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Chiral P,N-bidentate ligands in coordination chemistry and organic catalysis involving rhodium and palladium

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Abstract. Published data on the synthesis of rhodium and palladium complexes with optically active P,N-bidentate ligands and their applications in homogeneous asymmetric catalysis are summarised and discussed. The effect of the nature of the P,N-bidentate compounds on the structure of the metal complexes and on enantioselectivity in catalysis is examined. Allylic substitution, cross-coupling, hydroboration and hydrosilylation catalysed by Rh or Pd complexes with optically active P,N-bidentate ligands are considered. The prospects for the development of this field of chemistry are demonstrated. The bibliography includes 186 references.

I. Introduction

A fundamental problem studied at the border of chemical disciplines is the coordination behaviour of bi- and polyfunctional ligands. This problem includes competition of ligands for metal atoms, donor – acceptor interactions, isomerism of complexes, stereo- and regioselective synthesis of coordination compounds and specific complex formation in biologically important objects.[1] Of particular interest are phosphorus-containing compounds, which play an extremely important role in the development of views on coordination bonds, the geometry and the structure of complexes and on the mutual influence of inner-sphere ligands as well as in metal complex catalysis.[2,3] Systems containing an electron-donating centre of a different nature, apart from the phosphorus centre, are being vigorously studied. P,N-Bidentate ligands are highly important. They simultaneously exhibit properties of both soft and hard bases and promote redistribution of functions in a catalytic cycle, formation of bimetallic structures and a specific arrangement of the metal coordination sphere. Thus P,N-bidentate ligands can provide *cis*- or *trans*-chelation, bridging binding in either the 'head-to-tail' or 'head-to-head' fashions (in particular, in structures with metal – metal bonds) and P-monodentate coordination. The particular type of coordination depends, first of all, on the length of the bridge linking the donor atoms. Systems with two linking units are typical chelating agents; the bridging type of coordination is barely known for them, whereas three-unit species are capable of bridging coordination. Coordination of a P,N-system to a central atom gives rise to two moieties differing in kind, containing electron-donating centres with different steric and electronic characteristics. Being structurally asymmetric, P,N-bidentate ligands also possess clear-cut electronic asymmetry. In addition, both steric and electronic parameters of the electron-donating centres and the nature of the bridge linking them can be varied over wide limits. The features listed above are important in asymmetric catalysis in which very fine structural and electronic changes in the ligand nature can be significant. Therefore, it is quite natural that the greatest progress in the enantioselective catalysis of cross-coupling, allylation, hydroboration, hydrosilylation and other processes has been achieved by the use of metal complexes with P,N-bidentate chiral ligands.

Data on the role of optically active P,N-bidentate ligands in the coordination chemistry and catalysis are reported in several monographs and reviews.[4–10] However, the information presented there concerns either a particular narrow group of compounds (for example, ferrocenyl systems [8]) or a particular catalytic reaction. The present review is the first attempt to summarise and describe systematically the role of chiral P,N-bidentate ligands in coordination chemistry and asymmetric catalysis. Attention is concentrated on the studies published over the last 15 years, most of all, in the 1990s, which were the years of vigorous development of the field of chemistry in question. This review deals only with P,N-bidentate systems with no additional electron-donating centres (*i.e.* devoid of O, S, Se and As or additional N or P atoms), only rhodium and palladium complexes being considered. Although examples of the use of W(0),[11] Au(I),[12,13] Ir(I)[14] and Pt(II)[15] complexes in enantioselective catalysis do exist, the leading position of the two above-mentioned metals is beyond doubt.

We have classified the published data on the basis of the ligand structure. This approach appears expedient because it allows one to cover the achievements of both coordination chemistry and catalysis. Classification in terms of the types of organic reactions is more reasonable in considering the problems of enantioselective catalysis, whereas that accepted in coordination chemistry is based on the nature of the metal and the main initial metal complexes used. When these two aspects are discussed simultaneously, the nature of the P,N-bidentate ligand is a unifying point. Phosphorus-substituted ferrocenes and dihydrooxazoles are the subjects of separate Sections. This is due to the outstanding role of

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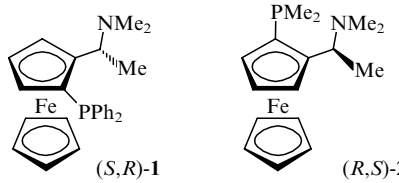
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these derivatives in asymmetric catalysis. Ligands of this type ensure high yields and high enantioselectivity of processes and provide the possibility of investigating some aspects of the catalysis mechanisms, for example, the role of the planar chirality of the ferrocenyl fragment. Phosphorus-substituted dihydrooxazoles represent a specific group of ligands developed for highly efficient allylation. The change in the steric and electronic parameters of the sp^2-hybridised donor nitrogen atom incorporated in the five-membered ring influences the properties of the ligand and the catalytic activity of its metal complexes. The rather patchy group of other ligands is classified according to the nature of the electron-donating nitrogen centre; compounds with the phosphite donor centre are distinguished as a separate group. In addition, in arranging the information, we attempted, whenever possible, to group studies of the most productive scientific schools chronologically and to consider comprehensively the most important catalytic processes.

II. P,N-Bidentate phosphorus-substituted ferrocenes

1. Ligands with sp^3-hybridised electron-donating nitrogen atoms. Aminoalkylferrocenylphosphines

In 1974, in the very beginning of the development of metal complex asymmetric catalysis, a publication appeared [16] dealing with the synthesis of (*S*,*R*)-1-(1-dimethylaminoethyl)-2-diphenylphosphinoferrocene [(*S*,*R*)-**1**, (*S*,*R*)-PPFA][†] and (*R*,*S*)-1-(1-dimethylaminoethyl)-2-dimethylphosphinoferrocene [(*R*,*S*)-**2**, (*R*,*S*)-MPFA], which were the first representatives of chiral P,N-bidentate phosphorus-containing ligands.



(*S*,*R*)-**1** (*R*,*S*)-**2**

The novel ligands were tested [16] in enantioselective hydrosilylation of a series of prochiral ketones. The best result (yield 89%, *ee* 49%) was obtained in the reaction of acetophenone with diphenylsilane in the presence of $[Rh(C_6H_{10})Cl]_2 \cdot 4L$, where L = (*R*,*S*)-MPFA [(*R*,*S*)-**2**].

$$PhCOMe + Ph_2SiH_2 \xrightarrow[2)\ H_3O^+]{1)\ Cat} PhCH(OH)Me$$

Cat = $[Rh(C_6H_{10})Cl]_2 \cdot 4$(*R*,*S*)-MPFA.

The compound (*R*,*S*)-**2** was found to be markedly more efficient than the best mono- and bidentate phosphorus-containing ligands known at that time, namely, (*R*)-PhCH$_2$(Ph)(Me)P* and 2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane [(−)-DIOP].[16] It was also found that replacement of the dimethylamino group in the side chain of the ligand (*R*,*S*)-**2** by a hydrogen atom results in a sharp decrease in the stereoselectivity. These studies opened up a new line in the search for bidentate chiral ligands for metal complex catalysis. The researchers used simultaneously two fruitful concepts, namely, combination of two different electron-donating centres (phosphorus and nitrogen) and two types of chirality (central and planar) in the molecule of an optically active ligand. PPFA [(*S*,*R*)-**1**] has been modified, for example, by replacing the methyl substituents at the nitrogen atom by Et, Pr^i, Bu^i, *etc*.[17] P,N-Bidentate ligands have been assayed in other asymmetric catalytic processes. Cross-coupling of (1-phenylethyl)magnesium chloride with vinyl bromide catalysed by the complex PdCl$_2$[(*S*,*R*)-PPFA] gave (*S*)-3-phenylbut-1-ene in 82% yield (*ee* 61%).[17,18]

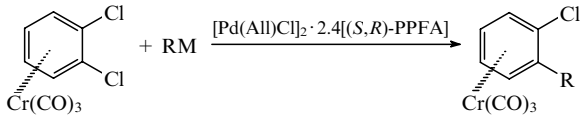
$$PhCH(Me)MgCl + BrCH{=}CH_2 \xrightarrow{PdCl_2[(S,R)\text{-PPFA}]} PhCH(Me)CH{=}CH_2$$

The enantiomer of the ligand (*S*,*R*)-**1**, namely, (*R*,*S*)-PPFA, also as a complex with PdCl$_2$, ensures an even higher enantioselectivity in this type of reaction.[19]

$$Me_3SiCH(Ph)MgCl + Br{-}CR^1{=}CHR^2 \xrightarrow{PdCl_2[(R,S)\text{-PPFA}]} Me_3Si(Ph)(H)C{-}CR^1{=}CHR^2$$

R^1 = Me, R^2 = H (*ee* 85%); R^1 = Ph, R^2 = H (*ee* 95%);
R^1 = R^2 = H (*ee* 96%).

The bidentate ligand (*S*,*R*)-**1** is able to induce not only central but also planar chirality.[20]

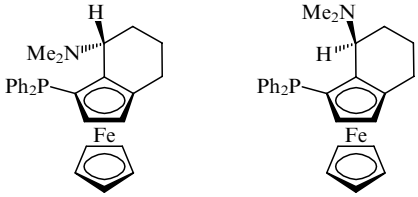


(*ee* < 44%)

R = CH=CH$_2$, C(Me)=CH$_2$, CH=CHBu;
M = SnBu$_3$, MgCl, ZnCl, B(OH)$_2$; All = CH$_2$=CHCH$_2$.

For (*S*,*R*)-**1** and for its close analogue having two *tert*-butyl substituents at the phosphorus atom, a number of rhodium(I) cationic complexes, including $[(NBD)Rh(L)]^+X^-$ (NBD is norbornadiene, $X^- = PF_6^-$, ClO_4^-), $[(COD)Rh(L)]^+Y^-$ (COD is cyclooctadiene, $Y^- = BF_4^-$, BPh_4^-), have been prepared. The complexes have been thoroughly studied by ^{1}H NMR, ^{31}P NMR and IR spectroscopy and conductometry. The structure of the complex $\{(NBD)Rh[(R,S)\text{-PPFA}]\}^+PF_6^-$ was established by X-ray diffraction analysis.[21] The formation of a metal-containing chelate ring was demonstrated in all cases. The use of these complexes as catalysts of hydrogenation of *N*-acetyl-α-aminocinnamic acid ensures *ee* of up to 84%.[21,22]

The further investigation into chiral phosphorus-containing ferrocenes has been mostly carried out by two research groups, namely, Weissensteiner's [23–28] and Togni's [29–39] groups. Thus Weissensteiner *et al*.[23,24] synthesised epimeric ferrocenyl P,N-bidentate ligands, (*R*,*R*)-PTFA **3a** and (*R*,*S*)-PTFA **3b**.



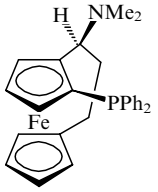
3a **3b**

In the model cross-coupling of (1-phenylethyl)magnesium chloride with vinyl bromide, the complex PdCl$_2$[(*R*,*R*)-PTFA] provides an *ee* of 79% for a nearly quantitative chemical yield of 3-phenylbutene; in the presence of PdCl$_2$[(*R*,*S*)-PTFA], the *ee* is only 4%. Thus, in this case, the process enantioselectivity is governed by the central chirality of the ligands **3a,b**. This outcome contrasts sharply with the results obtained in the catalysis by nickel complexes, which gave close values of the optical yield in the presence of (*R*,*S*)- and (*R*,*R*)-PPFA.[17] The structure of the catalyst PdCl$_2$[(*R*,*R*)-PTFA] was studied by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy. According to X-ray diffraction data, the Pd−P bond length [2.207(2) Å] is close to the average values observed in *cis*-palladium(II) dichloride complexes with aminophosphine ligands.[24] Subsequently, the palladium(II) complex $\{Pd(\eta^3\text{-}C_4H_7)[(R,R)\text{-PTFA}]\}^+Tf^-$ and the palladium(0) complex $\{Pd[(R,R)\text{-PTFA}]\}L$, where Tf = CF_3SO_3, L is maleic anhydride or dimethyl fumarate, have been studied in detail [25] using multinuclear NMR data (including the INDOR and EXSY techniques)

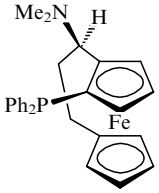
[†] Hereinafter, the first character denotes the configuration of the ferrocenyl core.

and X-ray diffraction analysis. It was concluded that PTFA, which is conformationally more rigid than PPFA, possesses also stronger chelating properties. An attempt [26] to use (*S*,*S*)-PTFA as a ligand in asymmetric hydroformylation of styrene proved unsuccessful: for rhodium(I)-based catalyst, *ee* was 0.5%, while in the case of platinum(II)-based catalyst, it is 7% – 21%. This was explained [26] by the fact that the chelate angle formed by PTFA is rather small, especially in the case of complexation with platinum(II).

Enantiomeric ferrocenyl bidentate ligands **4a,b**, related in structure to PPFA and PTFA, have been prepared.[27,28] Complexes of the ligand **4a** with $PdCl_2$ and the ligand **4b** with PdClMe, $PdMe_2$ and $PdPh_2$ were synthesised.



(*S*,*S*)-**4a**



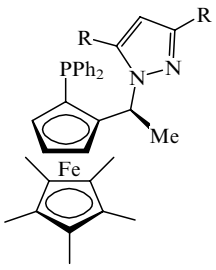
(*R*,*R*)-**4b**

The structures of the ligands **4a,b** and complexes derived from them, which are promising in asymmetric catalysis, were studied by X-ray diffraction analysis and multinuclear NMR spectroscopy including low-temperature procedures. Broadening of the resonance signals of the diastereotopic methyl groups in the palladium complexes of **4a,b** suggests [28] that the energy barrier to the rupture of the Pd – N bond is low.

