Novel Highly Efficient *P*-Chiral Ferrocenylimino Diamidophosphite Ligands for Pd-Catalysed Asymmetric Allylation

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Keywords: Allylic substitution / Asymmetric catalysis / Palladium / *P*,*N*-Bidentate ligands / Rhodium

Novel P^*-chiral *P*,*N*-bidentate ligands were synthesized by treatment of ferrocene-based imino alcohols with chlorophosphites derived from (*S*)-2-anilinomethylpyrrolidine or (*S*)-prolinol. Metal chelate complexes with the ligands – [Rh(CO)(PN)Cl] and [Pd(PN)(allyl)]$^+$X$^-$ (X$^-$ = BF$_4^-$, Cl$^-$, I$^-$, CH$_{12}$B$_{11}^-$) – were obtained and all new compounds were fully characterized by ^{1}H, ^{13}C, ^{31}P NMR, IR, MS (EI, CI, FAB, ESI and plasma desorption techniques) and X-ray analysis (imino alcohol **2d** and complex **7**). P^*-Chiral diamidophosphites gave up to 97 % *ee* in the Pd-catalysed allylic substitution of 1,3-diphenylallyl acetate with dimethyl malonate and *para*-toluenesulfinate.

Introduction

Chiral ligands incorporating ferrocene have been widely used in asymmetric catalysis.[1] Ferrocene is suitable for use as a scaffold for chiral ligands thanks to its appropriate rigidity, planar chirality, steric bulkiness and stability, while it is also inexpensive and readily available[2] and can be easily derivatized. All these distinctive features are also characteristic of imino alcohols, easily available by condensation of formylferrocene and amino alcohols,[3] and we recently obtained *P*,*N*-bidentate arylphosphites based on these and possessing axial or(and) central chirality.[4] Notably, *P*,*N*-phosphite ligands are known to be highly stereoselective in Cu-catalysed conjugate addition, Ir-catalysed hydrogenation and Rh-catalysed hydrosilylation, thanks to their increased π-acidity.[5] In addition, chiral phosphites are stable towards oxidation, readily obtainable and comparatively inexpensive: the cost of monophosphite derivatives of BINOL, highly efficient in asymmetric hydrogenation, is 50 times less than that of the well known diphosphane BINAP.[6]

Taking all this into account, we develop in this article an attractive idea of designing diamidophosphite ligands each possessing a P^*-stereocentre and a distant ferrocenylimino group. Since ligands with asymmetric donor centres are particularly efficient stereoinductors, their chiral phosphorus atoms seem to be crucial.[7] We also tested the new ligands in the Pd-catalysed asymmetric allylation with 1,3-diphenylallyl acetate, for known *P*,*N*-phosphites have not been properly investigated in this theoretically and practically important process.[8] Their application in the alkylation of 1,3-diphenylallyl acetate with dimethyl malonate, for example, resulted in enantioselectivities no higher than 88 % *ee*.[9]

Results and Discussion

Novel *P*,*N*-bidentate diamidophosphites were synthesized by direct phosphorylation of the corresponding imino alcohols (Scheme 1).

It should be noted that compounds **2a**–**d**, similarly to 2-formylpyridine-derived imino alcohols,[10] exist in equilibrium with their corresponding oxazolidine tautomers **2a′**–**d′** in organic solvents. In the case of **2d**, the tautomers (ca. 1:1 ratio in both C$_6$D$_6$ and CDCl$_3$) can easily be seen by ^{1}H and ^{13}C NMR and IR spectroscopy (see Table 1 and Experimental) (Figure 1).

On the other hand, X-ray analysis of **2d** demonstrated that only the imino form is observed in the solid state (Figure 2).

The ^{1}H NMR spectra of **2a**–**c** are more complex, as the oxazolidines represent mixtures of two epimers. Nevertheless, comparison of the integral intensities of the H$_i$ and H$_o$

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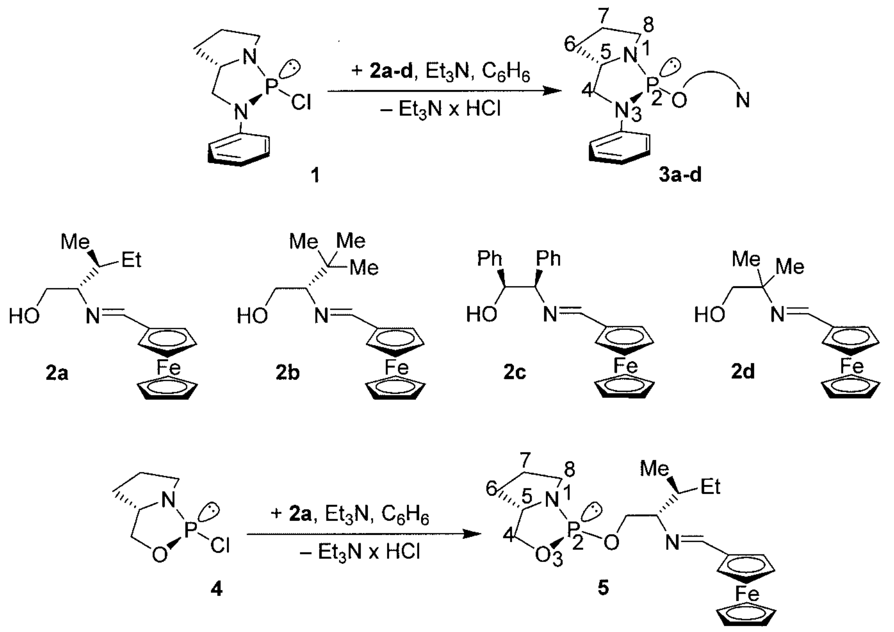
Supporting information for this article is available on the WWW under http://www.eurjoc.org or from the author.

DOI: 10.1002/ejoc.200400780



Scheme 1.

Table 1. ^{1}H, ^{13}C NMR and IR spectral parameters of compound **2d**.

	^{1}H NMR, δ_H, J [Hz] (CDCl$_3$)							IR [cm^{-1}] (CHCl$_3$)
	HC= (H$_i$)	OCHN (H$_o$)	C$_5$H$_4$	C$_5$H$_5$	CH$_2$O	NH	CH$_3$	
2d (45%)	8.16 (s, 1 H)	–	4.63 (t, 2 H, ^3J = 1.8) 4.36 (t, 2 H, ^3J = 1.8)	4.14 (s, 5 H)	3.45 (s, 2 H)	–	2.0 (s, 6 H)	ν(OH) = 3476
2d′ (55%)	–	5.29 (s, 1 H)	4.28 (br. s, 2 H) 4.15 (br. s, 2 H)	4.19 (s, 5 H)	3.64 (d, 1 H, ^2J = 7.5) 3.46 (d, 1 H, ^2J = 7.5)	2.08 (br. s, 1 H)	1.32 (s, 3 H) 1.26 (s, 3 H)	ν(NH) = 3286
	^{13}C NMR, δ_C (CDCl$_3$)							
	HC=	OCHN	C$_5$H$_4$	C$_5$H$_5$	CH$_2$O	*C*Me$_2$	CH$_3$	
2d	157.5	–	87.7 68.8 68.5	70.2	71.3	60.0	23.9	
2d′	–	89.1	80.9 67.7 67.6 66.2 65.8	68.2	77.1	59.5	26.4 25.9	

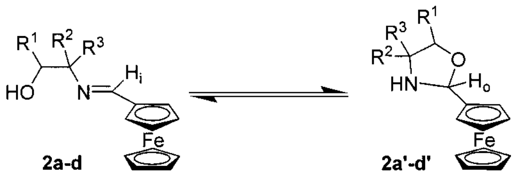


Figure 1. Equilibration of compounds **2a**–**d** and their oxazolidine tautomers **2a′**–**d′**.

peaks reveals significant amount of oxazolidine tautomers (see Experimental). Interestingly, the phosphorylation reaction proceeds selectively and no phospha derivatives of oxazolidines were detected in the reaction products. In addition, the synthesis of **3a**–**d** and **5** is also highly stereoselective, since only epimers with pseudoequatorial orientations of their exocyclic substituents at the phosphorus atom were formed. In the cases of **3a**–**d** this corresponds to the (*R*) configuration of the *P**-stereocentre, while the *P** atom in **5** has (*S*) absolute configuration according to the characteristic[11] $^2J_{C(8),P}$ values (35.1–38.5 Hz) in their ^{13}C NMR spectra (see Experimental).

