 (m), 514 (m), 482 (s), 460 (m) cm^{-1}. MS (ESI+): *m*/*z* = 678 [M – Cl]$^+$; the isotopic envelope agrees with the calculated one.

Preparation of (*SP*-4-2)-{(*R*,R_p)-*N*-Benzyl-2-[1-(diphenylphosphanyl)ethyl]ferrocenecarboxamido-κ^2*O*,*P*}chloro(methyl)palladium(II) (13): A solution of amide **6** (64 mg, 0.12 mmol) in dichloromethane (5 mL) was added to a solution of [PdCl(Me)(cod)] (33 mg, 0.12 mmol) in the same solvent (5 mL) and the mixture was stirred in the dark for 20 h. The reaction solution was then filtered through a PTFE syringe filter (0.45 μm). The product crystallised upon diffusion of diethyl ether to afford **12** as an orange crystalline solid, which was filtered off and dried in vacuo. Yield: 60 mg (70%). ^{1}H NMR ($CDCl_3$): δ = 0.60 (d, $^3J_{P,H}$ = 2.8 Hz, 3 H, PdCH_3), 1.41 (dd, $^3J_{P,H}$ = 11.5, $^3J_{H,H}$ = 7.2 Hz, 3 H, CHCH_3), 3.43 (m, 1 H, C_5H_3), 4.04 (s, 5 H, C_5H_5), 4.05 (m, 1 H, C_5H_3), 4.16 (dq, $^3J_{H,H} \approx {}^2J_{P,H} \approx 7.5$ Hz, 1 H, C*H*CH$_3$), 4.68 (dd, $^2J_{H,H}$ = 14.4, $^3J_{H,H}$ = 5.1 Hz, 1 H, CH_2Ph), 4.99 (m, 1 H, C_5H_3), 5.14 (dd, $^2J_{H,H}$ = 14.4, $^3J_{H,H}$ = 6.5 Hz, 1 H, CH_2Ph), 7.15 (br. t, $^3J_{H,H} \approx 6$ Hz, 1 H,

N*H*), 7.28–7.72 (m, 15 H, P*Ph*$_2$ and CH$_2$*Ph*) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = –1.26 (Pd*C*H$_3$), 14.53 (d, $^2J_{P,C}$ = 6 Hz, CH*C*H$_3$), 31.21 (d, $^1J_{P,C}$ = 20 Hz, *C*HCH$_3$), 45.11 (*C*H$_2$Ph), 68.42 (C$_5$H$_3$ *C*H), 69.93 (C$_5$H$_3$ *C*H), 70.38 (C$_5$H$_5$), 70.45 (C$_5$H$_3$ *C*H), 73.06 (d, $^3J_{P,C}$ = 2 Hz, C$_5$H$_3$ *C*-CONH), 88.38 (d, $^2J_{P,C}$ = 9 Hz, C$_5$H$_3$ *C*-CH), 125.11 (d, $^1J_{P,C}$ = 48 Hz, PPh$_2$ *C*$_{ipso}$), 127.65 (CH$_2$Ph *C*H$_p$), 127.66 (d, $J_{P,C}$ = 11 Hz, PPh$_2$ *C*H), 128.78 (CH$_2$Ph *C*H$_o$), 128.83 (CH$_2$Ph *C*H$_m$), 128.89 (d, $J_{P,C}$ = 9 Hz, PPh$_2$ *C*H), 130.11 (d, $^4J_{P,C}$ = 2 Hz, PPh$_2$ *C*H$_p$), 130.67 (d, $^1J_{P,C}$ = 40 Hz, PPh$_2$ *C*$_{ipso}$), 131.23 (d, $^4J_{P,C}$ = 2 Hz, PPh$_2$ *C*H$_p$), 131.40 (d, $J_{P,C}$ = 10 Hz, PPh$_2$ *C*H), 136.23 (d, $J_{P,C}$ = 12 Hz, PPh$_2$ *C*H), 138.35 (CH$_2$Ph *C*$_{ipso}$), 175.45 (*C*ONH) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 54.3 (s) ppm. IR (Nujol): $\tilde{\nu}$ = 3262 (m, N–H), 1573 and 1545 (vs, C=O), 1439 (s), 1408 (w), 1352 (m), 1307 (s), 1207 (w), 1178 (m), 1106 (s), 1059 (w), 1000 (m), 820 (m), 750 (m), 743 (s), 700 (s), 693 (s), 627 (w), 537 (m), 499 (m) cm^{-1}. $C_{33}H_{33}ClFeNOPPd$ (688.5): calcd. C 57.58, H 4.83, N 2.04; found C 57.27, H 4.62, N 1.95.