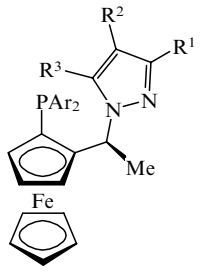
2. Ligands with sp^2-hybridised electron-donating nitrogen atoms

a. Ferrocenylphosphinopyrazoles

Researches into ferrocene-based P,N-bidentate ligands have gained a new incentive due to the studies of Togni *et al.*[29–39] Having started with minor structural changes, *i.e.* introduction of one or five methyl groups into the unsubstituted ring of (*S*,*R*)- or (*R*,*S*)-PPFA,[29] they used subsequently a fairly advantageous expedient, namely, they replaced the dimethylamino group by a pyrazole ring. This gave rise to a series of 1-diarylphosphino-2-[1-(pyrazol-1-yl)ethyl]ferrocenes **5a,b** [29] and **6a – g**.[30–32]



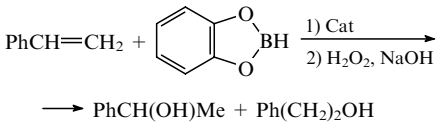
(*R*,*S*)-**5a,b**
R = H (**a**), Me (**b**)



(*R*,*S*)-**6a – γ**

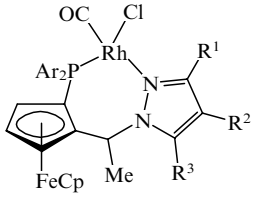
Compound **6**	R^1	R^2	R^3	Ar
a	H	H	H	Ph
b	Me	H	Me	Ph
c	CF_3	H	CF_3	Ph
d	Me	Me	Me	Ph
e	CF_3	H	Me	Ph
f	Pr^i	H	Pr^i	Ph
g	Me	Br	Me	Ph
h	Ph	H	Me	Ph
i	Me	NO_2	Me	Ph
j	Ph	H	Me	cyclo-C_6H_{11}
k	Me	H	Me	4-FC_6H_4
l	Me	H	Me	4-$CF_3C_6H_4$
m	Me	H	Me	4-$MeOC_6H_4$
n	Me	H	Me	3,5-$Me_2C_6H_3$
o	Me	H	Me	4-MeC_6H_4
p	Me	H	Me	4-PhC_6H_4
q	Me	H	Me	3,5-$(CF_3)_2C_6H_3$
r	Me	H	Me	4-$NMe_2C_6H_4$
s	CF_3	H	CF_3	4-$MeOC_6H_4$
t	1-naphthyl	H	Me	Ph
u	1-adamantyl	H	H	Ph
v	cyclo-C_6H_{11}	H	Me	Ph
w	Ph	H	H	Ph
x	2-naphthyl	H	Me	Ph
y	4-pyridyl	H	Me	Ph
z	3-$NO_2C_6H_4$	H	H	Ph
α	2,4-$(MeO)_2C_6H_3$	H	Me	Ph
β	9-anthryl	H	Me	Ph
γ	9-tripticyl	H	H	Ph

The ligands **6a – t** were tested [30,31] in the hydroboration–oxidation of styrene with catecholborane.



Cat = {$[Rh(COD)_2]^+BF_4^-$} – (**6a – t**).

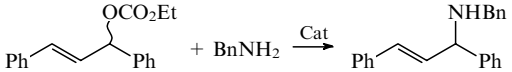
In some cases, the reaction gives a substantial amount of an achiral primary alcohol but, in general, the enantioselectivity is high. The optical yield was found to be clearly dependent on the electronic properties of substituents at the donor centres — electron-withdrawing substituents in the pyrazole nucleus decrease the optical yield, whereas substituents in the phenyl groups at the phosphorus atom increase the optical yield [the *ee* values for the formation of (*R*)-1-phenylethanol in the presence of the ligands **6c**, **e**, **a**, **l**, **q** are 33%, 44%, 65%, 98% and 98.5%, respectively]. Rhodium(I) chloro carbonyl complexes **7a – t** were synthesised by reactions of **6a – t** with $[Rh(CO)_2Cl]_2$. They were characterised by the data of ^1H, ^{31}P ($^1J_{P-Rh}$ = 161 – 176 Hz) and ^{13}C NMR and IR spectroscopy (ν_{CO} = 1980 – 2008 cm^{-1}) and mass spectrometry.[31] X-ray diffraction analysis of the compounds **7n**, **o** was performed.[31]



7a – t

An acceptable correlation has been found between the ν_{CO} and *ee* values for the complexes **7a – t**; the frequency of the carbonyl group vibrations is affected by changes in the σ-donor properties of the nitrogen centre and in the π-acceptor properties of the phosphorus centre. The cationic complexes $[Rh(COD)(L)]^+BF_4^-$ have been prepared (L = **6b**, **c**) and also studied by multinuclear magnetic resonance and X-ray diffraction analysis. As in the complexes **7a – t**, in this case, too, a seven-membered chelate metallacycle is formed.

The ligands **6t – γ** have found application in a reaction significant from the synthetic standpoint, namely, allylic amination [32] (the enantioselectivity reaches 99%).

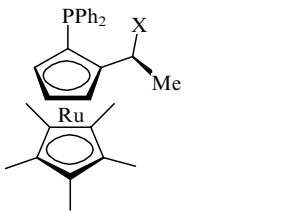


Cat = $[Pd_2(dba)_3]\cdot 3L$, dba is dibenzylideneacetone; L = **6t – γ**.

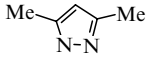
The reaction mechanism, including allylic intermediates $[Pd(\eta^3\text{-}PhC_3H_3Ph)(L)]^+PF_6^-$, was studied in detail using X-ray diffraction analysis and 2D NMR. It was found that the attack of a nitrogen-containing nucleophile is directed at the carbon atom in the allylic ligand located in the *trans*-position relative to the phosphorus centre of the coordinated P,N-bidentate ligand. The activation barrier to the formation of the C–N bond in the *trans*-position relative to the phosphorus atom is 3 kcal mol^{-1} lower than that for the *trans*-position to nitrogen.[32] Calculation methods[33] and conformational analysis[34] [using ^{31}P, ^{13}C and ^{1}H (NOESY) data] of model allylic complexes have also been invoked to study the reaction mechanism and stereochemical features of the process.

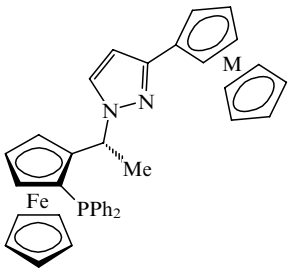
The ligand **6u**, containing an adamantyl substituent in the pyrazole ring, proved to be the most efficient in allylic amination (*ee* 99%).[32,35] By the addition of coordinating anions, F^-, BH_4^- or OH^-, in co-catalytic amounts, a virtually quantitative optical yield can be attained (>99.5%).[36]

Similar derivatives of ruthenocene **8a**,**b**[37] and bimatallic systems **9a**,**b**, in which the pyrazole ring contains a second ferro- or rutheno-cene fragment, have been synthesised.[38]



(*R*,*S*)-**8a**,**b**

X = NMe_2 (**a**),  (**b**)

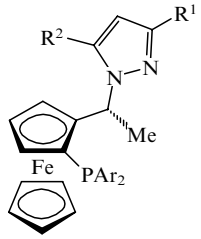


(*S*,*R*)-**9a**,**b**

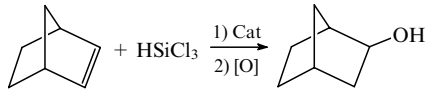
M = Fe (**a**), Ru (**b**)

The efficiencies of the ligands **6u** and **9a**,**b** in the catalysed allylic amination are comparable (*ee* >99.5%).[38] In catalytic hydroboration–oxidation, the ligand **8b** is somewhat inferior to the ferrocenyl analogue **5b** (the optical yields for 100% conversion of styrene are 87% and 94%, respectively).[37]

Recently,[39] ligands **10a**–**d**, close analogues of the compounds **6a**–**γ**, have been proposed. In the presence of these ligands, asymmetric hydrosilylation–oxidation of norbornene has been carried out.



(*S*,*R*)-**10a**–**d**



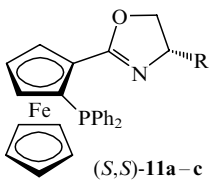
Cat = $PdCl_2 \cdot L$, L = **10a**–**d**.

Compound **10**	R^1	R^2	Ar	Optical yield of hydroxynorbornane (%)
a	Ph	Me	Ph	39
b	2,4,6-$(MeO)_3C_6H_2$	H	Ph	82
c	2,4,6-$Me_3C_6H_2$	H	Ph	91
d	2,4,6-$Me_3C_6H_2$	H	3,5-$(CF_3)_2C_6H_3$	99

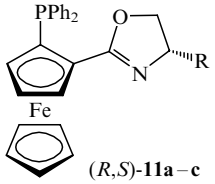
In the case of the ligands **10**, the optical yield increases on passing from **10a** to **10d**. It has been concluded[39] that optimisation of the ligand regarding steric factors should be done with allowance for its electronic asymmetry because the σ-basicity of the pyrazole fragment and the π-acidity of the phosphine fragment are important in hydroxylation–oxidation, as well as in hydroboration–oxidation.

b. Phosphinoferrocenyl-4,5-dihydrooxazoles

Phosphinodihydrooxazole ligands will be discussed in Section III. This Section is devoted to structures related to the ligands **6a**–**γ** but having a second chiral centre in the heterocyclic fragment. In particular, epimeric ligands of type **11a**–**c** have been synthesised.[40–43] They are designated by the common abbreviation DPOF.



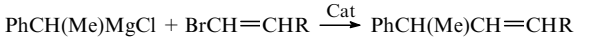
(*S*,*S*)-**11a**–**c**



(*R*,*S*)-**11a**–**c**

R = Pr^i (**a**), Bu^t (**b**), Me (**c**).

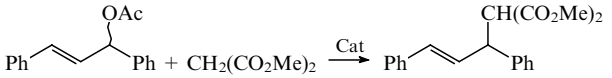
The reaction of the compounds (*S*,*S*)- and (*R*,*S*)-**11b** with $PdCl_2(MeCN)_2$ gave complexes {$PdCl_2$[(*S*,*S*)-**11b**]} and {$PdCl_2$[(*R*,*S*)-**11b**]}; the latter was characterised by X-ray diffraction analysis.[40] These complexes were used as cross-coupling catalysts.



R = H, Ph; Cat = $[Pd(All)Cl_2]L$, L = (*S*,*S*)-**11a**, (*S*,*S*)-**11c**, (*S*,*R*)-**11a**.

The complex {$PdCl_2$[(*S*,*S*)-**11a**]} provides a higher enantioselectivity of this process than its epimer (*ee* 45% and 8%, respectively). The chemical yield is also substantially greater in the former case (74% and 23%, respectively). Thus, unlike the ligands (*R*,*R*)-PTFA **3a** or (*R*,*S*)-PTFA **3b**, in this case, the enantioselectivity is mainly due to planar chirality.

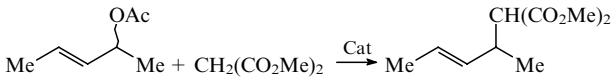
In the classical alkylation of malonates with allyl esters catalysed by $[Pd(All)Cl]_2$, the ligand (*S*,*S*)-**11b** ensures *ee* 90%; in the case of the ligand (*S*,*S*)-**11c**, the enantioselectivity is more than 99% (the chemical yield is nearly quantitative in both cases). In the presence of (*R*,*S*)-**11b,** *ee* is only 73%.[42,43] In this reaction, the crucial role is also played by the stereochemistry of the ferrocenyl core of the ligand.



12

Cat = $[Pd(All)Cl]_2L$, L = (*S*,*S*)-**11b**, (*S*,*S*)-**11c**, (*R*,*S*)-**11b**.

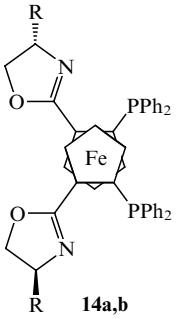
The enantioselectivity of the reaction depends also on the steric requirements of the substrate. On passing from 1,3-diphenylprop-2-enyl acetate **12** to the methyl analogue **13**, the optical yield sharply drops (it is not more than 36%).



13

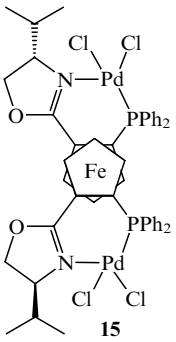
Cat = $[Pd(All)Cl]_2L$, L = (*S*,*S*)-**11b**.

Tetrasubstituted ferrocenyl ligands **14a**,**b**, constructed as combinations of two fragments of the ligands **11a** or **11b**, have also been synthesised.[44]



14a,b

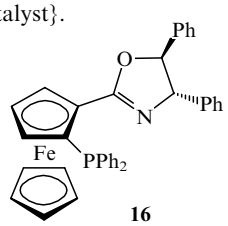
R = Pr^i (**a**), Bu^t (**b**).



15

The compound **14a** was converted into the palladium complex **15**; unfortunately, this complex was only scantily characterised by spectroscopic data (data on ^1H NMR and mass spectra were reported). Interestingly, the ligand prepared by replacement of the dihydrooxazole rings in the structure **14a** by the $CH(Me)NMe_2$ groups behaves as a P,P- rather than a P,N-bidentate ligand with respect to Pd(II) because the amino-group nitrogen atom is bound to palladium more weakly than the dihydrooxazole nitrogen.[44] In the Pd(II)-catalysed alkylation of the allyl acetate **12**, the ligands **14a**,**b** provide *ee* 96% – 99%, the chemical yield being more than 90%; the epimer of compound **14a** with the opposite planar configuration displays the same enantioselectivity. Thus, in this case, unlike the ligands **11**, the planar chirality does not have a governing influence on the product configuration; this might be due to different reaction mechanisms.

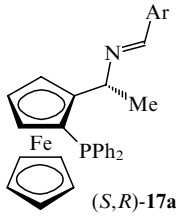
Ligand (*S,S,S*)-DIPOF **16** has been studied [14, 45] in the asymmetric reduction of a series of prochiral aromatic and aliphatic ketones with diphenylsilane {with $[Rh(COD)Cl]_2$ as the pre-catalyst}.



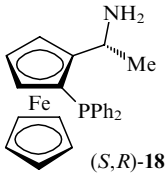
16

The chemical yields in these reactions were 45% – 100%, while the optical yields were 57% – 91%. The best results were attained in the reduction of acetophenone to (*R*)-1-phenylethanol. In the presence of (*R,R,R*)-DIPOF, the reaction affords (*S*)-1-phenylethanol with *ee* 91%. The use of $[Ir(COD)Cl]_2$ as the pre-catalyst increases the optical yield to 96%.

In the hydrosilylation of acetophenone with diphenylsilane, the use of related dihydrooxazole systems, namely, arylideneaminoalkylferrocenylphosphines **17a** – **d** leads to commensurable results (*ee* 87% – 90% for chemical yields of 86% – 94%) [46] {with $[Rh(NBD)Cl]_2$ as the pre-catalyst}.



(*S,R*)-**17a** – **d**

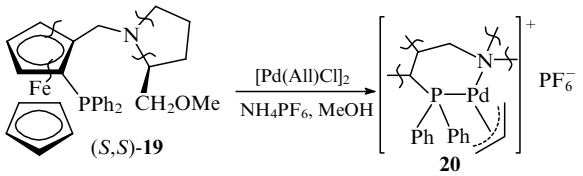


(*S,R*)-**18**

Ar = Ph (**a**), 3-$CF_3C_6H_4$ (**b**), 4-$CF_3C_6H_4$ (**c**), C_6F_5 (**d**)

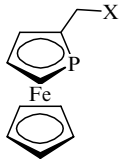
The presence of the imino group in the ligand structure is of prime importance. Indeed, in the presence of the amine (*S,R*)-**18**, *ee* is 39%, while in the presence of (*S,R*)-PPFA [(*S,R*)-**1**], it is only 16%. However, the nature of the arylidene group barely influences the optical yield.

In conclusion, we would like to mention several other P,N-bidentate phosphorus-substituted ferrocenes which hold prospects as asymmetric catalysts. The first one is ligand **19**, for which cationic complex **20** has been obtained.[47] The P,N-bidentate manner of binding to palladium(II) in the complex **20** was established by ^1H, ^{31}P and ^{13}C NMR spectroscopy and X-ray diffraction analysis.



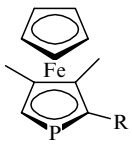
(*S,S*)-**19** **20**

Phosphaferrocenes **21a** – **c**, representing a new class of ligands with planar chirality,[48] and analogous compounds **22**,[49] containing peripheral aza heterocycles have been synthesised.