Compounds **3a**–**d** and **5** are readily soluble in common organic media and stable under inert atmosphere. No traces of decomposition products could be detected in ^{31}P NMR spectra of **3c** after 1 year of storage.

Neutral and cationic *cis*-chelate metal complexes with the new *P*,*N*-ligands were obtained (Scheme 2).

In addition, cationic Pd(II) complexes **10a**, **11a** and **12a** were obtained, in order to investigate the influence of a counterion on the efficiency of the catalyst (Scheme 3).

Some important spectroscopic data of the complexes are summarized in Tables 2–4. According to the $^1J_{P,Rh}$ and ν(CO) parameters of **6a**–**d** and **7** (Table 2), the diamidophosphites **3a**–**d** and **5** occupy an intermediate position between phosphanes and phosphites in a spectrochemical sequence of organophosphorus ligands.[12] Very close values

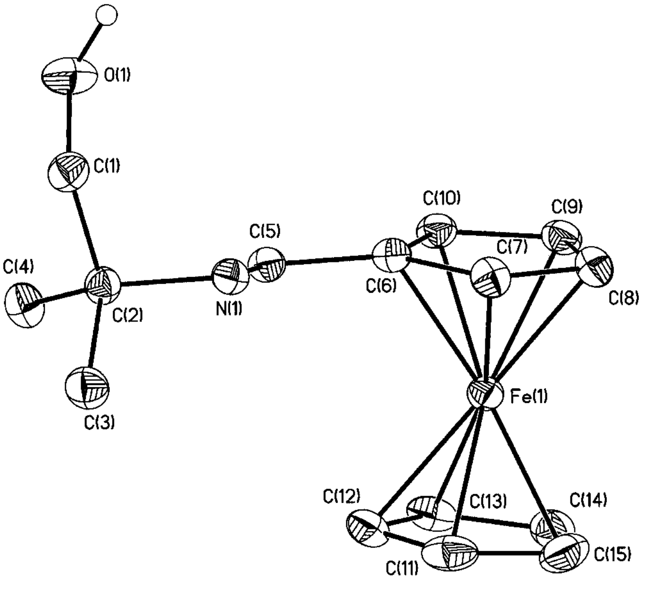
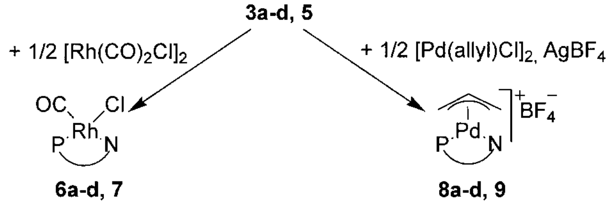


Figure 2. Molecular structure of **2d**. Atoms are presented by thermal ellipsoids drawn at 50% probability. Hydrogens are omitted for clarity. Selected bond lengths [Å]: O(1)–C(1) 1.415(3), N(1)–C(5) 1.267(3), N(1)–C(2) 1.484(3), Fe–C (averaged) 2.040(2); selected bond angles [°]: O(1)C(1)C(2) 110.82(17), C(5)N(1)C(2) 120.43(18).



Scheme 2.

Table 2. IR and ^{31}P NMR spectroscopic data for complexes **6a**–**d** and **7** (in $CHCl_3$).

	^{31}P NMR		IR, ν(CO) [cm^{-1}]
	δ_P	$^1J_{P,Rh}$ [Hz]	
6a	118.9	233.1	2010
6b	120.7	234.0	2006
6c	132.9	227.1	2012
6d	136.8	223.8	2008
7	141.5	240.3	2014

Table 3. ^{31}P NMR spectroscopic data for complexes **8a**–**d**, **9** and **10a**–**12a** (in $CDCl_3$).

	8a	**8b**	**8c**	**8d**	**9**	**10a**	**11a**	**12a**
δ_P (%)	114.7 (11), 112.1 (89)	116.6 (63), 113.2 (25)	130.1 (63), 128.7 (37)	127.9 (57), 126.8 (43)	140.7	122.6 (48), 122.2 (53)	120.5 (47), 119.9 (53)	115.5 (34), 113.1 (66)

of $^1J_{P,Rh}$ and ν (CO) for **6a** and **7** indicate that the electronic properties of ligands **3a** and **5** are practically identical despite the distinct phosphorus atom environments.

Duplication of peaks in the ^{31}P NMR spectra of compounds **8a**–**d** and **10a**–**12a** (Table 3) indicates the presence of their *exo* and *endo* isomers.[4] The sharp singlet in the ^{31}P NMR spectrum of **9** can be explained either by fast interconversion of the isomers or by the absence of one of them.

Rather large $^2J_{C(8),P}$ values (14.2–17.2 Hz) in the ^{13}C NMR spectra of **7** and **8a** (see Exp. Part) point to unchanged pseudoequatorial orientations of exocyclic substituents after complexation (and therefore unchanged absolute configurations of *P** atoms). Another notable feature is the significant coordination shift [$\Delta\delta_C = \delta_C$(complex) – δ_C(ligand)] for the imine carbon atoms in **7** and **8a** (10.0–12.6 ppm).

P,*N*-Bidentate coordination of diamidophosphite **3a** with palladium in complex **8a** is also supported by a significant increase in E_b P_{2p} and E_b N_{1s}, caused by binding of both donor atoms to palladium (Table 4).

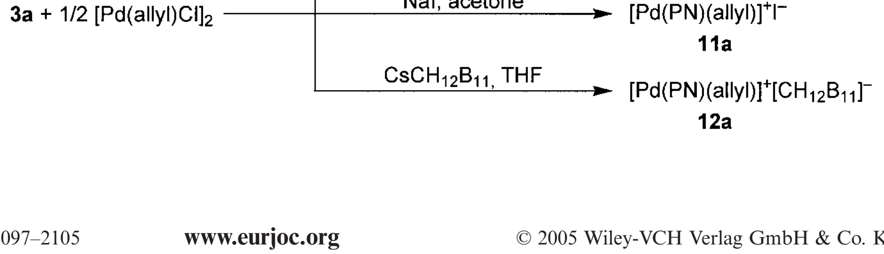
Table 4. XP spectroscopic data for compounds **3a** and **8a**.

	E_b [eV]					
	P 2p	N 1s	Fe $2p_{3/2}$	Pd $3d_{5/2}$	B 1s	F 1s
3a	132.1	398.9	708.4	–	–	–
8a	132.7	399.5	708.5	338.0	193.4	685.9

Chlorocarbonyl complex **7** was analysed by single-crystal X-ray diffraction (Figure 3).

Molecules of **7** in the crystal are characterized by (*S*) configurations at the asymmetric atoms P(2), C(5), C(2′) and C(4′). The Rh(1)N(1′)C(2′)C(1′)O(1′)P(2) metallacycle adopts a distorted sofa conformation with deviation of the C(1′) and C(2′) atoms by 1.27 and 0.92 Å, respectively. The iminoferrocenyl substituent occupies a pseudoequatorial position with respect to P(2).

Analogous metallacycles in previously investigated palladium complexes with ferrocenyl,[4b] 1-azatricyclo[2.2.2]octane and 1,3-azaphosphabicyclooctane substituents[13] are characterized by nearly the same conformation as seen in the structure of **7**, while in rhodium and palladium complexes without such bulky substituents the conformations



Scheme 3.