Catalytic Experiments. Rhodium-Catalysed Hydrogenation: Hydrogenation of methyl (*Z*)-acetamidocinnamate was performed as described in ref.[34] using [Rh(cod)$_2$]BF$_4$ or [{(μ-Cl)Rh(cod)}$_2$] as the metal source and **1**, **6**, (*R*)-**7** and (*S*)-**7** as the ligands. However, no reaction occurred even after 1 d. Racemic *N*,*N*-dimethyl{[2-(diphenylphosphanyl)ferrocenyl]methyl}amine[35] utilized as the ligand in a parallel run showed 80% conversion under otherwise identical conditions.

Allylic Substitution. General Procedure:[36] Ligand (25 μmol) and [{Pd(η^3-C$_3$H$_5$)Cl}$_2$] (4.8 mg, 13 μmol) were dissolved in dry dichloromethane (3 mL). The solution was stirred at room temperature for 10 min and then added to a mixture of *rac*-1,3-diphenyl-2-propenyl acetate (126 mg, 0.5 mmol), potassium acetate (5 mg, 0.05 mmol) and dichloromethane (3 mL). After stirring for another 5 min, *N*,*O*-bis(trimethylsily)acetamide (BSA; 0.37 mL, 1.5 mmol), and dimethyl malonate (0.17 mL, 1.5 mmol) were added successively and the reaction mixture was stirred at room temperature for 20 h. The reaction solution was then washed with saturated aqueous NH_4Cl solution (2 × 5 mL), the organic layer was dried with $MgSO_4$ and the solvents were evaporated in vacuo. Purification by column chromatography (silica gel, hexane/ethyl acetate, 3:1) afforded the product mixture (in the case of an incomplete conversion, mixtures with the starting allyl acetate were collected). Enantiomeric excesses were determined from ^{1}H NMR spectra recorded in C_6D_6 in the presence of chiral lanthanide shift reagent tris(3-trifluoroacetyl-*d*-camphorato)europium(III), Eu(facam)$_3$, while the configuration of the major component was assigned on the basis of optical rotation of the mixture.[37]

X-ray Crystallography: Crystals suitable for single-crystal X-ray diffraction analysis were selected directly from the reaction batch (**2**: orange prism, 0.13 × 0.20 × 0.28 mm) or grown by recrystallisation from hot hexane (**3**: yellow prism, 0.09 × 0.13 × 0.28 mm), ethyl acetate/hexane (**9**: dark red prism, 0.13 × 0.20 × 0.33 mm; **11**: yellow plate, 0.08 × 0.15 × 0.38 mm), or chloroform/diethyl ether (**13**: orange prism, 0.10 × 0.13 × 0.25 mm). X-ray quality crystals of phosphane oxides **5** and (*R*)-**8** formed during prolonged recrystallisation of the respective phosphanes from ethyl acetate/hexane (**5**: orange block, 0.18 × 0.25 × 0.35 mm; (*R*)-**8**: red-brown block, 0.08 × 0.25 × 0.45 mm). Full-set diffraction data ($\pm h \pm k \pm l$; $2\theta \leq 55°$ for **2**, **3**, **9**, **11**, and **13**; $2\theta \leq 54°$ for **5**) were collected with a Nonius KappaCCD diffractometer equipped with a Cryostream Cooler (Oxford Cryosystems) at 150(2) K using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) and analysed with the HKL program package.[38] When appropriate, the data were corrected for absorption by using the Gaussian absorption correction incorporated in the diffractometer software; the transmission factor ranges are given in Table 7. The structures were solved by direct methods (SIR97[39]) and refined by weighted full-matrix least-squares procedure on F^2 (SHELXL97[40]). All non-hydrogen atoms were refined with anisotropic thermal motion parameters, whilst the hydrogen atoms were included in their calculated positions and refined as riding atoms with U_{iso}(H) assigned to a multiple of U_{eq} of their bonding atom. Selected crystallographic data are given in

Table 7. Crystallographic data and data collection and structure refinement parameters for **2**, **3**, **5**, (*R*)-**8**, **9**, **11** and **13**.