21a – **c**

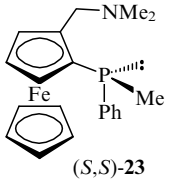
X = NMe_2 (**a**), CH_2NH_2 (**b**), CH_2NMe_2 (**c**)



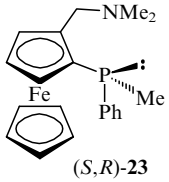
22a,b

R = 2-pyridyl, 8-quinolyl

A recent publication [50] describes the synthesis and resolution of diastereomers (*S,S*)-**23** and (*S,R*)-**23** with a chiral centre on the phosphorus atom.



(*S,S*)-**23**



(*S,R*)-**23**

A complex of the compound (*S,R*)-**23** with PdI_2 — [(1-MePhP-2-$Me_2HN^+CH_2C_5H_3$)FeC_5H_5)]PdI_3^- — has been prepared.[50] X-Ray diffraction analysis showed a P-monodentate binding to palladium of the ligand protonated at the nitrogen atom. The researchers suggested that the complex was formed upon opening of the chelate ring on treatment with the hydrogen iodide, resulting from decomposition of PdI_2, followed by the reaction of I_2 with traces of water. Hence, it was concluded that the six-membered metallacycle involving the ligand (*S,R*)-**23** is relatively unstable. However, this statement seems arguable because lots of metal complexes formed by related systems, for example, PPFA **1**, PTFA **3** or the ligands **4a**,**b** are known. The wrong choice of the initial palladium(II) compound appears to be a more probable reason.

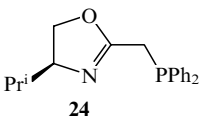
Thus, the use of nitrogen-and-phosphorus-containing ferrocenes in asymmetric metal complex catalysis makes it possible to attain more than 90% optical yields in some important reactions such as cross-coupling, hydroboration – oxidation and hydrosilylation – oxidation of alkenes, hydrosilylation of ketones, and allylic substitution.

III. P,N-Bidentate phosphorus-containing 4,5-dihydrooxazoles

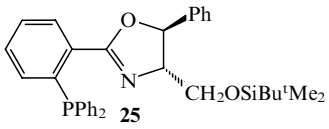
This group of ligands includes compounds containing an sp^2-hybridised donor nitrogen atom.

In 1993, three research groups working independently, namely, Helmchen's group [51] from the Institute of Organic Chemistry of Heidelberg University, Williams' group [52] from the Technological University (Lawboro), and Pfaltz's [53] group from the Institute of Organic Chemistry of Basel University, reported almost simultaneously the synthesis and the use in enantiomeric catalysis of the first representatives of a new class of P,N-bidentate

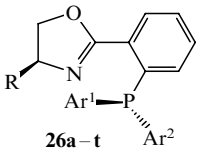
ligands — phosphorus-containing 4,5-dihydrooxazoles. There is an opinion,[54] however, that Williams *et al*.[55] came out with the main concepts a year earlier. Subsequently, the effort of the three groups mentioned above resulted in the synthesis of a large series of phosphorus-substituted dihydrooxazoles such as **24**, **25** and **26a–t**.[56–76]



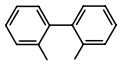
24



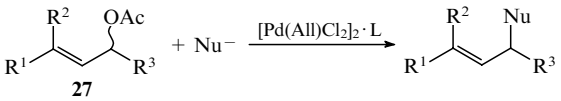
25



26a–t

Compound **26**	Ar[1]	Ar[2]	R
a	Ph	Ph	Me
b	Ph	Ph	Pr^i
c	Ph	Ph	Bu^t
d	Ph	Ph	Bu^i
e	Ph	Ph	Ph
f	Ph	Ph	CH_2Ph
g	Ph	Ph	1-naphthyl
h	Ph	Ph	CH_2Bu^t
i	Ph	Ph	CH_2SBu^i
j	Ph	Ph	$CMe_2SCH_2Pr^i$
k	Ph	Ph	$(CH_2)_2SMe$
l	Ph	Ph	(3-indolyl)methyl
m	Ph	1-naphthyl	Pr^i
n	1-naphthyl	Ph	Pr^i
o	1-naphthyl	1-naphthyl	Pr^i
p	2-biphenylyl	Ph	Pr^i
q	2-biphenylyl	Ph	Ph
r	3,5-$(CF_3)_2C_6H_3$	3,5-$(CF_3)_2C_6H_3$	Pr^i
s	cyclo-C_6H_{11}	cyclo-C_6H_{11}	Pr^i
t			Pr^i

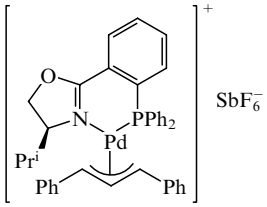
When ligands of the type **26** are employed in the model alkylation of dimethyl malonate with the allyl acetate **12** {with $[Pd(All)Cl]_2$ as the pre-catalyst},[51–53,56] optical and chemical yields reach 99%. The highest enantioselectivity is exhibited by the chiral substituted dihydrooxazoles **26b**, **c**, **e**. Other nucleophilic substitution reactions at the allylic carbon atom in the allyl acetates **27** were also performed with high enantioselectivity in the presence of these compounds. The results are summarised in Table 1.



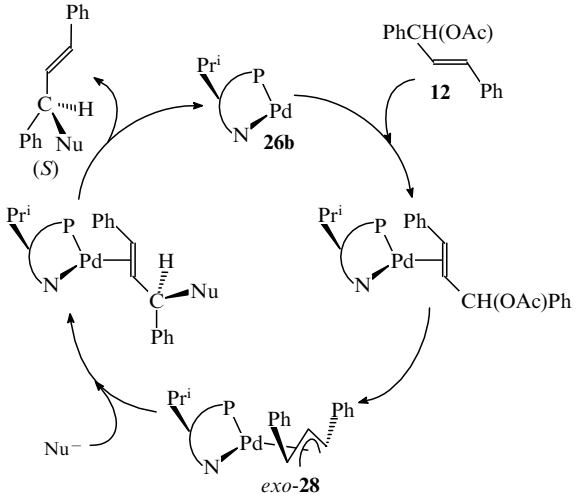
27

It should be noted that, in the presence of the epimeric compounds **26m**,**n**, the corresponding derivatives are formed in the same optical yield (77%) and with the same (*S*) absolute configuration, *i.e*. the asymmetric induction is accomplished by the dihydrooxazole fragment.[56] The distance between the electron-donating centres is also significant — the ligand **24**, which forms a five-membered metal-containing chelate ring, provides a moderate selectivity (*ee* 73%).[51]

Several palladium-catalysed intramolecular alkylation reactions have also been successfully performed;[67] the best result was attained with the ligand **26e** (*ee* 80%–87%). Enatioselective allylic substitution is utilised to prepare natural products including optically active starting compounds for the synthesis of α- and β-amino acids and their derivatives.[58,66] A palladium(II) cationic complex was prepared from the compound **26b** and characterised by ^1H NMR spectroscopy (NOESY, ROESY) and X-ray diffraction analysis.



Resorting to low-temperature 2D NMR spectroscopy made it possible to propose a catalytic cycle for the alkylation of dimethyl malonate with the acetate **12** in the presence of the ligand **26b**.[68]

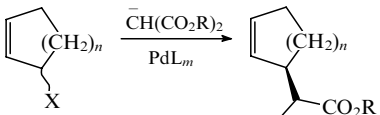


Nu = $CH(CO_2Me)_2$.

The predominant (*S*)-enantiomer of the reaction product is formed *via* an attack by the nucleophile on the C(3) atom of the allylic fragment, located in the *trans*-position relative to the phosphorus centre, in the *exo*-**28**.

Detailed investigation of the reaction mechanism using model reactions permitted ligands of the type **26** to be employed in other asymmetric allylic substitution processes. Thus *ee* values of more than 99.9% are attained in some cases in the alkylation of nitromethane with the allyl carbonates RCH=CHCH(R)O.CO_2Me (R = Me, Et, Ph).[69] Among the ligands **26b**,**c**,**e**,**i**,**m**,**n**,**o** tested {with $[Pd_2(dba)_3]\cdot CHCl_3$ as the pre-catalyst}, the best results were obtained for **26b**,**c**,**i**.

In the case of cyclic substrates **29**, the best results were obtained for the ligands **26p**,**q**.[70] The epimeric compounds **26m**,**n** provide close enantioselectivities.



29a–d

n = 1 (**a**), 2 (**b**), 3 (**c**), 4 (**d**); X = OAc, OCO_2Me, Br; R = Me, Et; *m* = 1.5–3; L = **26b**,**m**,**n**,**p**,**q**.

Phosphorus-containing cymantrenyldihydrooxazoles **30a–i** and **31a**,**b**[71] ensure better asymmetric induction in some cases {with $[Pd(All)Cl]_2$ as the pre-catalysts}.

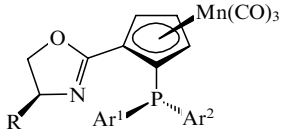
In the reaction of the cyclic allyl acetates **29a**,**b**,**c** (X = OAc) with the anion derived from dimethyl malonate in the presence of the ligand **30d**, the optical yields are 96%, 93% and >99%, respectively. The configuration of the phosphorus centre is of fundamental importance in this case: in the presence of the epimeric ligand **30c**, the reaction with the compound **29b** results in *ee* of only 31%. Compounds achiral at phosphorus (including

Table 1. Enantioselectivity in allylic substitution in the compounds **27** in the presence of the ligands **26b,c,e**.

Compound **27**	R^1	R^2	R^3	HNu	L	Yield (%)	*ee* (%)	Ref.
a	Ph	H	Ph	$CH_2(SO_2Ph)_2$	**26b**	78	93	57
				$H_2NSO_2C_6H_4$-4	**26b**	84	90	58
					**26b**	65	96	58
				$(Ph)_2C{=}NCH_2P(O)(OEt)_2$	**26b**	98	96	59
				$(Ph)_2C{=}NCH_2CO_2Bu^t$	**26c**	89	97	60
				$CH_2(CO_2Me)_2$	**26e**	98	97	53
				H_2NNHBz	**26c**	95	97	61
				$CH(NHAc)(CO_2Et)_2$	**26e**	98	97	53
				HO_2SBu^t	**26b**	69	91	62 [a]
				HO_2SBu^t	**26c**	70	90	62
				HO_2SBu^t	**26e**	71	93	62
b	Et	H	Ph	$CH_2(CO_2Me)_2$	**26c**	98	79	63
c	Me	H	Ph	$CH_2(CO_2Me)_2$	**26c**	96	71	57, 63
				H_2NBn	**26c**	87	89	61
d	Pr^i	H	$P(O)(OEt)_2$ (see [b])	$HN(Boc)_2$ [c]	**26c**	29	97	61
e	Ph	Ph	Me	$CH_2(CO_2Me)_2$	**26b**			64–66
f	Ph	Ph	Ph	$CH_2(CO_2Me)_2$	**26b**			64–66
g	Ph	Ph		$CH_2(CO_2Me)_2$	**26b**			64–66
h	Ph	Ph	Mes	$CH_2(CO_2Me)_2$	**26b**			64–66
i	Pr^i	H	Ph	$CH_2(CO_2Me)_2$	**26c**	88	96	53

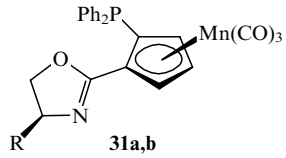
[a] Pre-catalyst is $[Pd_2(dba)_3]\cdot CHCl_3$; [b] the corresponding phosphate was used; [c] Boc is Bu^tOCO.

30a,**b**) are relatively ineffective, the *ee* values being not more than 44%.[71]



30a–i

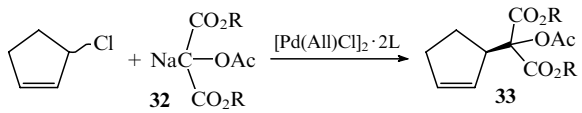
Compound **30**	Ar^1	Ar^2	R
a	Ph	Ph	Pr^i
b	Ph	Ph	Bu^t
c	Ph	2-biphenylyl	Bu^t
d	2-biphenylyl	Ph	Bu^t
e	3,5-$Me_2C_6H_3$	2-biphenylyl	Bu^t
f	2-biphenylyl	3,5-$Me_2C_6H_3$	Bu^t
g	3,5-$(CF_3)_2C_6H_3$	2-biphenylyl	Bu^t
h	2-biphenylyl	3,5-$(CF_3)_2C_6H_3$	Bu^t
i	2-biphenylyl	2-biphenylyl	Bu^t



31a,b

R = Pr^i (**a**), Bu^t (**b**)

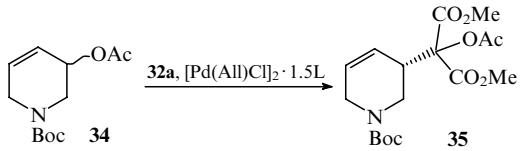
The ligand **30d** was also found to be highly effective in related reactions. Thus, when 3-chlorocyclopentene reacts with the sodium salt **32**, the reaction product **33** is formed in >94% yield and *ee* >98.5%.[72]



32 **33**

R = Me (**a**), Et (**b**); L = **30d**.

A similar reaction with the *N*-substituted tetrahydropyridine acetate **34** results in a product yield of 84% and *ee* 98%.[73]

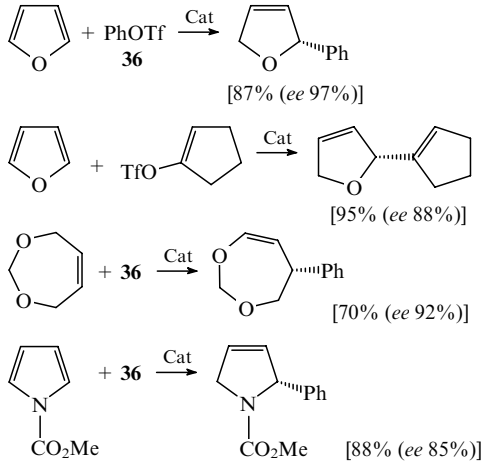


34 **35**

L = **30d**.

Compound **35** is a valuable optically active initial compound for the preparation of aza sugars and (*R*)-nicotinic acid.

The use of phosphorus-containing dihydrooxazoles in the formation of the C–C bond according to the Heck reaction is equally effective. Thus the ligand **26c** ensures a fairly good enantioselectivity in the reactions with triflates.[58, 74, 75]

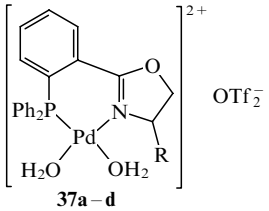


Cat = $[Pd(dba)_2]\cdot 2L$, L = **26c**.

In this reaction, phosphorus-substituted dihydrooxazoles are preferred over diphosphines including the known BINAP ligand [2,2′-bis(diphenylphosphino)-1,1′-dinaphthalene] because they do not induce undesirable side processes of double bond migration.[75]

Complexes **37a–d**, prepared from the corresponding ligands and $PdCl_2(MeCN)_2$ [followed by treatment with Ag(OTf) and water], have been employed for copolymerisation of styrene with CO.[76] This yielded poly(1-oxo-2-phenylpropane-1,3-diyl) with a molecular mass of ~ 20 000.