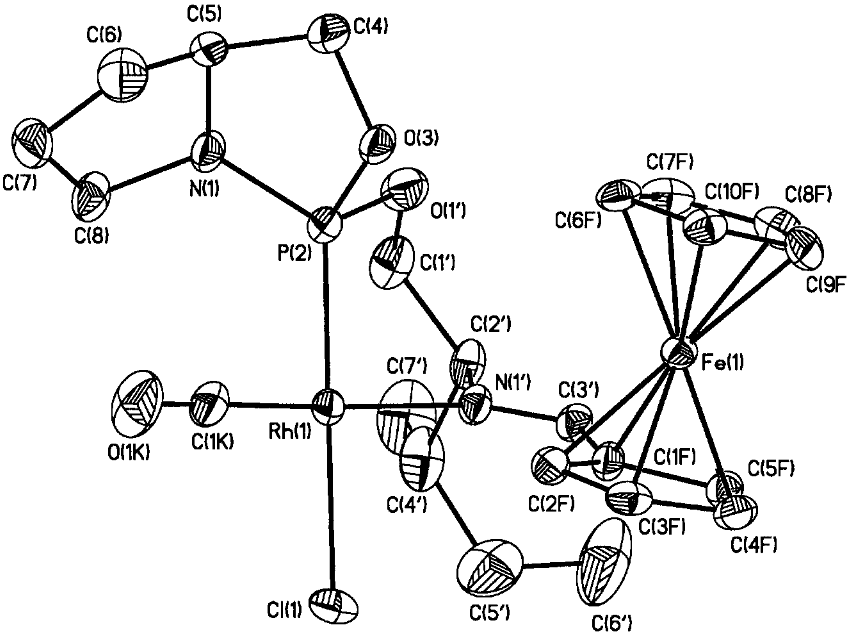


Figure 3. X-ray structure of complex **7** and numbering scheme. All hydrogen atoms linked to carbon atoms are omitted for clarity.

of metallacycles may be described as chair.[4b] We may therefore propose that the distorted sofa conformation of the metallacycle in **7** is caused by steric overcrowding due to the ferrocenyl moiety. The phospholidine and pyrrolidine cycles have envelope conformations, atoms C(5) and C(4) deviating from the basal plane by 0.43 and 0.54 Å, correspondingly.

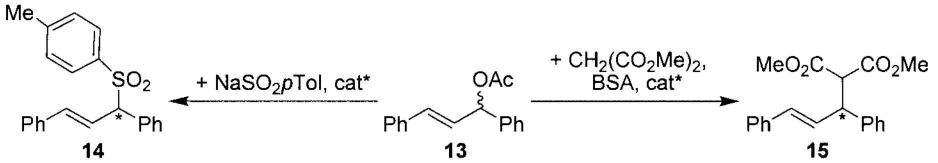
The environment of the Rh(1) atom has an almost ideal square-planar configuration, with deviation of this atom from the basal plane equal to 0.01 Å. It is noteworthy that Rh(1) forms a short contact with the C(2F)–H(2FA) bond: Rh(1)···H(2FA) 2.60, Rh(1)C(2F)H(2FA) 122°, C(2F)–H(2FA) distance normalized to 1.08 Å (according to neutron diffraction data[14]). The bonds lengths of the coordination polyhedra of the rhodium atom are close to those in rhodium and palladium complexes with *P,N*-bidentate aryl phosphites.[4b] Similarly to those in the compounds described in the literature,[4b,13] the phosphorus atoms in **7** have tetrahedral configurations (the sum of basal N–P–O angles is 300°, close to the values observed in a previously examined compound[13]).

Basically, ligands **3a**–**d** and **5** form rather stable metal chelates, so their treatment with $[Rh(CO)_2Cl]_2$ (Scheme 2) did not produce any *trans*-$[Rh(\eta^1\text{-}PN)_2(CO)Cl]$ complexes that are usual by-products in cases of weakly chelating ligands.[4] Even when 4 equivalents of ligand **3a** were allowed to react with 1 equivalent $[Pd(allyl)Cl]_2$ (+ 2 $AgBF_4$, in $CDCl_3$/THF), signals of chelate **6a** and unreacted **3a** were found together with signals of $[Pd(\eta^1\text{-}PN)_2(allyl)]^+BF_4^-$ (δ_P 115.8 (52%)) and $[Pd(\eta^1\text{-}PN)(\eta^2\text{-}PN)(allyl)]^+BF_4^-$ (δ_P 97.4, d, $^2J_{P,P'}$ 35.6 Hz and δ_P 81.6, d, $^2J_{P,P'}$ 35.6 Hz (18%)). These observations are in good agreement with the assumption of high stability of six-membered metal chelates with *P,N*-bidentate ligands.[15] Nevertheless, the nature of ligand should be taken into account, for it can cause significant effects. Thus, the ^{31}P NMR spectrum of $[Pd(allyl)Cl]_2$/4 L (L = **3d**, $CDCl_3$/THF, 2 $AgBF_4$) shows major signals for the complexes $[Pd(\eta^1\text{-}PN)_2(allyl)]^+BF_4^-$ (δ_P 116.9 (82%)) and $[Pd(\eta^1\text{-}PN)(\eta^2\text{-}PN)(allyl)]^+BF_4^-$ (δ_P 85.7, d, $^2J_{P,P'}$ 38.0 Hz and δ_P 81.2, d, $^2J_{P,P'}$ 38.0 Hz (9%)) and only traces of **6d** and unreacted **3d**.

Ferrocenylimino diamidophosphites **3a**–**d** and **5** were then tested in asymmetric Pd-catalysed allylic substitution (Scheme 4).

The results of allylic sulfonylation are summarised in Table 5. Best results were achieved with use of ligands **3a** and **3d** (Entries 5 and 18, correspondingly). It is clear that the bicyclic (2*R*,5*S*)-phosphorus-containing fragment is responsible for their efficiency, as ligands **3a** and **3d** display practically identical enantioselectivity. At the same time, **3b** and **3c** are inferior stereoinductors, probably because of the mismatched combination of the (2*R*,5*S*)-phosphocentre with additional C-stereogenic atoms in the peripheral imino group. Prolinol-based ligand **5** gave a practically racemic product (Entries 19–20). In view of the basically identical electronic properties of **3a** and **5** (see above), such a dramatic decrease in enantioselectivity is likely to be caused by substitution of the NPh fragment in the phosphacycle of **3a** with an oxygen atom in **5**. Application of $[Pd_2(dba)_3]\cdot CHCl_3$ instead of $[Pd(allyl)Cl]_2$ as a catalytic precursor resulted in generally lower optical and chemical yields of product **14**.

It is well known that optical and chemical yields of catalytic reactions often strongly depend on the nature of a counterion in the cationic catalyst.[16] Among the cationic complexes **8a**–**12a**, the highest enantioselectivity was observed with compounds **8a** and **12a**, bearing the noncoordinating BF_4^- and $CH_{12}B_{11}^-$ counterions (Table 5, Entries 5, 7–9). The lower enantioselectivity of **12a** (Entry 9) than of **8a** (Entry 5) is probably due to the bulkiness of its carbor-



Scheme 4.

Table 5. Enantioselective allylic sulfonylation as shown in Scheme 4.