	2	**3**	**5**	(*R*)-**8**	**9**	**11**	**13**
Empirical formula	$C_{24}H_{22}BrFeP$	$C_{24}H_{22}BrFePS$	$C_{25}H_{23}FeO_3P$	$C_{33}H_{32}FeNO_2P$	$C_{35}H_{38}Cl_2FeO_2PRh$	$C_{44}H_{55}FeO_3P_2Rh$	$C_{33}H_{33}ClFeNOPPd$
M [g mol^{-1}]	477.15	509.21	458.25	561.42	751.28	852.58	688.27
Crystal system	orthorhombic	orthorhombic	monoclinic	orthorhombic	orthorhombic	monoclinic	monoclinic
Space group	$P2_12_12_1$ (no. 19)	$P2_12_12_1$ (no. 19)	$P2_1$ (no. 4)	$P2_12_12_1$ (no. 19)	$P2_12_12_1$ (no. 19)	$P2_1$ (no. 4)	$P2_1$ (no. 4)
T [K]	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
a [Å]	7.2823(2)	7.0056(1)	11.3855(3)	7.6157(2)	12.8470(1)	11.1809(2)	10.0973(3)
b [Å]	7.3882(1)	17.5052(3)	7.7313(2)	16.1930(3)	16.3555(1)	10.3941(3)	11.1269(2)
c [Å]	38.7068(8)	17.6365(3)	12.4535(3)	22.2013(4)	30.6572(2)	17.2950(4)	13.2474(3)
β [°]			100.742(2)			99.552(1)	94.703(1)
V [Å^3]	2082.55(8)	2162.84(6)	1077.01(5)	2737.8(1)	6441.66(8)	1982.08(8)	1483.36(6)
Z	4	4	2	4	8	2	2
$D_{calcd.}$ [g mL^{-1}]	1.522	1.564	1.413	1.362	1.549	1.429	1.541
μ(Mo-K_α) [mm^{-1}]	2.725	2.723	0.798	0.641	1.209	0.902	1.266
T[a]	0.506–0.705	0.379–0.865	–[b]	–[b]	0.702–0.906	0.812–0.948	0.753–0.925
Total relections, R_{int} [%][c]	21276, 3.42	27159, 4.71	16974, 4.1	35364, 4.7	99821, 4.82	30126, 4.79	25673, 4.02
Unique/observed[d] reflections	4731/4487	4952/4369	4727/4297	6239/5801	14752/13499	9082/7984	6798/6228
R (observed data) [%][e]	2.10	2.81	3.52	3.16	3.46	3.42	2.82
R, wR (all data) [%][e]	2.40, 4.62	3.74, 5.70	4.20, 8.15	3.65, 7.48	4.14, 8.56	4.66, 6.60	3.46, 5.79
Flack's parameter	–0.006(5)	–0.008(6)	–0.00(2)	0.04(1)	–0.02(2)	–0.01(1)	–0.03(1)
$\Delta\rho$ [e Å^{-3}]	0.35, –0.24	0.24, –0.47	0.45, –0.44	0.20, –0.28	1.76,[f] –1.06	0.58, –0.60	0.58, –0.64
CCDC reference no.	633611	633612	633613	633614	633615	633616	633617

[a] Range of transmission coefficients. [b] Not corrected. [c] $R_{int} = \Sigma|F_o^2 - F_o^2(\text{mean})|/\Sigma F_o^2$, where F_o^2(mean) is the average intensity for symmetry-equivalent reflections. [d] Reflections with $I_o > 2\sigma(I_o)$. [e] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma w(F_o^2)^2]^{1/2}$. [f] Residual positive electron density in the vicinity of the rhodium atom.

Table 7. Geometric parameters and structural drawings were obtained with a recent version of Platon.[41] CCDC-633611 to -633617 (for compounds **2**, **3**, **5**, **8**, **9**, **11** and **13**, respectively) 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/data_request/cif.

Supporting Information (see footnote on the first page of this article): View of the crystal structure of **2** (Figure S1).

Acknowledgments

This work was supported financially by the Grant Agency of Charles University (grant no. 318/2005/B-CH/PrF) and forms part of the project "Centre for Structure and Synthetic Application of Transition Metal Complexes" from the Ministry of Education, Youth and Sports of the Czech Republic (project no. LC 06070).

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Received: January 24, 2007
Published Online: April 25, 2007