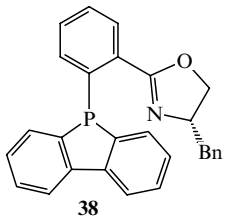
In the presence of the achiral complex **37a**, an atactic polymer is formed, whereas catalysis by the optically active complexes **37b–d** results in a stereoregular isotactic polymer.



37a–d

R = H (**a**), Bu^i (**b**), Ph (**c**), Bn (**d**).

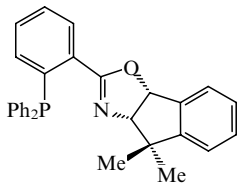
Ligand **38** has been employed for copolymerisation of styrene and ethylene with CO in the presence of the complex $[Pd(OAc)LS]^+TfO^-$, where L = **38** and S is a solvent.[77]



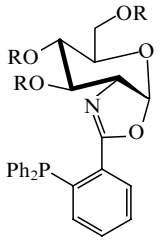
38

Other researchers working independently of the three leading groups mentioned above used successfully the ligands **26b,e** in allylic sulfonylation,[78] while the ligand **26c** was used in the intramolecular Heck reaction.[79] The allylation mechanism was analysed theoretically by the extended Hückel method.[80]

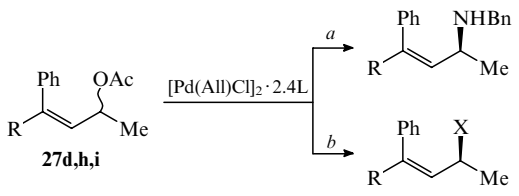
New phosphorus-containing oxazolines **39** and **40** have been synthesised. The ligand **39** [81] ensures *ee* of 95% – 99% in the allylic amination of the acetates **27d,h,i** with benzylamine or phthalimide.



39

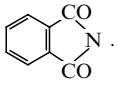


40 (R = Bu^{t}CO)

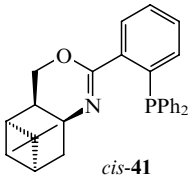


27d,h,i

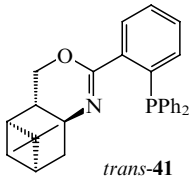
R = Ph (**d**, 43%, *ee* 99%), 4-ClC_6H_4 (**h**), 4-BrC_6H_4 (**i**); L = **39**;

(*a*) $BnNH_2$; (*b*) HX, X = .

The compound **40**, containing a carbohydrate fragment fused with a dihydrooxazole fragment, has been used as a ligand in the alkylation of dimethyl malonate with the allyl acetates **12** (*ee* 98%) and **13** (*ee* 69%) in the presence of $[Pd(All)Cl]_2$.[82] This resulted in the synthesis of phosphorus-containing dihydro-1,3-oxazine isomers **41**. In the reaction with the allyl acetate **12** {$[Pd(All)Cl]_2$ as the pre-catalyst}, *ee* depends on the ligand: it is 95% in the presence of *cis*-**41** and only 64% in the presence of *trans*-**41**.[83]

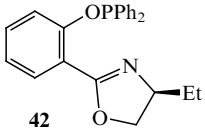


cis-**41**



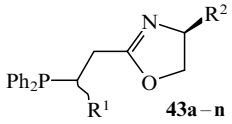
trans-**41**

On the basis of the compound **42**, neutral and cationic palladium(II) complexes have been prepared.[84] To the best of our knowledge, **42** is the only P,N-bidentate ligand of the dihydrooxazole type containing a phosphinite group. It would be of interest to study this compound in the asymmetric catalysis and to compare it with analogous phosphine systems.



42

Recently, a series of phosphorus-containing dihydrooxazoles **43a–n** have been synthesised. Unlike the ligands **26–42**, in this case, the diphenylphosphine fragment is not attached to the aromatic nucleus.[85,86]

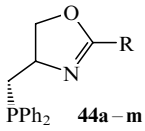


43a–n

R^1 = H: R^2 = Me (**a**), Bn (**b**), Pr^i (**c**), Ph (**d**); R^1 = (*S*)-Me, R^2 = Pr^i (**e**); R^1 = (*R*)-Me, R^2 = Pr^i (**f**); R^1 = (*S*)-Ph: R^2 = Bn (**g**), Pr^i (**h**), Ph (**i**), Bu^t (**j**); R^1 = (*R*)-Ph: R^2 = Bn (**k**), Pr^i (**l**), Ph (**m**), Bu^t (**n**).

The alkylation with the allyl acetate **12** {$[Pd(All)Cl]_2$ as the pre-catalyst} in the presence of the ligands **43a–d** provides *ee* of 11% – 90%, while this reaction in the presence of **43e–n** results in *ee* of 22% – 98%. The best results were attained in the presence of the ligands **43c** and **43n**. The optical yield depends on the solvent; for example, with the ligand **43c** in CH_2Cl_2, the *ee* is 90%, whereas that in MeCN is only 11%. Acetonitrile is the optimal solvent for ligands with two chiral centres such as **43e–n**. The researchers [85,86] did not explain this fact. Apparently, the chiral centre of the dihydrooxazole ring in the compounds **43e–n** is responsible for the asymmetric induction because the diastereomers **43h** and **43l** provide *ee* of 90% and 93%, respectively, all other factors being the same.

A number of phosphorus-substituted dihydrooxazoles **44a–m**, differing in the nature of the substituent R in the 2-position, have been synthesised.[87]

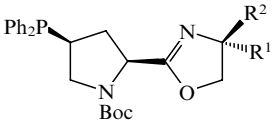


44a–m

R = Me (**a**), Bu^t (**b**), $CHPh_2$ (**c**), CPh_3 (**d**), 1-adamantyl (**e**), 3,5-$Bu^t_2C_6H_3$ (**f**), ferrocenyl (**g**), CF_3 (**h**), Ph (**i**), 4-$MeOC_6H_4$ (**j**), 4-MeC_6H_4 (**k**), 4-$NO_2C_6H_4$ (**l**), C_6F_5 (**m**).

These ligands ensure *ee* of up to 94% in the alkylation of dimethyl malonate with the allyl acetate **12** in the presence of $[Pd(All)Cl]_2$, the compound **44e** being the most effective. Electron-donating substituents in the dihydrooxazole ring were found to increase the optical yield. In general, the enantioselectivity attained with the ligands **44a–m** is somewhat lower than that observed with the ligands **26a–t**. This was attributed [87] to the fact that the relative strain and the tendency for opening of the five-membered chelate metallacycles formed by the ligands **44** are

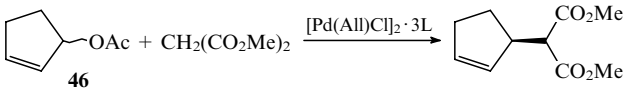
greater than those in the case of **26**. Indeed, according to ^{31}P NMR spectroscopy, the reaction of $[Pd(All)Cl]_2$ with the compound **44k** taken in a twofold excess relative to the palladium complex results in a complex containing two organophosphorus ligands in the palladium coordination sphere, while the reaction of the compound **26e** with the same Pd complex yields a metallacycle with only one phosphorus-containing ligand. In view of these data together with the results obtained using the ligand **24**, one can formulate a general rule: the phosphorus-substituted dihydrooxazoles forming five-membered chelate metallacycles are less effective than those forming six-membered rings. In this connection, compounds **45a–f** synthesised recently [88] are worthy of note.



45a–f

R^1 = H: R^2 = Pr^i (**a**), Ph (**b**), Bu^t (**c**); R^1 = Pr^i: R^2 = H (**d**); R^1 = Ph, R^2 = H (**e**); R^1 = R^2 = Me (**f**).

For example, in the alkylation of dimethyl malonate with cyclopent-2-enyl acetate (**46**), *ee* reaches 96%, the yield of the final product being 79%–99%.



46

L = **45a–f**.

The optical yield and the absolute configuration of the reaction product are controlled by the pyrrolidine fragment because in the presence of the ligand **45f**, *ee* is only 80%. The ligands **45a–f** should form complexes containing seven-membered metallacycles, which are moreover rather strained; nevertheless, they ensure a high level of asymmetric induction. Thus, the enantioselectivity in this reaction does not depend on the size of the metal ring.

In addition to the two, to some extent, related processes, *i.e.*, allylic substitution and Heck reaction, phosphorus-containing dihydrooxazole P,N-bidentate ligands have found application in the asymmetric version of catalytic hydrosilylation. Thus the ligands **26a–c**,**f**,**i**,**k**,**o**,**r–t** have been studied in the reduction of a series of prochiral aromatic and aliphatic ketones with diphenylsilane {with $[Rh(COD)Cl]_2$ as the pre-catalyst}.[89,90] In the hydrosilylation of acetophenone, the degree of conversion is 80%–99% and the optical yield is up to 86%. The highest enantioselectivity was found for the ligands **26b** (*ee* 82%) and **26r** (*ee* 86%); the latter ligand, which contains electron-withdrawing substituents at the phosphorus centre ensures also the highest catalytic activity.[90] It should be noted that in the presence of the ligand **26c**, which displayed very good properties in allylic alkylation, *ee* is only 40%. Too bulky substituents at the phosphorus centre do not enhance the enantioselectivity. Indeed, with the ligand **26o**, *ee* is only 17%. It is noteworthy that the replacement of the PAr^1Ar^2 fragment in the compounds **26** by SPh or SePh almost eliminates the asymmetric induction.

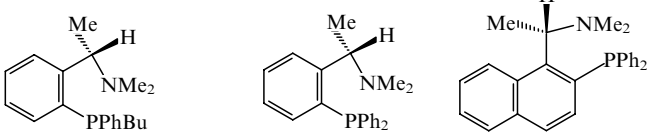
The use of the ligand **39** for the reduction of acetophenone with diphenylslane {the catalytic system $[Rh(COD)Cl]_2 \cdot 4L$} [91] proved especially successful (*ee* 94%). In the general case, the selectivity is inversely proportional to the size of the substituent at the 4-position of the dihydrooxazole fragment of the ligand. However, the asymmetric induction provided by the ligand **39** was found to be abnormally high, despite the fact that the two methyl substituents in the compound **39** create greater steric hindrance than one *tert*-butyl substituent in the compound **26c**. In the opinion of the investigators cited,[91] interpretation of these effects requires further research into the mechanism of the rhodium-catalysed hydrosilylation and the structure of intermediates.

IV. Other groups of chiral P,N-bidentate ligands

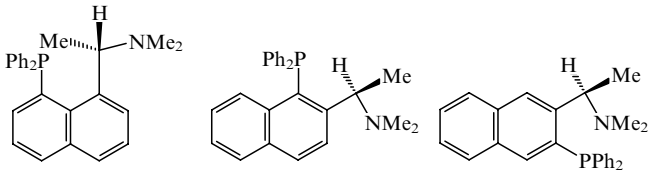
The two classes of optically active P,N-bidentate ligands considered above mainly include particular series of compounds prepared specially to be investigated in catalytic reactions. The other compounds used as P,N-bidentate ligands are difficult to classify because they belong to different classes and types. We classified these compounds in terms of the structures of the nitrogen and phosphorus electron-donating centres; three groups of ligands were thus distinguished. Within each group, the data are mainly arranged according to the type of the catalytic reaction.

1. Ligands with sp^3-hybridised electron-donating nitrogen atoms

Chiral P,N-bidentate ligands with sp^3 hybridised electron-donating nitrogen atoms became known earlier than other compounds (except for aminoalkylferrocenylphosphines). Back in 1977, syntheses of compound **47a** with two asymmetric centres, carbon and phosphorus, and the complex of the phosphine **47a** with $PdCl_2$ were reported.[92] The formation of the metal chelate ring and the absolute configuration of the chiral centres in the complex were proved by X-ray diffraction analysis. Subsequently,[93] several more aminophosphines with benzene or naphthalene nuclei have been reported, for example, (*S*)-AMPHOS **48**, 1,2-DPNEA **49**, 1,8-DPNEA **50**, 2,1-DPNEA **51** and 2,3-DPNEA **52**.



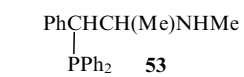
(S_C, R_P)-**47a**, (S_C, S_P)-**47b** (*S*)-**48** **49**



50 **51** **52**

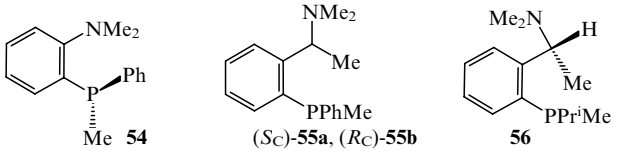
Neutral or cationic Rh(I) complexes with ligands of the type **47b** and **48–51** were used as catalysts of hydrogenation of prochiral unsaturated acids. Thus hydrogenation of itaconic acid in the presence of 1,2-DPNEA **49** proceeds with an optical yield of up to 43%.[93]

Other ligands, for example, the phosphorus-containing ephedrine derivative **53**, have also found application in the hydrogenation of prochiral unsaturated acids. The reduction of *N*-acetyl-α-aminocinnamic acid in the presence of $[Rh(C_8H_{14})Cl]_2$ and the ligand **53** gives the product in an optical yield reaching 77%.[94]

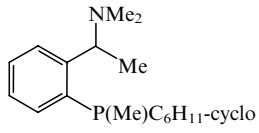


53

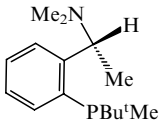
Ligands **54**, **55a**,**b**, **56**, **57a**,**b**, **58** and **59a**,**b** [95,96] have been used in the hydrogenation of *N*-acetyl-α-aminocinnamic and *N*-benzoyl-α-aminocinnamic acids in the presence of $[Rh(C_6H_8)Cl]_2$. The maximum optical yield (68%) was attained in the case of (*S*)-1-[2-(methyl-*tert*-butylphosphino)phenyl]ethylamine (**58**).[96]



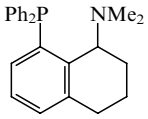
54 (S_C)-**55a**, (R_C)-**55b** **56**



(S_C)-**57a**,(R_C)-**57b**

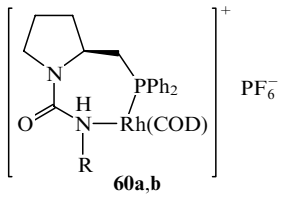


58



(*S*)-**59a**, (*R*)-**59b**

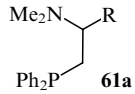
The cationic rhodium(I) complexes **60a**,**b** have been synthesised and characterised in detail by ^1H, ^{31}P and ^{13}C NMR and IR spectroscopy and conductometry.[97] The ligands present in these complexes contain rarely encountered carbamide donor centres. However, the reduction of *Z*-(α)-ethylacetaminocinnamic acid in the presence of the complex **60b** resulted in only a moderate enantioselectivity (*ee* 34%).



60a,**b**

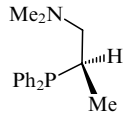
R = But (**a**), $(CH_2)_3Si(OEt)_3$ (**b**).