Entry	Catalyst	L*/Pd	Yield [%]	*ee* [%]
1	[Pd(allyl)Cl]$_2$/**3a**	1:1	99	79 (*S*)
2	[Pd(allyl)Cl]$_2$/**3a**	2:1	78	84 (*S*)
3	[Pd$_2$(dba)$_3$]·CHCl$_3$/**3a**	1:1	29	88 (*S*)
4	[Pd$_2$(dba)$_3$]·CHCl$_3$/**3a**	2:1	98	79 (*S*)
5	**8a**	1:1	99	96 (*S*)
6	**8a**[a]	1:1	6	92 (*S*)
7	**10a**	1:1	94	70 (*S*)
8	**11a**	1:1	11	21 (*S*)
9	**12a**	1:1	16	72 (*S*)
10	[Pd(allyl)Cl]$_2$/**3b**	1:1	34	75 (*S*)
11	[Pd$_2$(dba)$_3$]·CHCl$_3$/**3b**	1:1	0	0
12	**8b**	1:1	30	86 (*S*)
13	[Pd(allyl)Cl]$_2$/**3c**	1:1	16	58 (*S*)
14	[Pd$_2$(dba)$_3$]·CHCl$_3$/**3c**	1:1	17	37 (*S*)
15	**8c**	1:1	14	10 (*S*)
16	[Pd(allyl)Cl]$_2$/**3d**	1:1	36	94 (*S*)
17	[Pd$_2$(dba)$_3$]·CHCl$_3$/**3d**	1:1	16	91 (*S*)
18	**8d**	1:1	85	97 (*S*)
19	[Pd(allyl)Cl]$_2$/**5**	1:1	32	9 (*S*)
20	[Pd(allyl)Cl]$_2$/**5**	2:1	29	8 (*S*)
21	[Pd$_2$(dba)$_3$]·CHCl$_3$/**5**	1:1	31	12 (*S*)
22	**9**	1:1	17	3 (*S*)

[a] At 0 °C.

ane anion. Complexes **10a** and, especially, **11a**, with coordinating Cl$^-$ and I$^-$ counterions are generally less efficient (Entries 7, 8). The same trend can be seen for the ligand **3b** (Entries 10, 12), while for ligand **3c** chloride anion was found to be the best. In the case of diamidophosphite **3d**, no influence of the anion on optical yield was found (Entries 16, 18).

It should be noted that chiral allylic sulfones are exceptionally versatile intermediates in organic synthesis[8a] and that the 97% enantioselectivity achieved with **3a–d** (Table 5, Entry 18) is superior to the highest previously known result (93% *ee*) for allylic sulfonylation obtained with chiral phosphanyloxazolines.[17]

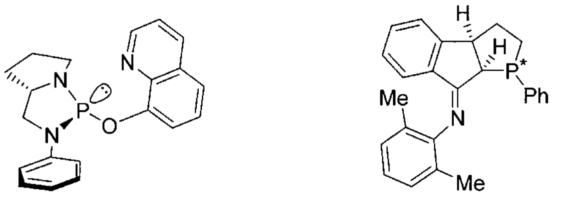
In asymmetric allylic alkylation (Scheme 4) all diamidophosphites **3a–d** provide excellent conversion and >90% *ee* (Table 6). Ligand **5** was again found to be the least efficient, providing (*R*)-**15** (Entries 19, 20) in contrast to the others. The applied solvent and L/Pd ratio were found to influence the results for certain ligands. Unlike in the case of the allylic sulfonylation reaction, use of [Pd$_2$(dba)$_3$]·CHCl$_3$ instead of [Pd(allyl)Cl]$_2$ as a catalyst precursor proved to be a good idea in the case of ligand **3a** (compare Entries 1 and 3).

Ligands **3a–d** gave *ee* values of up to 97% for the allylic alkylation of **13** (Scheme 4), which is the best result for all known chiral *P,N*-phosphite ligands and very close to the maximum enantioselectivities overall.[5d,5e,8a,18] For comparison, optical yields for the synthesis of **15** (Scheme 4) achieved with ligands related to **3a–d** are shown in Figure 4.

Moreover, in contrast to **3a–d**, *P**-chiral imino phosphane **17** requires a complex multi-step synthesis with the use of organozirconium reagents.

Table 6. Enantioselective allylic alkylation according to Scheme 4.

Entry	Catalyst	L*/Pd	Solvent	Conversion [%]	*ee* [%]
1	[Pd(allyl)Cl]$_2$/**3a**	1:1	THF	94	70 (*S*)
2	[Pd(allyl)Cl]$_2$/**3a**	2:1	THF	99	87 (*S*)
3	[Pd$_2$(dba)$_3$]·CHCl$_3$/**3a**	1:1	THF	98	90 (*S*)
4	**8a**	1:1	THF	76	60 (*S*)
5	**8a**	1:1	CH$_2$Cl$_2$	97	65 (*S*)
6	**12a**	1:1	THF	93	85 (*S*)
7	[Pd(allyl)Cl]$_2$/**3b**	1:1	THF	99	96 (*S*)
8	[Pd(allyl)Cl]$_2$/**3b**	2:1	THF	98	96 (*S*)
9	[Pd$_2$(dba)$_3$]·CHCl$_3$/**3b**	1:1	THF	87	95 (*S*)
10	**8b**	1:1	THF	78	83 (*S*)
11	**8b**	1:1	CH$_2$Cl$_2$	99	86 (*S*)
12	[Pd(allyl)Cl]$_2$/**3c**	1:1	THF	64	92 (*S*)
13	[Pd(allyl)Cl]$_2$/**3c**	2:1	THF	37	91 (*S*)
14	[Pd$_2$(dba)$_3$]·CHCl$_3$/**3c**	1:1	THF	28	94 (*S*)
15	**8c**	1:1	THF	56	90 (*S*)
16	**8c**	1:1	CH$_2$Cl$_2$	28	68 (*S*)
17	**8d**	1:1	THF	99	97 (*S*)
18	**8d**	1:1	CH$_2$Cl$_2$	96	96 (*S*)
19	**9**	1:1	THF	44	65 (*R*)
20	**9**	1:1	CH$_2$Cl$_2$	89	26 (*R*)



16, 85% *ee*[8c]

17, 57% *ee*[16]

Figure 4. Optical yields for the synthesis of **15** (Scheme 4) achieved with ligands related to **3a**–**d**.

Experimental Section

General Remarks: All reactions were carried out under dry argon in freshly dried and distilled solvents. Infrared spectra were recorded on a Specord M80 spectrophotometer with samples prepared as KBr pellets, as Nujol mulls between CsI plates, as $CHCl_3$ solutions between KBr plates or in polyethylene cells. ^{31}P, ^{13}C, and ^{1}H NMR spectra were recorded with a Bruker AMX 400 instrument (162.0 MHz for ^{31}P, 100.6 MHz for ^{13}C and 400.13 MHz for ^{1}H). Complete assignment of all the resonances in ^{13}C NMR spectra was achieved by the use of DEPT techniques. Chemical shifts (ppm) are given relative to Me_4Si (^{1}H and ^{13}C NMR) and 85% H_3PO_4 (^{31}P NMR). The X-ray photoelectron spectra (XPS) were measured on a Kratos XSAM 800 spectrometer calibrated against the Ag line at 368.3 eV, the Cu line at 932.7 eV and the Au line at 84.0 eV; correction for the sample charging was performed at C_{1s} = 284.6 eV; the accuracy of the line maximum determination was ± 0.1 eV. Mass spectra were recorded with a Kratos MS 890 spectrometer (EI), an MSVKh TOF spectrometer with ionization by Cf-252 fission fragments (plasma desorption technique, PD), an AMD 402 spectrometer (FAB and CI), and a Micromass Bio Q II-ZS spectrometer (electrospray ionization technique, ESI). Elemental analyses were performed at the Laboratory of Microanalysis (Institute of Organoelement Compounds, Moscow).

PCl_3 was distilled immediately before use. Et_3N was distilled twice from over KOH and then over a small amount of $LiAlH_4$ before use. (*S*)-Prolinol (Aldrich) was azeotropically dried with benzene and distilled before use. (2*R*,5*S*)-2-Chloro-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane (**1**) was prepared as published.[11c] Imino alcohol **2a** was synthesized as published.[4b] The syntheses of imino alcohols **2b**–**d** were performed by techniques similar to those used for **2a**. Compounds **2a**–**d** were dried under vacuum (2 Torr, 3 h) immediately before use.