Yet another traditional field of application of chiral aminophosphines with an sp^3-hybridised nitrogen atom is cross-coupling. Both acyclic (**61a**–**g**, **62**) and heterocyclic (**63**, **64**) aminophosphines have been employed in these reactions.[98,99]

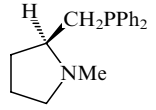


61a–**g**

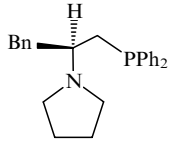
Compound **61**	R	Abbreviation
a	Me	(*S*)-ALAPHOS
b	Pri	(*S*)-VALPHOS
c	Bui	(*S*)-LEUPHOS
d	But	(*R*)-t-LEUPHOS
e	Ph	(*R*)-PhGLYPHOS
f	Bn	(*S*)-PHEPHOS
g	cyclo-C_6H_{11}	(*R*)-ChGLYPHOS



62

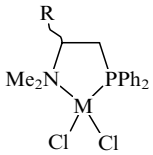


63 (*S*)-PROPHOS



64

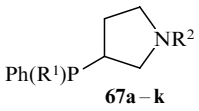
Cross-coupling of 1-phenylethylmagnesium chloride with vinyl bromide in the presence of complexes of $PdCl_2$ with the ligands **61a**–**g**, **62**, **63** and **64** proceeds with a moderate enantioselectivity [*ee* up to 55% for (*S*)-PHEPHOS **61f**]. The catalytic system $NiCl_2 \cdot L$ was found to be more efficient; indeed, in the case of the ligand **61d**, the optical yield reaches 94%. It should be noted that movement of the chiral centre towards the phosphorus atom results in a decrease in the asymmetrising activity (*ee* 38% for **61a** and *ee* 25% for **62**).[99] For example, in the cross-coupling of 1-phenylethylmagnesium chloride with β-bromostyrene, the Ni complex (*S*)-AMPHOS **48** exhibits no catalytic effect, while $PdCl_2 \cdot$[(*S*)-AMPHOS] ensures a 95% chemical yield and a 40% optical yield.[100] Palladium(II) *cis*-dichloro compounds **65a,b** have been synthesised and characterised by X-ray diffraction data.[101] These complexes and nickel complexes **66a,b** having a similar structure were tested in the cross-coupling of 1-phenylethylmagnesium chloride with vinyl bromide. In the presence of the palladium complexes **65a**,**b**, the optical yield was moderate (*ee* up to 45%). The use of the nickel complexes **66a**,**b** resulted in a higher enantioselectivity (for **66b**, *ee* 88%).



65a,**b**, **66a**,**b**

Compound	R	M
65a	(*S*)-$(CH_2)_2SMe$	Pd
65b	(*R*)-$(CH_2)_2SMe$	Pd
66a	(*S*)-$(CH_2)_2SMe$	Ni
66b	(*R*)-$(CH_2)_2SMe$	Ni

The synthesis of P,N-bidentate ligands **67a**–**k**, containing a pyrrolidine ring, has been described.[102,103]

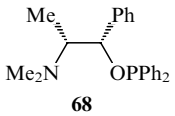


67a–**k**

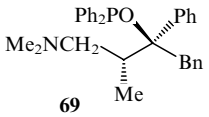
Compound **67**	R^1	R^2
a	Ph	H
b	Ph	Bn
c	Ph	2-$MeOC_6H_4CH_2$
d	Ph	Et
e	H	H
f	2-$MeOC_6H_4CH_2$	H
g	2,4,6-$(MeO)_3C_6H_2CH_2$	H
h	2-$MeOC_6H_4CH_2$	Bn
i	2,4,6-$(MeO)_3C_6H_2CH_2$	Bn
j	H	Bn
k	H	Ph

The compounds **67b**,**c**,**g**,**h**,**i** were used to prepare the *cis*-diiodo metal chelates $PdI_2 \cdot L$, having a heteronorbornane skeleton; diastereomeric palladium complexes with the ligands **67a**–**g** were separated by column chromatography. The structure of the complex compounds was convincingly proved by IR spectroscopy and ^1H, ^{13}C and ^{31}P NMR spectroscopy (including the use of solid-state techniques), FAB mass spectrometry and X-ray diffraction analysis. However, these products were not selective in cross-coupling, the *ee* values being not more than 10%. Meanwhile, in the case of $NiCl_2 \cdot$ **67b**, the chemical yield is 98% and the optical yield is 75%.[103]

P,N-Bidentate ligands **68** and **69**, containing a phosphinite group, have been described.[104]



68

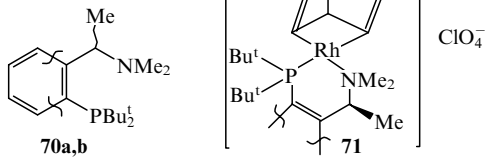


69

Palladium complexes formed by the ligands **68** and **69** proved to be inefficient in the cross-coupling of 1-phenylethylmagnesium bromide with vinyl bromide; the optical yield was only 6%–9% for a degree of conversion of 60%–74%.[104] This outcome was explained by insufficient rigidity of six- and seven-membered palladacycles and by lower basicity of the phosphinite group in comparison with the phosphine group. However, this interpretation is quite debatable. The palladium complexes were characterised only by ^{31}P and ^1H NMR spectra. No data of long-wavelength IR spectroscopy which would provide information on the arrangement of the chloro ligands at the Pd atom based on the position of the ν_{Pd-Cl} band are available. No data on the molecular masses of the complexes can be found either. Therefore, it cannot be ruled out that the reaction of the ligand **69** with $PdCl_2$ gives a bi- or poly-nuclear compound $[PdCl_2 \cdot L]_n$, in which the P,N-bidentate ligands function as bridges linked according to the 'head-to-tail' pattern, rather than a chelate. As regards the basicity of the phosphorus centre in cross-coupling catalysts, the statistical data available to date do not permit an unambiguous conclusion about its role in the enantioselectivity. It is quite probable that in the case of aminophosphinites **68** and **69**, an appropriate catalytic system has not been chosen.

Several chiral aminophosphines have been tested in asymmetric hydrosilylation. For instance, the reduction of acetophenone with diphenylsilane with participation of (*S*)-AMPHOS **48** {$[Rh(C_2H_4)_2Cl]_2$ as the pre-catalyst} gave the corresponding alcohol with *ee* 33%, and in the case of reduction of *tert*-butyl methyl ketone, *ee* was 72%.[105] Subsequently,[106] this result was somewhat improved: catalysis by $[Rh(COD)Cl]_2 \cdot 10L$, where L = (*S*)-AMPHOS **48**, gave α-phenylethyl alcohol in an optical yield of 51% and a chemical yield of 97%. Other pre-catalysts proved to be less efficient: for $Pd(COD)Cl_2$, *ee* reaches 50.5% but the degree of conversion is only 13%, while for $Pt(COD)Cl_2$ and $[Ir(COD)Cl]_2$, *ee* does not exceed 27%.

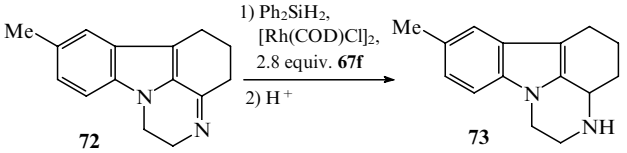
It should be noted that close analogues of (*S*)-AMPHOS **48** containing a di(*tert*-butyl)phosphine group in the benzene ring, instead of the diphenylphosphine group, are known,[107] namely, (*S*)- (**70a**) and (*R*)-DIBUTPHOS **70b**. According to X-ray diffraction analysis,[107] in the rhodium complex **71**, the ligand (*R*)-DIBUTPHOS **70b** forms a metal chelate.



70a,b **71**

However, the use of the ligands **70a**,**b** in the hydrosilylation of acetophenone with phenyldimethylsilane {with $[Rh(C_2H_4)_2Cl]_2$ as the pre-catalyst} gave a quite unexpected result: for a chemical yield of up to 92%, no enantioselectivity was observed at all.

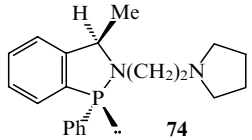
The ligand (*S*)-PHEPHOS **61f** ensures an optical yield of 54% in the hydrosilylation of acetophenone with diphenylsilane {the $[Rh(COD)Cl]_2 \cdot 4L$ system}.[108] When cyclic imine **72** was subjected to hydrosilylation with diphenylsilane in the presence of the $[Rh(COD)Cl]_2 \cdot 2.8L$ system, where L = (*S*)-PHEPHOS **61f**, compound **73**, the enantiomer of the antidepressant pyrazidol, was obtained in 69% yield and *ee* 73%.[109]



72 **73**

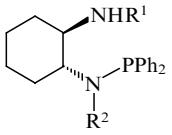
The behaviour of (*S*)-PHEPHOS **67f** and (*S*)-AMPHOS **48** in the reaction with $[Rh(COD)Cl]_2$ and $[Rh(CO)_2Cl]_2$ has been studied.[110] The reaction products, binuclear Rh(I) complexes of the $[Rh(L)Cl]_2$ type and mononuclear complexes of the Rh(CO)Cl(L) type, were isolated and characterised by spectroscopy (IR, X-ray electron, ^1H NMR, ^{31}P NMR and mass spectra).

To summarise the foregoing, it should be noted that rhodium and palladium derivatives of chiral aminophosphines with an sp^3-hybridised peripheral nitrogen atom provide moderate enantioselectivity as catalysts of hydrogenation, cross-coupling and hydrosilylation. However, they are more effective in allylic substitution. Specifically, amino-substituted phosphinous amide **74**, in which the asymmetric phosphorus atom is incorporated in a heterocycle, ensured a chemical yield of 99% and an optical yield of 62% in the alkylation of dimethyl malonate with the acetate **12** {with $[Pd(All)Cl]_2$ as the pre-catalyst}.[111]



74

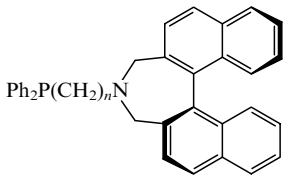
The same model reaction was used to test a series of amino phosphinous amides **75a**–**j**, in which the phosphorus atom is achiral {$[Pd(All)Cl]_2$ as the pre-catalyst}.[112] In the presence of these ligands, *ee* is 76% for a chemical yield of 41%–82%. The best optical yield was attained with the ligand **75h**, having no substituents at the amide nitrogen atom.



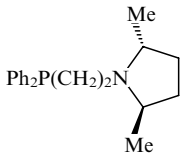
75a–**j**

Compound **75**	R^1	R^2
a	H	H
b	Me	Me
c	Bn	Bn
d	Pr^i	Pr^i
e	$CH_2CH_2Pr^i$	$CH_2CH_2Pr^i$
f	2-$MeC_6H_4CH_2$	2-$MeC_6H_4CH_2$
g	3-$MeC_6H_4CH_2$	3-$MeC_6H_4CH_2$
h	Bn	H
i	2-$MeC_6H_4CH_2$	H
j	Bu^tCH_2	H

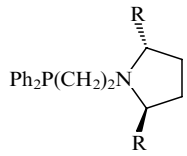
Ligands **76a,b**, **77**, **78a,b** and **79** with axial or central chirality of the peripheral nitrogen atom have been prepared.[113]



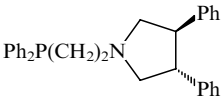
76a,**b**
n = 2 (**a**), 3 (**b**)



77

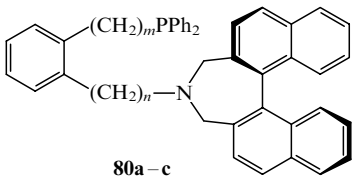


78a,**b**
R = Et (**a**), Bn (**b**)



79

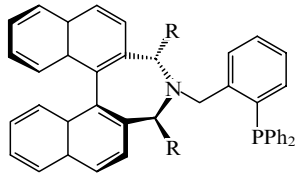
In the model allylic alkylation using $[Pd(All)Cl]_2$ as the pre-catalyst, the use of the ligands **76a**,**b** results in *ee* values of 93% and 96%, respectively. The chemical yields are 96%. An increase in the optical yield on passing from the compound **76a** to **76b**, was attributed [113] to an increase in the size of the chelate metallacycle it forms. The ligands **77**, **78a**,**b** and **79** are much less enantioselective (*ee* up to 39%). In the presence of the ligands **80a**–**c**, in which the phosphorus center is further removed from the nitrogen centre, the asymmetric induction decreases with an increase in the distance between the donor centres.[113]



80a–**c**

Compound **80**	n	m
a	1	0
b	2	0
c	1	1

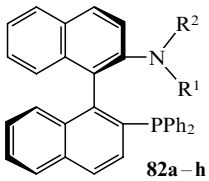
In the alkylation of dimethyl malonate with the acetate **12**, the ligands **80a**–**c** [with $Pd(OAc)_2$ as the pre-catalyst] ensure *ee* of 96%, 79% and 18%, respectively.[114] The low optical yield observed in the last-mentioned case was explained by assuming monodentate coordination of the compound **80c** for the formation of the intermediate. The ligands **80a**–**c** were also employed in the cross-coupling of (1-phenylethyl)magnesium chloride with vinyl bromide. The best result (*ee* 46%) was observed for the ligand **80b**; in other cases, *ee* did not exceed 9%. Compounds **81a,b**, having a similar structure and containing additional chiral centres in the dihydroazepine ring, offer no advantages over the ligands **80a**–**c**.[115]



81a,b [R = Me (**a**), Et (**b**)]

In the same model allylic alkylation reaction {with $[Pd(All)Cl]_2$ as the pre-catalyst}, *ee* is 59% for the ligand **81a** and 37% for the ligand **81b**. A higher enantioselectivity (*ee* 68%) was achieved in the alkylation of dimethyl malonate with the sterically less shielded acetate **13** {the $[Pd(All)Cl]_2 \cdot$ **81a** catalytic system}.

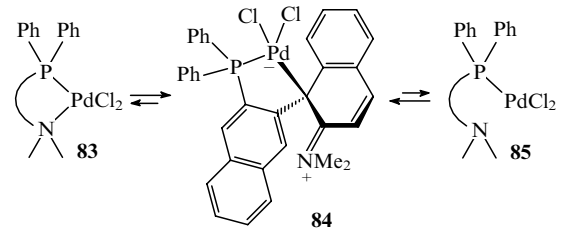
When dinaphthalene derivatives **82a–h**, which also have a chiral axis, are employed in allylic alkylation [the acetate **12**, pre-catalyst $Pd(dba)_2$], the chemical yields are 77%–95% and the optical yields are 53%–73% (the ligand **82f** is the most effective).



82a–h

Compound **82**	R^1	R^2
a	H	H
b	Me	Me
c	H	Et
d	H	Pr^i
e	H	cyclo-C_6H_{11}
f	Me	Pr^i
g	Me	cyclo-C_6H_{11}
h	cyclo-C_6H_{11}	cyclo-C_6H_{11}

The reaction of aminophosphine **82b** with $PdCl_2(PhCN)_2$ has been studied.[116] According to the ^1H, ^{13}C and ^{31}P NMR spectra, the reaction gives an equilibrium mixture of three complexes, **83**, **84** and **85**, in a ratio of 10 : 85 : 5.

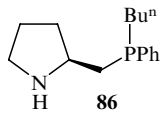


83 **84** **85**

It was demonstrated by X-ray diffraction analysis that the complex **84**, which predominates in the mixture, is a chelate formed due to the $P-C_\sigma$ binding. It was noted that this type of binding can play an essential role in the formation of intermediates in allylation processes.

Chiral N-sp^3-hybridised aminophosphines, which have not yet found application in catalysis but, in our opinion, hold considerable promise, deserve special consideration. Most of these compounds contain asymmetric phosphorus and/or nitrogen atoms.

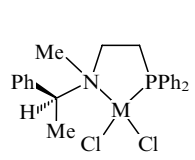
In particular, the reaction of compound **86** with $PdCl_2(MeCN)_2$ results in two epimers of the palladium chelate complexes, $PdCl_2 \cdot$ [(S_N, S_C, S_P)-**86**] and $PdCl_2 \cdot$ [(S_N, S_C, R_P)-**86**], which were separated by fractional crystallisation.[117]



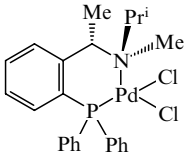
86

Palladium and platinum *cis*-dichloro complexes **87a**,**b** with two chiral centres have also been described.[118]

Whereas the platinum complex **87a** exists as a single diastereomer (the asymmetric nitrogen atom has only one configuration), the palladium analogue **87b** undergoes epimerisation with a half-transformation period of 30 min (according to ^1H NMR spectra and polarimetry). Unlike the complex **87b**, compound **88** contains a configurationally stable chiral nitrogen centre due to the stereochemical assistance of the neighbouring endocyclic carbon centre.[119]

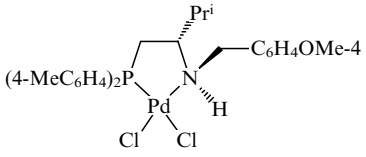


87a,b [M = Pt (**a**), Pd (**b**)]

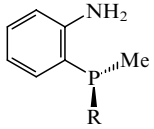


88

The chiral nitrogen centre in the compound **89** also possesses configurational stability, as shown[120] by the data of ^1H (2D NOESY), ^{13}C, ^{15}N and ^{31}P NMR, IR and mass spectra and X-ray diffraction analysis.



89

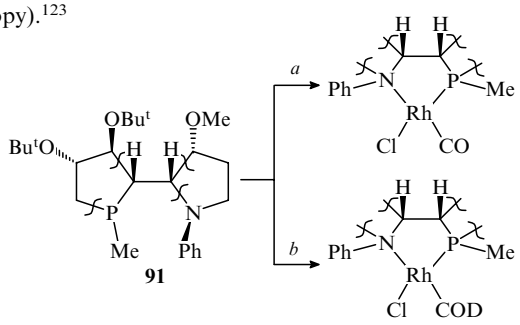


90a,b [R = Ph (**a**), 2-ClC_6H_4 (**b**)]

The complex exists as a single diastereomer both in solution and in the solid state but the palladacycle retains configurational mobility. The conformers differ little in energy, which detracts from the potential use of the compound **89** as a ligand in stereoselective catalysis.

Some aminophosphines with chiral centres at the phosphorus atom also appear interesting, for example, compounds **90a**,**b**, for which both neutral and cationic palladium(II) chelates have been obtained.[121,122]

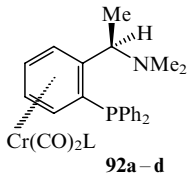
The original bicyclic compound **91** contains five asymmetric carbon atoms in addition to the chiral phosphorus atom. This compound can bind to a metal as both a P-monodentate or a P,N-bidentate ligand (according to ^{31}P, ^{13}C and ^1H NMR spectroscopy).[123]



91

(*a*) 0.5 equiv. $[Rh(CO)_2Cl]_2$; (*b*) 0.5 equiv. $[Rh(COD)_2Cl]_2$.

The complex PdBr(R)(L), where L = (*R*)-AMPHOS [(*R*)-**48**], R = Me, C≡CSiMe_3, has been synthesised.[124] Several ligands **92a–d** based on (*R*)-AMPHOS [(*R*)-**48**] have been prepared.[125]



92a–d

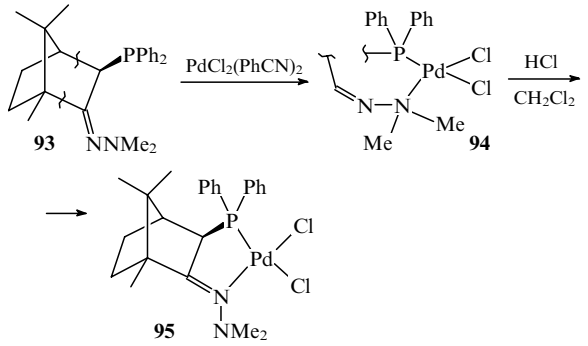
L = CO (**a**), PPh_3 (**b**), $P(OMe)_3$ (**c**), $P(OPh)_3$ (**d**).

The complexes **92a–d** have found application so far only in the amination of 4-bromotoluene with piperidine catalysed by

palladium complexes; however, they are also of interest for asymmetric synthesis, especially in view of the possibility of changing the electronic properties of the phosphorus centre by changing the nature of the ligand L.[125]

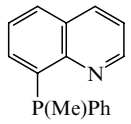
The dimethylhydrazone of the phosphorus-substituted (*R*)-camphor **93** reacts with $PdCl_2(PhCN)_2$ to give initially six-membered chelate metallacycle **94** (according to the IR spectra, ^{31}P and ^1H NMR spectra and X-ray diffraction analysis).[126]

On treatment of a solution of the complex **94** in CH_2Cl_2 with dry hydrogen chloride, the metal chelate rearranges giving rise to complex **95** with a coordinated sp^2-hybridised nitrogen atom.



2. Ligands with sp^2-hybridised electron-donating nitrogen atoms

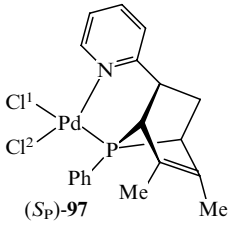
The interest in ligands with sp^2-hybridised donor nitrogen atoms arose somewhat later than that in compounds with sp^3-hybridised nitrogen centres. In 1982, phosphines **96a**,**b** and their neutral palladium derivatives $PdCl_2(L)$ were synthesised.[127] Later,[128] the cationic complexes $[Pd(L)_2]^{2+}(PF_6^-)_2$ and $[PdCl(L)_2]^+X^-$ (X = Cl, PF_6) were prepared.



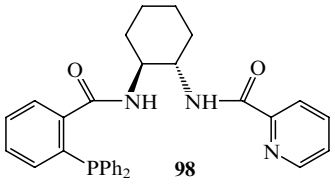
(*R*$_P$)-**96a**, (*S*$_P$)-**96b**

Several other fairly interesting ligands and complexes based on them, for example, **97**–**99**, have been reported.[129–131] X-ray diffraction analysis[129] showed that the Pd–Cl(1) bond length in the complex **97** [2.394(2) Å)] is markedly greater than the typical value, due to the strong *trans*-effect of the phosphorus centre with an unusual geometry.

The ligand **98** has a nine-atom bridge between phosphorus and nitrogen. It is thus able to form 12-membered macrometallacycles.[130] Nevertheless, the enantioselectivity (*ee* 86%) in the model alkylation of dimethyl malonate with the allyl acetate **12** {with $[Pd(All)Cl]_2$ as the pre-catalyst} is quite comparable with the enantioselectivity attained when using catalysts with a standard size of the chelate ring.

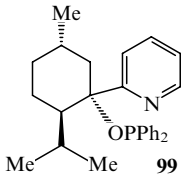


(*S*$_P$)-**97**



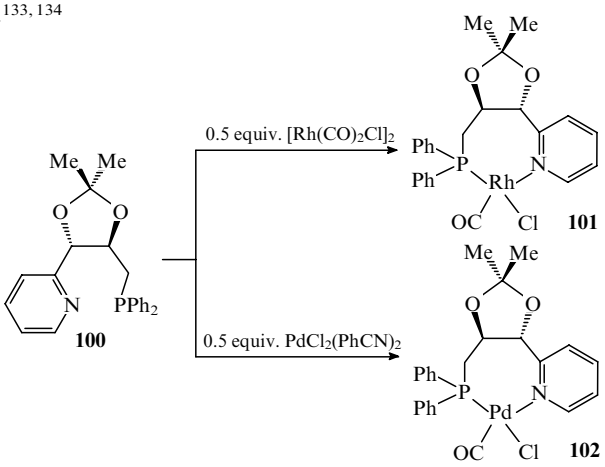
98

Cationic complexes of the phosphinite **99**, $[Rh(CO).(PPh_3)(L)]^+ClO_4^-$ and $[Rh(COD)(L)]^+ClO_4^-$ (the latter was studied by X-ray diffraction analysis), have found use as catalysts of hydroformylation of a number of unsaturated substrates such as vinyl acetate, styrene, vinylnaphthalene and methyl acrylate.[131] The optical yields were 12%, 6%, 78% and 92%, respectively for rather high degrees of conversion and regioselectivities. However, later it was shown[132] that the last-mentioned value was erroneous.



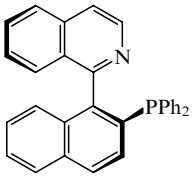
99

The formation of complexes by phosphine **100** (PYDIPHOS) was thoroughly studied by spectral methods (IR spectroscopy, ^{31}P, ^1H and ^{13}C NMR spectroscopy) and mass spectrometry.[133, 134]

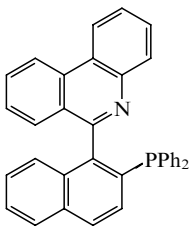


Both rhodium (**101**) and palladium (**102**) metal complexes were described as chelates (the structure of the complex **102** was confirmed by X-ray diffraction analysis); however, the data obtained for the complex **101** do not rule out unambiguously an alternative highly symmetrical binuclear structure with bridging coordination of the P,N-bidentate ligands of the 'head-to-tail' type.[134] The enantioselectivity observed in catalytic reactions involving PYDIPHOS (**100**) is moderate. For hydroformylation of styrene in the presence of the complex **101**, the *ee* is 28%; ethoxycarbonylation in the presence of the complex **102** results in *ee* of 20%; in the model allylic alkylation {the $[Pd(All)Cl]_2 \cdot 4L$ system}, *ee* is 9%.[135]

Studies by Brown *et al.*[136–141] deserve special attention. These researchers proposed effective ligands QUINAP **103** and PHENAP **104a**,**b**.

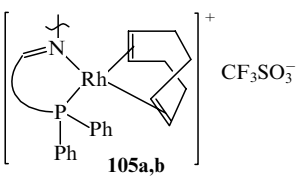


103

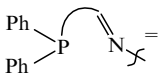


(*R*)-**104a**, (*S*)-**104b**

Cationic rhodium complexes **105a**,**b** with these ligands have found successful use as catalysts of hydroboration of vinylarenes with catecholborane.[137, 138] The optical yields were 64%–95% and the chemical yields were 21%–71%. For example, in the hydroboration of styrene in the presence of the complexes **105a**,**b**, the *ee* values were 91% and 67%, respectively.[138]



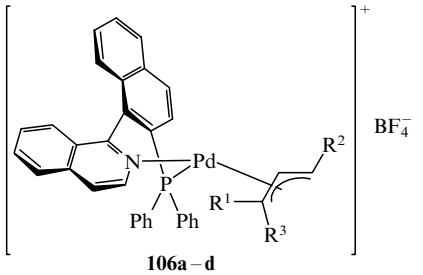
105a,b



= **103** (**a**), **104a** (**b**).

The complex **105a** has also been used as the catalyst for hydroboration–amination of vinylarenes;[139] the corresponding primary amines were obtained in optical yields of 77%–98% and in chemical yields of 50%–64%.

Allylic palladium complexes **106a–d** with the P,N-bidentate ligand **103** have been synthesised. Their structure was established based on the spectral data (IR spectroscopy and ^{31}P, ^{13}C and ^{1}H NMR spectroscopy and mass spectrometry).[140]

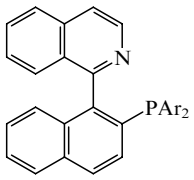


106a–d

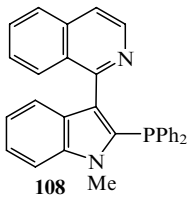
Compound **106**	R^1	R^2	R^3
a	H	H	H
b	Ph	H	H
c	Ph	Ph	H
d	Ph	Ph	Ph

In the classical alkylation of dimethyl malonate with the allyl acetate **12** catalysed by the complex **106a**, the optical yield fluctuates from 67% to 98%, depending on the reaction conditions. For other allylic substrates, the optical yield varies from 47% to 67%. The replacement of dimethyl malonate by diethyl malonate decreases somewhat the enantioselectivity (*ee* 75%–78%). The use of the neutral complex $PdCl_2 \cdot$ **103** instead of the cationic complex **106a** increases the optical yield (*ee* 79%).[140] A similar complex in which $[Pd(All)(\mathbf{104a})]^+BF_4^-$ is used instead of QUINAP **103** ensures a commensurable level of asymmetric induction in this reaction (*ee* 95%).[141]

Ligands **107a–d** [142] used in hydroboration and compound **108** [143] containing an indole fragment have been prepared recently.



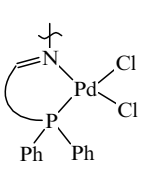
107a–d



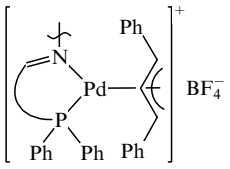
108

Compound **107**	Configuration	Ar
a	*S*	3-MeC_6H_4
b	*S*	3,5-$Me_2C_6H_3$
c	*R*	2-biphenylyl
d	*R*	2-furyl

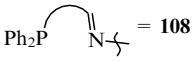
Unfortunately, both the ligand **108** itself and its complex with $PdCl_2$ **109** are readily racemised. The corresponding cationic allylpalladium complex **110** is the only diastereomer.



109



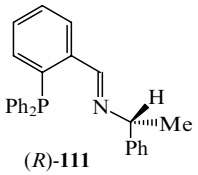
110



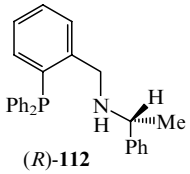
= **108**

The structures of **109** and **110** were studied [143] using spectral methods (IR and ^{31}P, ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry). The complex **110** was studied by X-ray diffraction analysis. The metal atoms in both complexes were found to be coordinated to the isoquinoline nitrogen atom. The configurational stability of the allylic cationic complexes of Pd(II) of the type **110** gives hope for their successful use in asymmetric allylic substitution.[143]

In addition to ligands with a pyridine or isoquinoline fragment, a large group of ligands with a peripheral imino group, iminophosphines, have been described. They were studied by Brunner *et al.*[144, 145, 148–150] In particular, (*R*)-IMINPHOS **111** and (*R*)-AMINPHOS **112** (prepared by the reduction of **111** with $NaBH_4$) were compared in the hydrogenation of *N*-acetyl-α-aminocinnamic acid {$[Rh(C_2H_4)_2Cl]_2$ as the pre-catalyst} and hydrosilylation of acetophenone with diphenylsilane {$[Rh(COD)Cl]_2$ as the pre-catalyst}.[144]

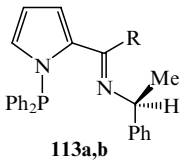


(*R*)-**111**

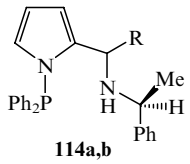


(*R*)-**112**

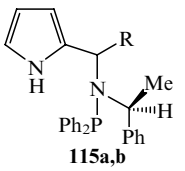
The ligand (*R*)-**111** was more enantioselective in hydrogenation than (*R*)-**112** (*ee* 17% and 14%, respectively). The *ee* value attained in hydrosilylation is 29% in the presence of (*R*)-IMINPHOS **111** and 53% for (*R*)-AMINPHOS **112**.[144] Note that the ferrocene arylideneaminophosphines **17a–d** and the aminophosphines (*S*,*R*)-**18** exhibit a diametrically opposite pattern of dependence (see Section II.2.b). Subsequently,[145] other imino- and amino-phosphines such as **113a**,**b**–**115a**,**b** and **116** have been studied in the hydrosilylation of acetophenone {$[Rh(COD)Cl]_2$ as the pre-catalyst}; however, they all proved to be middling asymmetric inductors because they ensured *ee* of not more than 20%. The best results were obtained with the ligands **113a** and **115a**.