$[Rh(CO)_2Cl]_2$, $[Pd(allyl)Cl]_2$ and $[Pd_2(dba)_3]\cdot CHCl_3$ were synthesized as published.[19] Rhodium complexes **6a**–**d** were synthesized for the ^{31}P NMR and IR experiments in $CHCl_3$ medium analogously to the known procedures.[4b] The preparation of complexes **7**, **8a**–**d**, **9** and **10a** were performed by techniques similar to that reported.[4]

$NaSO_2pTol$, $CH_2(CO_2Me)_2$ and BSA (*N*,*O*-bis(trimethylsilyl)acetamide) were purchased from Acros Organics. Compound **13** was synthesized as published.[19b]

(2*S*)-2-(Ferrocenylideneamino)-3,3-dimethylbutan-1-ol (2b): Yield: 3.036 g, 97%; yellow solid, m.p. 130–132 °C. ^{1}H NMR [$CDCl_3$, δ_H ($J_{H,H}$), Hz]; for **2b**: δ_H = 0.95 (s, 9 H, CH_3), 2.78 (m, 1 H, CHN), 3.78 (m, 2 H, CH_2O), 4.18 (s, 5 H, C_5H_5), 4.34 (br. s, 1 H), 4.36 (br. s, 1 H), 4.53 (t, ^3J = 1.1 Hz, 1 H), 4.73 (t, ^3J = 1.2 Hz, 1 H), 8.01 (s, 1 H, CH (H_i)) (66%) ppm; for **2b′**: δ_H = 0.98 (s, 9 H, CH_3), 1.82 (br. s, 1 H, NH), 3.19 (m, 1 H, CHN), 3.52 (m, 1 H, CH_2O), 3.81 (m, 1 H, CH_2O), 4.20 (s, 5 H, C_5H_5), 4.13 (br. s, 2 H), 4.30 (br. s, 2 H), 5.16 (s, 1 H, OCHN (H_o)) (22%) and 0.92 (s, 9 H, CH_3), 1.82 (br. s, 1 H, NH), 3.18 (m, 1 H, CHN), 3.58 (m, 1 H, CH_2O), 3.96 (m, 1 H, CH_2O), 4.19 (s, 5 H, C_5H_5), 4.15 (br. s, 2 H), 4.27 (br. s, 2 H), 5.08 (s, 1 H, OCHN (H_o)) (12%) ppm. ^{13}C NMR ($CDCl_3$): δ_C = 26.1, 26.4, 27.1 (all s, CH_3), 31.5, 32.8, 32.9 (all s, *C*Me_3), 61.6, 66.5 (s, CH_2O), 66.1–80.4 (all C_{Fc}), 81.8, 81.9 (s, CHN), 90.1, 90.3 (s, OCHN), 162.1 (s, CH=N) ppm; elemental analysis: calcd. (%) for $C_{17}H_{23}FeNO$ (313.1): C 65.19, H 7.40, N 4.47; found C 65.35, H 7.16, N 4.21.

(1*S*,2*R*)-2-(Ferrocenylideneamino)-1,2-diphenylethan-1-ol (2c): Yield: 3.07 g, 75%; orange solid; m.p. 141–143 °C. ^{1}H NMR [$CDCl_3$, δ_H ($J_{H,H}$), Hz], for **2c**: δ_H = 3.93 (s, 5 H, C_5H_5), 4.32 (br. s, 2 H), 4.58 (br. s, 2 H), 4.41 (d, ^3J = 6.6 Hz, 1 H, CHN), 5.09 (d, ^3J = 6.6 Hz, 1 H, CHO), 7.23–7.35 (m, 10 H, CH_{Ph}), 8.02 (s, 1 H, CH (H_i)) (72%) ppm; for **2c′**: δ_H = 4.27 (s, 5 H, C_5H_5), 4.28 (d, ^3J = 6.5 Hz, 1 H, CHN); 4.60 (t, ^3J = 1.3 Hz, 2 H), 4.79 (t, ^3J = 1.2 Hz, 2 H), 4.77 (d, ^3J = 6.5 Hz, 1 H, CHO), 5.29 (s, 1 H, OCHN (H_o)), 7.24–7.36 (m, 10 H, CH_{Ph}) (28%) ppm. ^{13}C NMR ($CDCl_3$): δ_C = 77.4 (s, CHN), 68.1–80.0 (all C_{Fc}), 80.3 (s, CHO), 127.1–141.0 (C_{Ph}), 162.1 (s, CH=N) ppm; elemental analysis: calcd. (%) for $C_{25}H_{23}FeNO$ (409.3): C 73.36, H 5.66, N 3.42; found C 73.52, H 5.87, N 3.60.

2-(Ferrocenylideneamino)-2-methylpropan-1-ol (2d): Yield: 2.623 g, 92%; orange solid; m.p. 134–136 °C. ^{1}H NMR [C_6D_6, δ_H ($J_{H,H}$), Hz]; for **2d**: δ_H = 1.19 (s, 6 H, CH_3), 3.59 (s, 2 H, CH_2O), 4.06 (s, 5 H, C_5H_5), 4.16 (t, ^3J = 1.8 Hz, 2 H), 4.65 (t, ^3J = 1.8 Hz, 2 H), 8.10 (s, 1 H, CH (H_i)) (49%); for **2d′**: δ_H = 1.05 (s, 3 H, CH_3), 1.21 (s, 3 H, CH_3), 2.23 (br. s, 1 H, NH), 3.38 (d, ^2J = 7.4 Hz, 1 H, CH_2O), 3.56 (d, ^2J = 7.4 Hz, 1 H, CH_2O), 4.21 (s, 5 H, C_5H_5), 4.07 (br. s, 2 H), 4.41 (m, 1 H), 4.45 (m, 1 H), 5.49 (s, 1 H, OCHN (H_o)) (51%) ppm; elemental analysis: calcd. (%) for $C_{15}H_{19}FeNO$ (285.2): C 63.18, H 6.72, N 4.91; found C 62.91, H 6.58, N 5.18.

Preparation of Chlorophosphite 4: A solution of (*S*)-prolinol (0.61 mL, 6 mmol) and Et_3N (1.6 mL, 12 mmol) in benzene (30 mL) was added dropwise at 0 °C to a vigorously stirred solution of PCl_3 (0.528 mL, 6 mmol) in benzene (70 mL). The resulting mixture was warmed to 80 °C for a short time, and then cooled down to 20 °C. The solid $Et_3N\cdot HCl$ was filtered off and the filtrate was evaporated in vacuo. The residue was distilled in vacuo to obtain **4**.

(2*R*,5*S*)-2-Chloro-3,1-oxaza-2-phosphabicyclo[3.3.0]octane (4): Yield: 0.82 g, 82%; colourless oil; b.p. 65–68 °C (1 Torr). ^{13}C NMR [$CDCl_3$, δ_C ($J_{C,P}$), Hz]: δ_C = 28.4 (br. s, C (7)), 29.4 (s, C (6)), 43.9 (br. s, C (8)), 63.3 (br. s, C (5)), 73.8 [d, ^2J = 8.9 Hz, C (4)] ppm. ^{31}P NMR ($CDCl_3$): δ_P = 173.6 ppm. MS (70 eV, EI): *m*/*z* (%): 181 (70) $[M]^+$, 165 (56), 149 (55), 131 (44), 120 (100), 100 (44), 91 (53); elemental analysis: calcd. (%) for C_5H_9ClNOP (165.0): C 36.27, H 5.48, N 8.46; found C 35.98, H 5.61, N 8.70.