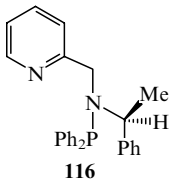
113a,b



114a,b



115a,b

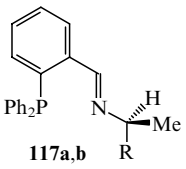


116

R = H (**a**), Me (**b**).

A later publication [146] describes the synthesis of the (*S*)-enantiomer of IMINOPHOS [(*S*)-**111**] and a large series of its palladium and platinum complexes such as PdCl(Me)(L), $[Pd(\eta^3\text{-All})(L)]^+X^-$ (η^3-All = 2-RC_3H_4, 2-MeC_3Me_4, 2-$RC_3H_2Me_2$; X = Cl, O_3SCF_3), $PdCl_2(L)$.[149] The chelating P,N-bidentate coordination of the ligand in these complexes was proved by ^{31}P, ^{1}H and ^{13}C NMR spectroscopy; neutral Pd(II) complexes were studied by X-ray diffraction analysis.

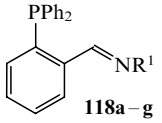
Close analogues of IMINPHOS **111**, compounds **117a,b**, are also known.[147] The enantioselectivity exhibited by these compounds in the alkylation of dimethyl malonate with the allyl acetate **12** catalysed by Pd complexes is also low (*ee* does not exceed 17%).



117a,b

R = cyclo-C_6H_{11} (**a**), 2-naphthyl (**b**).

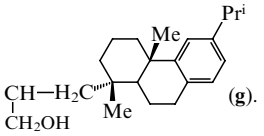
Quite recently, a new large series of iminophosphines **118a–g** have been proposed;[148–150] these products were used to prepare biologically active compound **119**, which belongs to the group of barbiturates.[149] In the reaction catalysed by palladium acetylacetonate in the presence of (*S*)-**118e**, the yield of the compound **119** was 89% (*ee* ~34%).



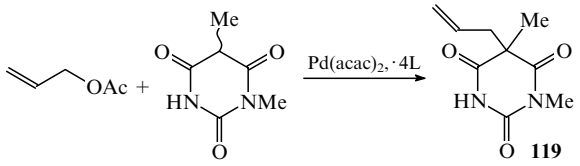
118a–g

R^1 = C(Ph)(H)Me (**a**), HC(Me)CH_2OH (**b**), HC(Et)CH_2OH (**c**),

HC(Pr^i)CH_2OH (**d**), HC(Bu^t)CH_2OH (**e**), HC(Ph)CH_2OH (**f**),



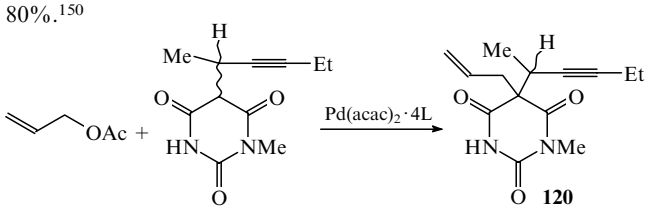
(**g**).



119

L = (*S*)-**118e**.

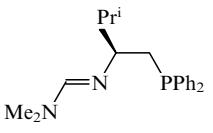
Although the optical yield attained is relatively low, this reaction opens up the way for accumulation of a valuable medicinal preparation, namely, the anesthetic metohexital **120**, which was prepared in the presence of the ligand (*S*)-**118e** in an optical yield of 80%.[150]



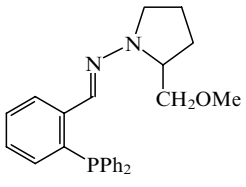
120

L = (*S*)-**118e**.

Chiral aminoiminophosphines **121** and **122a,b** were found to be fairly effective in the alkylation of dimethyl malonate with the allyl acetate **12**.[151–153]

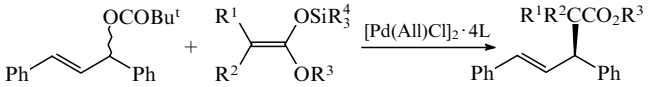


121



(*S*)-**122a**, (*R*)-**122b**

When the reaction was carried out with the ligand **121** {[Pd(All)Cl]$_2$ as the pre-catalyst}, the chemical yield was 85% and the optical yield was 92%. In the allylic palladium intermediate, the ligand was found[151] to be coordinated through the phosphorus atom and the imine nitrogen atom. The iminophosphines **122a,b** are also effective in this reaction {[Pd(All)Cl]$_2$·3L as the catalyst}: *ee* is 90%–92% for a nearly quantitative chemical yield.[152] The ligand **121** was used in processes in which ketene silyl acetals are used as nucleophiles.[153] The yields in these reactions reach 95% and *ee* is 93%.

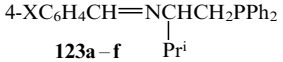


$R^1 = R^2 = R^3 = R^4$ = Me: $R^1–R^2 = (CH_2)_5$, $R^3 = R^4$ = Me;

$R^1 = R^2$ = H, R^3 = Me, $R^4_3 = Bu^tMe_2$; $R^1 = CO_2Me$, R^2 = H,

$R^3 = R^4$ = Me; L = **121**.

Recently, a new series of phosphorus-substituted imines **123a–f**, containing substituents of different nature in the arylmethylidene fragment, have been prepared.[154] In the alkylation of dimethyl malonate with 3-pivaloyloxy-1,3-diphenylprop-1-ene {catalysed by [Pd(All)Cl]$_2$·4L}, the catalytic activity was found to be directly correlated with the enantioselectivity, on the one hand, and the electron-donating capacity of the substituent X on the other hand.



123a–f

Compound **123**	X	Yield (%)	*ee* (%)
a	CO_2Me	42	19
b	CF_3	46	38
c	H	57	52
d	Me	76	74
e	OMe	88	85
f	NMe_2	99	92

In the author's opinion,[154] this is due to the increase in the stability of the Pd(II) cationic complexes on passing from the ligand **123a** to **123f**.

It should be noted that ligands with sp^2-hybridised donor nitrogen atoms have made a greater contribution to asymmetric catalysis than the ligands with sp^3-hybridised nitrogen because, in addition to allylic alkylation, they are effective in hydroboration–oxidation and hydroboration–amination processes.

3. P,N-Bidentate derivatives of phosphorous acid

About 250 chiral P,N-bidentate ligands are currently used in the synthesis of coordination compounds and in asymmetric catalysis. The natures of the nitrogen centres in these compounds are quite diverse, while the phosphorus centres are usually acyclic phosphines (a PAr_2 fragment is encountered most often). (Phosphinites such as **42**, **68**, **69** and **99** and phosphinous amides **74** and **113–116** are the scanty exceptions.) The introduction of electron-donating or electron-withdrawing substituents into the corresponding positions of the benzene nucleus is almost the only method of controlling the inductive effect of phosphorus. However, there exists another, more effective method different in kind, namely, replacement of the carbon atoms in the first coordination sphere of phosphorus by heteroatoms (oxygen and/or nitrogen). This method allows fine adjustment of the chemical stability, the donor–acceptor properties and steric requirements of the ligand. A phosphorus centre of this type is present in P,N-bidentate ligands derived from phosphorous acid.

It is noteworthy that, starting from the early 1990s, the number of publications devoted to the use of chiral phosphites and phosphorous amides, especially P,P-bidentate ones, in the coordination chemistry and catalysis, has substantially increased.[155,156] The obvious advantages of these ligands have been outlined.[157]

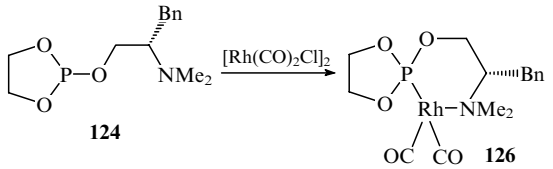
(i) They are readily available because most of them, including functionally substituted ones, can be prepared fairly easily (in one or two steps) and in a high yield from widely used optically active organic precursors, for example, amino alcohols or diols.

(ii) No P–C bonds, which would considerably hamper the oxidative destruction of the ligand, are present in the molecule.

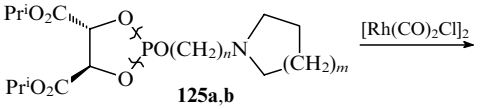
(iii) Owing to the clear-cut π-acceptor properties inherent in phosphites,[158] they are more electrophilic ligands; coordinated phosphites are able to stabilise low oxidation states of complex-forming metals.

It should be noted that chiral phosphinophosphites are the best ligands for asymmetric hydroformylation.[132,156] The introduction of an N-donor centre into the molecule of an ester or an amidoester of phosphorous acid extends the scope of application of chiral phosphites.

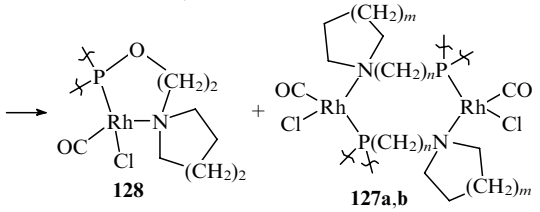
The first publication reporting the synthesis and complex formation of optically active aminoalkyl phosphites **124** and **125a**,**b** appeared in 1993.[159] The reaction of the compounds **124** and **125** with $[Rh(CO)_2Cl]_2$ afforded mono- and bi-nuclear Rh(I) chloro carbonyl complexes.[159,160] The ligand **124** forms metal chelate **126**, while the ligand **125b** gives dimer **127b**. The reaction of $[Rh(CO)_2Cl]_2$ with the ligand **125a** gives rise to a mixture of monomer **128** and dimer **127a**; during storage of the solution, the latter product gradually rearranges to complex **128**. It should be noted that the complexes **127a**,**b** and **128** have been studied only in solution.



124 **126**



125a,**b**

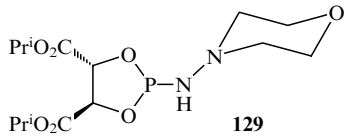


128 **127a**,**b**

$n = m = 2$ (**a**); $n = 3$, $m = 1$ (**b**).

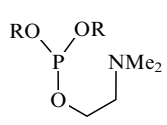
However, the use of the chiral P,N-bidentate derivatives of phosphorous acid **124** and **125a**,**b** in the hydrosilylation of acetophenone with diphenylsilane {$[Rh(CO)_2Cl]_2$ and $[Rh(COD)Cl]_2$ as pre-catalysts} was not very effective (*ee* did not exceed 8%).[159]

Ligand **129** was prepared [161] by successive phosphorylation of diisopropyl tartrate and 4-aminomorpholine. It is coordinated as a P-monodentate ligand in the complex (acac)Rh(CO)L.

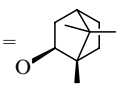
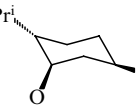
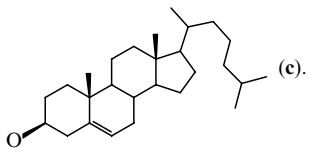


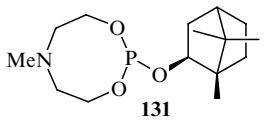
129

The complexes of phosphites **130**–**132** and phosphorous amide **133** with $Pd(COD)Cl_2$were studied by ^1H, ^{31}P and ^{13}C NMR, X-ray electron and IR spectroscopy and plasma desorption mass spectrometry.

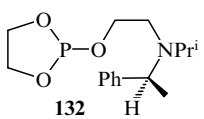


130a–**c**

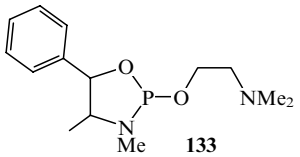
OR =  (**a**),  (**b**),  (**c**).



131



132

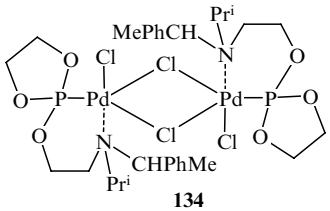


133

It was shown that the compounds **130a**–**c** [162–164] and **133** [165] form mononuclear chelates of the same type. According to X-ray diffraction data, the Pd—P distance in the palladium complex of the ligand **130a** (2.189 Å) is shorter than this bond in palladium dichloro complexes with P,N-bidentate ligands forming a six-membered metallacycle (2.205–2.241 Å).[162] The bond shortening is due to the π-acceptor properties of the phosphite centre.

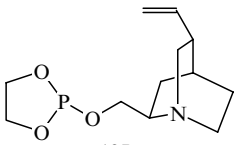
The resonance signals of phosphorus in the ^{31}P NMR spectra of Pd(II) *cis*-dichloro complexes with amino phosphites and amino phosphorous amides occur at a higher field than the signals of free ligands due to shielding of the phosphorus nucleus. However, in the case of similar aminophosphine complexes, the signals of the ^{31}P nuclei are located at a lower field than those for the free ligands.[166]

Dioxaazaphosphocane **131** forms a polynuclear compound of Pd(II), namely, *cis*-$[PdCl_2(L)]_{20}$, in which the P,N-bidentate ligands function as bridges arranged in the 'head-to-tail' manner.[167] From the 1,3,2-dioxaphospholane derivative **132**, the dimeric complex **134** with bridging chloro ligands and an intra-active palladium—nitrogen bond was synthesised.[168] This unusual pattern of complexation observed for the ligand **132** is due to the presence of the bulky substituent in the peripheral amino group of its molecule. As a consequence, the amino group becomes a very weak nucleophile, an analogue of Hünig bases.



134

Recently,[169] aminoalkyl phosphite **135** based on a unique amino alcohol, quincoridin, has been synthesised.



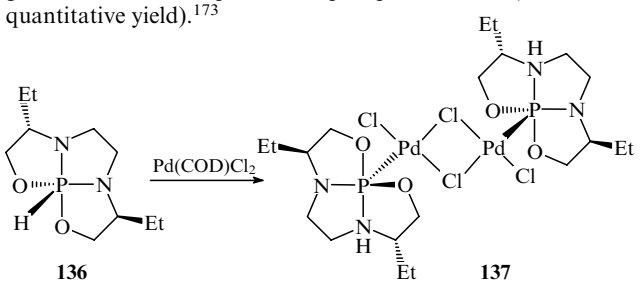
135

To the best of our knowledge, the compound **135** is the only known example of a P,N-bidentate ligand with a configurationally stable chiral nitrogen. This ligand was used to synthesise rhodium(I) chloro carbonyl chelate, [Rh(CO)Cl(L)].