Preparation of Ligands. General Technique: A solution of the appropriate imino alcohol (5.4 mmol) in benzene (10 mL) was added dropwise at 0 °C to a vigorously stirred solution of compound **1** or **4** (5.40 mmol) and Et_3N (0.73 mL, 5.40 mmol) in benzene (10 mL). The resulting mixture was warmed to 80 °C for a short time and then cooled down to 20 °C. The solution was filtered, and hexane (30 mL) was added to precipitate $Et_3N\cdot HCl$. The mixture was filtered again, the solvent was evaporated in vacuo, and the residue was dried in vacuo (1 Torr, 2 h).

(2*R*,5*S*,2′*S*,3′*S*)-2-[2′-(Ferrocenylideneamino)-3′-methylpentyloxy]-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane (3a): Yield: 2.792 g, 90%; orange solid; m.p. 117–119 °C; ^{13}C NMR [$CDCl_3$, δ_C ($J_{C,P}$), Hz]: δ_C = 10.9 (s, *C*H_3CH_2), 15.9 (s, *C*H_3CH), 24.9 (s,

$CH_3\mathit{C}H_2$), 25.9 [d, ^{3}J = 3.4 Hz, C(7)], 31.9 C(6), 36.0 (s, $CH_3\mathit{C}H$), 48.5 [d, ^{2}J = 38.5 Hz, C(8)], 54.7 [d, ^{2}J = 7.2 Hz, C(4)], 63.1 [d, ^{2}J = 8.8 Hz, C(5)], 63.5 [^{2}J = 5.3 Hz, $POCH_2$], 68.9 (s, C_{Cp}), 68.2, 68.3, 69.8, 69.9 (all s, C_{Fc}). 76.3 (s, NCH), 80.6 [s, $C_{Fc(\mathit{ipso})}$], 114.6 (d, ^{3}J = 11.8 Hz, CH_{Ph}), 118.5 (s, CH_{Ph}), 128.8 (s, CH_{Ph}), 145.6 (d, ^{2}J = 16.0 Hz, C_{Ph}), 160.6 (s, CH=N) ppm. ^{31}P NMR ($CDCl_3$): δ_P = 121.4 ppm. MS (CI): *m*/*z* (%): 517 (100) [*M*]$^+$, 433 (96), 368 (42), 212 (35), 205 (70). MS (70 eV, EI): *m*/*z* (%): 517 (12) [*M*]$^+$, 433 (100), 368 (80), 212 (35), 205 (41); elemental analysis: calcd. (%) for $C_{28}H_{36}FeN_3OP$ (517.2): C 64.99, H 7.01, N 8.12; found C 65.12, H 7.24, N 7.96

(2*R*,5*S*,2′*S*)-2-[2′-(Ferrocenylideneamino)-3′,3′-dimethylbutoxy]-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane (3b): Yield: 2.55 g, 91%; orange solid; m.p. 113–115 °C. ^{13}C NMR [$CDCl_3$, δ_C ($J_{C,P}$), Hz]: δ_C = 25.9 [d, ^{3}J = 3.8 Hz, C(7)], 27.0 (s, $C\mathit{C}H_3$), 31.9 (s, C(6)), 32.8 (s, $\mathit{C}CH_3$), 48.4 [d, ^{2}J = 38.5 Hz, C(8)], 54.8 [d, ^{2}J = 7.3 Hz, C(4)), 62.3 [d, ^{2}J = 5.7 Hz, $POCH_2$], 63.1 [d, ^{2}J = 9.2 Hz, C(5)), 68.8 (s, C_{Cp}), 68.0, 68.6, 69.7, 69.8 (all s, C_{Fc}), 80.4 [d, ^{3}J = 2.3 Hz, NCH], 81.3 (s, $C_{Fc(\mathit{ipso})}$), 114.7 (d, ^{3}J = 11.8 Hz, CH_{Ph}), 118.5 (s, CH_{Ph}), 128.9 (s, CH_{Ph}), 145.7 (d, ^{2}J = 15.6 Hz, C_{Ph}), 160.1 (s, CH=N) ppm. ^{31}P NMR ($CDCl_3$): δ_P = 121.6 ppm. MS (70 eV, EI): *m*/*z* (%): 517 (5) [*M*]$^+$, 433 (56), 368 (65), 313 (100), 205 (71); elemental analysis: calcd. (%) for $C_{28}H_{36}FeN_3OP$ (517.2): C 64.99, H 7.01, N 8.12; found C 64.85, H 7.18, N 7.95.

(2*R*,5*S*,1′*S*,2′*R*)-2-[2’-(Ferrocenylideneamino)-1′,2′-diphenylethoxy]-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane (3c): Yield: 2.814 g, 85%; dark orange solid; m.p. 125–127 °C. ^{13}C NMR [$CDCl_3$, δ_C ($J_{C,P}$), Hz]: δ_C = 26.1 [d, ^{3}J = 4.2 Hz, C(7)], 32.2 (s, C (6)), 47.2 [d, ^{2}J = 36.2 Hz, C(8)], 53.3 [d, ^{2}J = 8.4 Hz, C(4)], 63.2 [d, ^{2}J = 8.8 Hz, C(5)], 68.7 (s, C_{Cp}), 66.7, 69.4, 69.7, 69.9 (all s, C_{Fc}), 78.1 (s, NCH), 80.6 (s, $C_{Fc(\mathit{ipso})}$), 81.04 (s, POCH), 114.5 (d, ^{3}J = 13 Hz, CH_{Ph}), 118.1 (s, CH_{Ph}), 126.6 (s, CH_{Ph}), 126.8 (s, CH_{Ph}), 127.0 (s, CH_{Ph}), 127.5 (s, CH_{Ph}), 127.7 (s, CH_{Ph}), 127.9 (s, CH_{Ph}), 128.3 (s, CH_{Ph}), 140.1 (s, C_{Ph}), 142.1 (s, C_{Ph}), 145.1 (d, ^{2}J = 15.3 Hz, C_{Ph}), 160.8 (s, CH=N) ppm. ^{31}P NMR ($CDCl_3$): δ_P = 120.6. MS (CI): *m*/*z* (%): 614 (10) [*M* + H]$^+$, 433 (100), 392 (55), 205 (43). MS (70 eV, EI): *m*/*z* (%): 613 (4) [*M*]$^+$, 433 (76), 392 (12), 302 (15), 205 (100); elemental analysis: calcd. (%) for $C_{36}H_{36}FeN_3OP$ (613.2): C 70.48, H 5.91, N 6.85; found C 70.25, H 6.09, N 7.02.

(2*R*,5*S*)-2-[2’-(Ferrocenylideneamino)-2′-methylpropoxy]-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane (3d): Yield: 2.43 g, 92%; light orange solid; m.p. 120–122 °C. ^{13}C NMR [$CDC1_3$, δ_C ($J_{C,P}$), Hz]: δ_C = 24.1 and 24.8 (both s, CH_3), 30.0 [d, ^{3}J = 2.9 Hz, C(7)], 31.7 (s, C(6)), 48.5 [d, ^{2}J = 38.5 Hz, C(8)], 55.0 [d, ^{2}J = 6.7 Hz, C(4)], 59.7 (d, ^{3}J = 1.9 Hz, CN), 63.0 [d, ^{2}J = 8.9 Hz, C(5)], 69.2 (d, ^{2}J = 5.7 Hz, $POCH_2$), 68.9 (s, C_{Cp}), 68.0, 68.3, 68.5, 70.0 (all s, C_{Fc}), 81.3 (s, $C_{Fc(\mathit{ipso})}$), 114.5 (d, ^{3}J = 11.4 Hz, CH_{Ph}), 118.5 (s, CH_{Ph}), 128.8 (s, CH_{Ph}), 145.6 (d, ^{2}J = 16.2 Hz, C_{Ph}), 157.0 (s, CH=N) ppm. ^{31}P NMR ($CDC1_3$): δ_P = 121.7 ppm. MS (CI): *m*/*z* (%): 490 (61) [*M* + H]$^+$, 433 (100), 368 (44), 205 (87). MS (70 eV, EI): *m*/*z* (%): 489 (3) [*M*]$^+$, 433 (100), 368 (95), 212 (34), 205 (35); elemental analysis: calcd. (%) for $C_{26}H_{32}FeN_3OP$ (489.2): C 63.81, H 6.59, N 8.59; found C 64.02, H 6.88, N 8.27.

(2*R*,5*S*,2′*S*,3′*S*)-2-[2’-(Ferrocenylideneamino)-3′-methylpentyloxy]-3,1-oxaza-2-phosphabicyclo[3.3.0]octane (5): Yield: 90%; dark red oil. ^{13}C NMR [$CDCl_3$, δ_C ($J_{C,P}$), Hz]: δ_C = 10.9 (s, $\mathit{C}H_3CH_2$), 15.8 (s, $\mathit{C}H_3CH$), 25.1 (s, $CH_3\mathit{C}H_2$), 26.0 [d, ^{3}J = 3.0 Hz, C(7)], 30.8 (s, C(6)), 36.3 (s, $CH_3\mathit{C}H$), 46.9 [d, ^{2}J = 35.1 Hz, C(8)], 61.7 [d, ^{2}J = 3.4 Hz, C(5)], 64.0 (d, ^{2}J = 3.8 Hz, $POCH_2$), 68.8 (s, C_{Cp}), 68.1, 69.8, 69.9, 70.0 (all s, C_{Fc}), 73.6 [d, ^{2}J = 10.7 Hz, C(4)], 76.5 [d, ^{3}J = 4.2 Hz, NCH], 80.8 (s, $C_{Fc(\mathit{ipso})}$), 160.5 (s, CH=N) ppm. ^{31}P NMR ($CDCl_3$): δ_P = 151.5 ppm. MS (70 eV, EI): *m*/*z* (%): 442 (4) [*M*]$^+$, 313 (27), 213 (33), 66 (100); elemental analysis: calcd. (%) for $C_{22}H_{31}FeN_2O_2P$ (442.2): C 59.74, H 7.06, N 6.33; found C 59.67, H 6.91, N 6.19.

Rhodium and Palladium Complexes

[Rh(CO)(5)Cl] (7): Yield 0.161 g, 93%; orange-red powder; m.p. 165–167 °C (dec.) ppm. ^{13}C NMR [$CDCl_3$, δ_C ($J_{C,P}$), Hz]: δ_C = 10.3 (s, $\mathit{C}H_3CH_2$), 14.0 (s, $\mathit{C}H_3CH$), 25.3 (s, $CH_3\mathit{C}H_2$), 26.3 (s, C(7)), 29.6 [s, C(6)], 37.3 (s, $CH_3\mathit{C}H$), 45.4 [d, ^{2}J = 14.2 Hz, C(8)], 60.7 [d, ^{2}J = 5.1 Hz, C(5)], 66.2 (s, $POCH_2$), 69.6 (s, C_{Cp}), 68.3, 69.9, 72.6, 73.4 (all s, C_{Fc}), 71.6 [d, ^{2}J = 8.2 Hz, C(4)], 75.5 (s, NCH), 80.5 (s, $C_{Fc(\mathit{ipso})}$), 170.5 (s, CH=N) ppm. IR (Nujol): $\tilde{\nu}$(RhCl) = 304 cm^{-1}; elemental analysis: calcd. (%) for $C_{23}H_{31}ClFeN_2O_3PRh$ (608.0): C 45.38, H 5.13, N 4.60; found C 45.24, H 4.96, N 4.41.

[Pd(3a)(allyl)]$^+$BF$_4^-$ (8a): Yield 0.286 g, 95%; red powder; m.p. 142–144 °C (dec.). ^{13}C NMR [$CDCl_3$, δ_C ($J_{C,P}$), Hz]: δ_C = 10.8 (s, $\mathit{C}H_3CH_2$), 13.9 (s, $\mathit{C}H_3CH$), 25.8 (s, $CH_3\mathit{C}H_2$), 26.9 [d, ^{3}J = 6.5 Hz, C(7)], 30.5 (s, C(6)), 38.2 (s, $CH_3\mathit{C}H$), 46.8 [d, ^{2}J = 17.2 Hz, C(8)], 49.6 (s, $CH_{2(allyl)}$, *trans*-N), 54.3 (s, C(4)), 61.1 (s, C(5)), 70.0 (s, $POCH_2$), 69.9 (s, C_{Cp}), 68.3, 68.8, 71.3, 71.4 (all s, C_{Fc}), 73.3 (s, NCH), 78.7 (s, $C_{Fc(\mathit{ipso})}$), 81.8 [d, ^{2}J = 37.4 Hz, $CH_{2(allyl)}$, trans-P], 121.8 [d, ^{2}J = 7.6 Hz, $CH_{(allyl)}$], 117.8 (d, ^{3}J = 8.0 Hz, CH_{Ph}), 122.3 (s, CH_{Ph}), 129.3 (s, CH_{Ph}), 142.2 (d, ^{2}J = 12.2 Hz, C_{Ph}), 173.2 (s, CH=N) ppm. MS (PD): *m*/*z* (%): 664 (94) [*M* – BF$_4$]$^+$, 623 (41) [*M* – BF$_4$ – allyl]$^+$, 311 (36), 204 (100). MS (70 eV, EI): *m*/*z* (%): 751 (21) [*M*]$^+$, 710 (20) [*M* – allyl]$^+$, 66 (100); elemental analysis: calcd. (%) for $C_{31}H_{41}BF_4FeN_3OPPd$ (751.1): C 49.53, H 5.50, N 5.59; found C 49.12 H 5.73, N, 5.22.

[Pd(3b)(allyl)]$^+$BF$_4^-$ (8b): Yield 0.277 g, 92%; pale orange powder; m.p. 138–140 °C (dec.). MS (ESI): *m*/*z* (%): 664 (100) [*M* – BF$_4$]$^+$, 623 (7) [*M* – BF$_4$ – allyl]$^+$, 205 (9); elemental analysis: calcd. (%) for $C_{31}H_{41}BF_4FeN_3OPPd$ (751.1): C 49.53, H 5.50, N 5.59; found C 49.71, H 5.23, N 5.37.

[Pd(3c)(allyl)]$^+$BF$_4^-$ (8c): Yield 0.32 g, 94%; dark orange powder; m.p. 150–152 °C (dec.). MS (FAB): *m*/*z* (%): 760 (100) [*M* – BF$_4$]$^+$, 719 (8) [*M* – BF$_4$ – allyl]$^+$, 556 (28), 392 (30), 205 (57); elemental analysis: calcd. (%) for $C_{39}H_{41}BF_4FeN_3OPPd$ (847.1): C 55.25, H 4.87, N 4,96; found C 55.37, H 5.11, N 5,78.

[Pd(3d)(allyl)]$^+$BF$_4^-$ (8d): Yield 0.261 g, 90%; orange powder; m.p. 169–171 °C (dec). MS (FAB): *m*/*z* (%): 636 (100) [*M* – BF$_4$]$^+$, 595 (78) [*M* – BF$_4$ – allyl]$^+$, 368 (37), 205 (59); elemental analysis: calcd. (%) for $C_{29}H_{37}BF_4FeN_3OPPd$ (723.1): C 48.13, H 5.15, N 5.81; found C 48.47, H 4.91, N 5.48.

[Pd(5)(allyl)]$^+$BF$_4^-$ (9): Yield 0.257 g, 95%; red powder; m.p. 147–149 °C (dec.). MS (PD): *m*/*z* (%): 589 (100) [*M* – BF$_4$]$^+$, 548 (15) [*M* – BF$_4$ – allyl]$^+$, 314 (49), 130 (50); elemental analysis: calcd. (%) for $C_{25}H_{36}BF_4FeN_2O_2PPd$ (676.1): C 44.38, H 5.36, N 4.14; found C 44.12, H 5.51, N 3.91.

[Pd(3a)(allyl)]$^+$Cl$^-$ (10a): Yield 0.269 g, 96%; orange powder; m.p. 146–148 °C (dec); elemental analysis: calcd. (%) for $C_{31}H_{41}ClFeN_3OPPd$ (699.1): C 53.16, H 5.90, N 6.00; found C 52.97, H 6.17, N 5.78.

Preparation of Complexes 11a and 12a: A solution of NaI (0.075 g, 0.5 mmol) in dry acetone (10 mL) for **11a** or solution of $CsCH_{12}B_{11}$ (0.138 g, 0.5 mmol) in dry THF (10 mL) for **12a** was added dropwise to a stirred solution of complex **10a** (0.350 g, 0.5 mmol) in the same solvent (10 mL) at 20 °C. The reaction mixture was stirred at 20 °C for 1 h, filtered, concentrated to ca. 0.5 mL, and precipitated with ether. The obtained precipitate was separated by centrifugation, washed with diethyl ether (2 × 10 mL) and dried in air and in vacuo (1 Torr).

$[Pd(3a)(allyl)]^+I^-$ (11a): Yield 0.356 g, 90%; light orange powder; m.p. 138–140 °C (dec); elemental analysis: calcd. (%) for $C_{31}H_{41}FeIN_3OPPd$ (791.0): C 47.2, H 5.22, N 5.31; found C 47.36 H 5.57 N 4.98.

$[Pd(3a)(allyl)]^+[CH_{12}B_{11}]^-$ (12a): Yield: 0.375 g, 93%; deep red powder; m.p. 166–168 °C (dec.). MS (PD): *m/z* (%): 664 (20) [$M - CB_{11}H_{12}$]$^+$, 623 (12) [$M - CB_{11}H_{12}$ – allyl]$^+$, 204 (59), 133 (100); elemental analysis: calcd. (%) for $C_{32}H_{53}B_{11}FeN_3OPPd$ (809.3): C 47.57, H 6.61, N 5.20; found C 47.31, H 6.42, N 4.96.

Catalytic Experiments

Palladium-Catalysed Sulfonylation of 1,3-Diphenyl-2-propenyl Acetate with Sodium *p*-Toluenesulfinate: $[Pd(allyl)Cl]_2$ (3.6 mg, 10^{-2} mmol) or $[Pd_2(dba)_3]\cdot CHCl_3$ (10.3 mg, 10^{-2} mmol) and ligand **3a–d**, **5** (2–4 × 10^{-2} mmol) or complex **8a–d** to **12a** (2 × 10^{-2} mmol) were dissolved in THF (5 mL) at room temp. After the mixture had been stirred for 40 min, 1,3-diphenyl-2-propenyl acetate (0.1 mL, 5 × 10^{-1} mmol) was added. Stirring was continued for 15 min and a portion of $NaSO_2p$Tol (178 mg, 1 mmol) was added. After the mixture had been stirred for 48 h, brine (10 mL) was added, and the mixture was extracted with THF (3 × 7 mL). The organic phase was dried ($MgSO_4$) and concentrated in vacuo. Purification by recrystallisation from ethanol gave the product as milky white crystals. Enantiomeric excess was determined by HPLC ((*R*,*R*)Whelk-01, C_6H_{14}/*i*PrOH = 4:1, 1 mL min^{-1}, 254 nm) according to published data.[20]

Palladium-Catalysed Alkylation of 1,3-Diphenyl-2-propenyl Acetate with Dimethyl Malonate: $[Pd(allyl)Cl]_2$ (3.6 mg, 10^{-2} mmol) or $[Pd_2(dba)_3]\cdot CHCl_3$ (10.3 mg, 10^{-2} mmol) and ligand **3a–c** or **5** (2–4 × 10^{-2} mmol) or complex **8a–d** or **9** (2 × 10^{-2} mmol) were dissolved in the appropriate solvent (5 mL) at room temp. After the solution had been stirred for 40 min, 1,3-diphenyl-2-propenyl acetate (0.1 mL, 5 × 10^{-1} mmol) was added. Stirring was continued for 15 min and dimethyl malonate (0.1 mL, 8.7 × 10^{-1} mmol), BSA [*N*,*O*-bis(trimethylsilyl)acetamide] (0.22 mL, 8.7 × 10^{-1} mmol) and AcONa (2 mg) were then added to the catalyst solution, and the mixture was stirred for 48 h. The solution was diluted with THF (5 mL) and filtered through Celite. The solvent was removed in vacuo to afford a pale yellow oil that solidified on standing. Enantiomeric excess was determined by HPLC (Daicel Chiralcel OD-H, C_6H_{14}/*i*PrOH = 99:1; 0.5 mL min^{-1}, 254 nm) according to published data.[21]

X-ray Crystallographic Study: X-ray studies of **2d** and **7:** The principal experimental and crystallographic parameters are presented in Table 7. The structure of **2d** and **7** were solved by direct methods and refined by full-matrix techniques against F^2 in anisotropic approximation with use of the SHELXTL 5.1 program package.[22] The positions of hydrogen atoms were calculated geometrically and included in refinement in rigid body approximation. The absolute configuration of **7** was determined by use of the Flack parameter.

CCDC-250539 (for **2d**) and -250538 (for **7**) 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.

Acknowledgments

The authors gratefully acknowledge receiving *tert*-leucinol from Degussa AG (Germany) and $CsCH_{12}B_{11}$ from I. T. Chizhevsky (In-

Table 7. The principal experimental and crystallographic parameters of structures **2d** and **7**.

	2d	**7**
Diffractometer	Bruker Smart CCD 1000	Syntex $P2_1$
Molecular formula	$C_{15}H_{19}FeNO$	$C_{23}H_{31}ClFeN_2O_3PRh$
Formula mass	285.16	608.68
Colour, shape	red, prism	red, prism
Dimensions [mm]	0.2 × 0.2 × 0.2	0.2 × 0.2 × 0.1
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/c$	$P2_12_12_1$
a [Å]	9.290(4)	10.241(2)
b [Å]	18.902(8)	14.260(3)
c [Å]	7.689(3)	16.963(3)
β [°]	103.461(8)	
V [Å^3]	1313.2(9)	2477.3(9)
Z	4	4
$\rho_{calcd.}$ [g cm^{-1}]	1.442	1.632
Temperature [K]	120	153
Min./max. 2Θ [°]		1.00 and 28.05
Scan type	ω (0.3° step in ω and 10 s exposure per frame)	$\Theta/2\Theta$
Radiation, λ(Mo-K_α) [Å]		0.71072
Linear absorption (μ) [cm^{-1}]	11.35	14.51
Absorption correction	SADABS	none
$T_{min.}/T_{max.}$	0.805/0.805	
F(000)	600	1240
Total refl. (R_{int})	10092 (0.0265)	3385 (0.0007)
Number of independent refl.	3742	3385
Number of indepent refl. with $I > 2(\sigma)$	2958	2781
Parameters	169	289
wR_2	0.0964	0.1193
R_1	0.0437	0.0474
GOF	0.962	0.949
$\rho_{max.}/\rho_{min.}$ [e Å^{-3}]	1.071/–0.398	1.833/–1.466

stitute of Organoelement Compounds, Moscow). The authors thank Dr. A. V. Korostylev (Leibniz-Institut für Organische Katalyse, Rostock, Germany) for assistance in the preparation of the manuscript. This work was partially supported by the Russian Foundation for Basic Research (Grant No. 03-03-32181) and a Grant of the President of the RF for young scientists – doctors of sciences (No. MD-21.2003.03).

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Received: October 29, 2004