It should be noted that the increased (even in comparison with the most electron-withdrawing amino phosphites [31,160]) π-acidity of the aminoalkyl phosphites **124**, **125a**,**b** and **135** influences the spectral characteristics of chloro carbonyl complexes of rhodium with these ligands. Thus the $^1J_{P-Ph}$ spin–spin coupling constants observed for these complexes are, on the average, ~100 Hz greater, while ν(CO) values are greater by ~20 cm^{-1}.

Hydrophosphorane compounds are seldom used for the preparation of metal complexes with P,N-bidentate derivatives of phosphorous acid. Complex formation is accompanied by rupture of the P—H and P—N bonds and simultaneous formation of M—P and M—N bonds. The main studies dealing with the complexation of chiral hydrophosphoranes have been

surveyed in several publications.[155, 170, 171] Therefore, here we shall consider only the tricyclic hydrophosphorane **136**, prepared not long ago.[172] The reaction of this compound with $Pd(COD)Cl_2$ gave the first stable palladated phosphorane **137** (in an almost quantitative yield).[173]

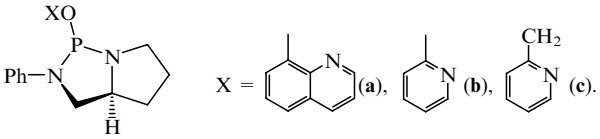


136 **137**

After the proton has migrated from phosphorus to nitrogen, the compound **136** acts as a P-monodentate phosphoranide ligand. When **136** is made to react with $Pt(COD)Cl_2$, the phosphorane ring is opened at the apical P–N bond. In the complex $[PtCl_2(L)]$, the ligand occurs in the 'open' form and is bound to the metal in the P,N-bidentate fashion.[174]

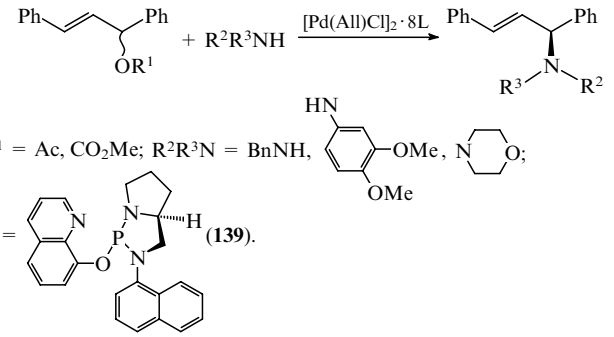
The synthesis and coordination to metals of phosphite and phosphorous amide derivatives of alkaloids, quinine and codeine, have been the subject of a detailed review;[175] therefore, we do not discuss them here.

In 1997, diastereospecific synthesis of three amino-substituted phosphorous diamide ligands **138a–c** was reported.[176]

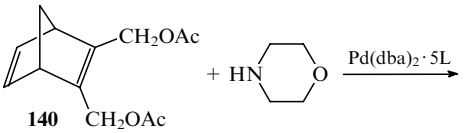


138a–c

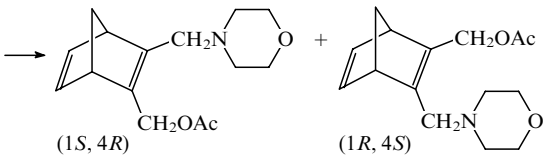
In the classical allylic alkylation with the allyl acetate **12** {with $[Pd(All)Cl]_2$ as the pre-catalyst}, the ligands **138a**,**b** ensured a degree of conversion of 100% and *ee* of 85%–87%, and the ligand **138c** provided 85% and 76%, respectively. Nearly identical results were attained in the related alkylation of dimethyl malonate with 3-methoxycarbonyloxy-1,3-diphenylprop-1-ene. Subsequently,[177] ligand **139** has been synthesised. The compounds **138a–c** and **139** (yields 70%–100%, *ee* 73%–94%) have found application as catalysts of allylic amination.



When diphenylallyl acetate is used as the substrate and benzylamine is employed as the nucleophile, the ligands **138a** and **138c** are the most effective (degree of conversion 95% and *ee* 93%). In the allylic amination of acetate **140** in the presence of the ligand **138a**, the yield is 93% and the optical yield is 89%.[178]



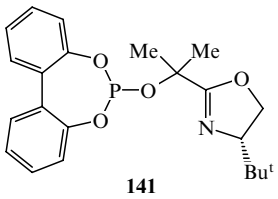
140



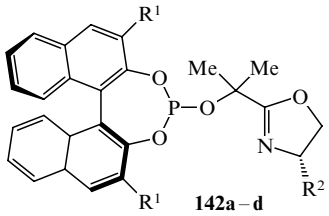
L = **138a**.

It is worth noting that known bisphosphines, (+)-DIOP and (−)-BINAP, ensure *ee* < 5% in this reaction.[178]

4,5-Dihydrooxazoles **141–143**, containing cyclic phosphite groups as substituents, are effective ligands for catalytic allylallylation.[179, 180] Thus alkylation of dimethyl malonate with the allyl acetate **27** in the presence of the $[Pd(All)Cl]_2 \cdot 2.5L$ catalytic system results in *ee* of 77%–92%.

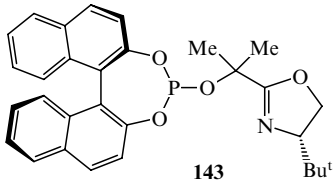


141

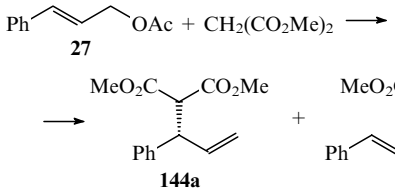


142a–d

R1 = H: R2 = Bu t (**a**), Pr i (**b**), Ph (**c**); R1 = Me, R2 = Bu t (**d**).



143



144a **144b**

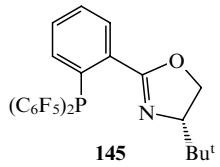
The best result was achieved in the presence of the ligand **142d**, the total yield of branched (**144a**) and linear (**144b**) reaction products being equal to 75%–92%

Asymmetric induction is mainly accomplished due to the dihydrooxazole fragment. Thus for the ligand **141**, the *ee* is 83% and for the ligand **143**, it is 79%. In addition, the enantio- and regioselectivity of the process increase with an increase in the size and, especially, electronegativity of substituents at the phosphorus atom. The results of alkylation of dimethyl malonate with the acetates **27a**,**b** are listed in Table 2. It can be seen that both an increase in the size of substituents in the ligand and an increase in

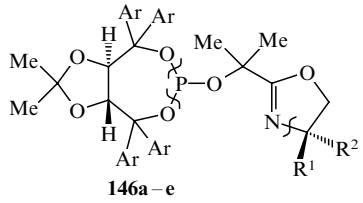
Table 2. Enantio- and regioselectivity of the alkylation of dimethyl malonate with the acetates **27** {$[Pd(All)Cl]_2$ as the pre-catalyst}.

Compound **27**	Ligand	*ee* (%)	The ratio **144a** : **144b**
a	**23c**	78	4 : 96
	145	84	47 : 53
	142a	90	76 : 24
b	**142a**	96	95 : 5

the steric requirements in the compound **27** results in higher enantioselectivity and regioselectivity of the reaction. It should be noted that the selectivity increases also on passing from the ligand **23c** to its analogue **145**, having perfluorophenyl groups attached to phosphorus.



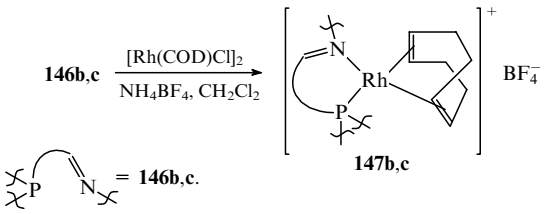
145



146a – e

Compound **146**	Ar	R^1	R^2
a	Ph	H	Ph
b	Ph	Ph	H
c	Ph	H	Pr^i
d	Ph	Pr^i	H
e	2-naphthyl	Pr^i	H

Ligands **146a – e**, prepared using widespread chiral inductors, α,α,α′,α′-tetraaryl-1,2-dioxolano-4,5-dimethanols (TADDOL), were employed [181] to prepare Rh(I) cationic complexes **147b,c** (the complex **147b** was characterised by X-ray diffraction analysis) and to carry out hydrosilylation of a series of aliphatic and aromatic ketones, including reduction of acetophenone with diphenylsilane {with $[Rh(COD)Cl]_2$ as the pre-catalyst}.



147b,c

The best results were obtained with the ligand **146d**: the *ee* value in the reduction of acetophenone was 88% (chemical yield 91%) and in the reduction of *tert*-butyl methyl ketone, the *ee* reached 95%.

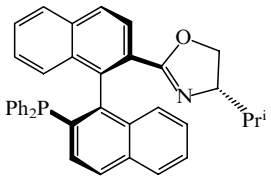
V. Conclusion

The data considered here demonstrate that the research into chiral P,N-bidentate ligands is developing rather vigorously. More than 270 compounds of this type are being used in asymmetric catalysis for allylic alkylation, cross-coupling, hydrosilylation of the C=O and C=C bonds, hydroboration – oxidation, hydroboration – amination and for the Heck reaction.

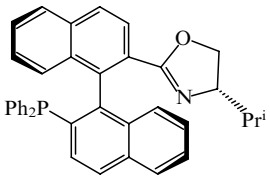
The use of rhodium and palladium complexes with optically active P,N-bidentate ligands in asymmetric catalysis is briefly summarised in Table 3. The table presents the results of the most thoroughly developed processes, namely, hydrosilylation, hydroboration – oxidation and allylic substitution. The enantioselective allylation was considered taking the model allylic alkylation of dimethyl malonate with the acetate **12** as an example. It follows from the data of Table 3 that phosphorus-substituted ferrocenes and dihydrooxazoles are the most effective in the hydrosilylation of the C=O bond; ferrocenylphosphinopyrazoles and QUINAP **103** are the best compounds for hydroboration – oxidation; and all the groups of chiral P,N-bidentate compounds proved efficient for allylic substitution. It should also be noted that ferrocenylaminoalkylphosphines are effective stereoselective ligands for some cross-coupling reactions.

However, several topical problems in the chemistry of P,N-bidentate ligands are still to be solved.

(i) Among the problems of design and synthesis of these ligands, preparation of compounds with a chiral carbon atom at the phosphorus centre deserves attention in the first place because at present, predominant structures are those having asymmetric carbon atoms at the nitrogen centre and/or in the bridge linking phosphorus and nitrogen. It is also important to synthesise ligands with asymmetric donor atoms, especially, with configurationally stable chiral nitrogen atoms. Combination in a chiral ligand molecule of asymmetric atoms with different absolute configurations and chemical natures as well as combination of different types of chirality (for example, central and planar chirality, central and axial chirality, *etc.*) can provide effective transfer of chiral information from the metal complex to the substrate. For example, recently, phosphinodihydrooxazoles **148a,b** with a chirality axis were synthesised;[182, 183] allylic amination of the acetate **27** with substituted hydrazines [183] in the presence of these compounds results in *ee* of up to 99%, while the allylic alkylation of the allyl acetate **12** [182] gives *ee* of up to 91%. It was shown [182] that the binaphthalene cage is responsible for the increase in the stereoselectivity.



148a



148b

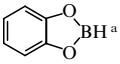
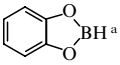
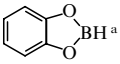
As noted above, an increase in the π-acidity of the phosphorus centre favours an increase in the chemical and optical yields in allylic substitution, hydroboration – oxidation and hydrosilylation – oxidation of alkenes and hydrosilylation of ketones. The inductive effect of the phosphorus centre increases on passing from aminophosphines to amino phosphites or amino phosphorous amides. In these compounds, the inductive effect can be readily optimised.

In the development of new chiral P,N-bidentate ligands, optically active natural products can be used such as steroids, amino acids and alkaloids. No P,N-bidentate derivatives of phosphorous acid having a plane of chirality or a peripheral imino group are known to date. However, the synthesis of these compounds is quite practicable.

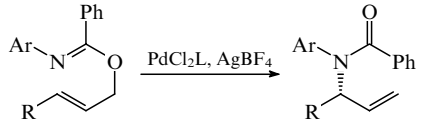
It should also be noted that the synthesis of phosphites and phosphorous amides involves phosphorylation of the corresponding proton-donating functional groups, which proceeds, as a rule, with high yields; therefore, one can expect that a new generation of P,N-bidentate ligands would contain a phosphite (or amino phosphite) centre, possess planar or axial chirality of the carbon framework, and the nitrogen-containing fragment would be represented by an oxazoline, oxazine, imine or pyrazoline group.

(ii) Regarding asymmetric catalysis, it is necessary to master those reactions in which optically active P,N-bidentate ligands have received little use, if any. This refers first of all to the addition of electrophilic reagents to alkenes (for example, hydrocyanation) and to hydroformylation and copolymerisation of alkenes or dienes in the presence of CO. Non-symmetrical phosphinophosphites,[156] *i.e.* systems with donor centres with different chemical natures, showed good results in these reactions. An example of using P,N-bidentate ligands in non-standard reactions is the aza Claisen rearrangement catalysed by the complexes $PdCl_2L$ [L = (*S*,*S*)-**11b**, **26b,c,f**].[184]

Table 3. Comparative efficiency of some P,N-bidentate ligands in model catalytic reactions.

Substrate	Reagent	Pre-catalyst	Ligand	Reaction product	Yield (%) [*ee* (%)]	Ref.
PhCOMe	Ph_2SiH_2	$[Rh(COD)Cl]_2$	(*S*,*S*,*S*)-DIPOF (**16**)	PhCH(OH)Me	100 (91)	45
	Ph_2SiH_2	$[Rh(NBD)Cl]_2$	(*S*,*R*)-**176**	PhCH(OH)Me	90 (90)	46
	Ph_2SiH_2	$[Rh(COD)Cl]_2$	**26r**	PhCH(OH)Me	99 (86)	90
	Ph_2SiH_2	$[Rh(COD)Cl]_2$	**39**	PhCH(OH)Me	84 (94)	91
	Ph_2SiH_2	$[Rh(COD)Cl]_2$	**146d**	PhCH(OH)Me	91 (88)	181
PhCH = CH_2	 [a]	$[Rh(COD)_2]^+BF_4^-$	**6g**	PhCH(OH)Me	68 (98.5)	31
	 [a]	$[Rh(COD)_2]^+BF_4^-$	**8b**	PhCH(OH)Me	100 (87)	87
	 [a]	$[Rh(COD)_2]^+SO_3CF_3^-$	QUINAP (**103**)	PhCH(OH)Me	71 (91)	138
$CH_2(CO_2Me)_2$	PhCH = CHCH(OAc)Ph	$[Pd(All)Cl]_2$	(*S*,*S*)-**11b**	PhCH = CHCH(Ph)$CH(CO_2Me)_2$	98 (99)	43
	PhCH = CHCH(OAc)Ph	$[Pd(All)Cl]_2$	**26b**,**c**,**e**	PhCH = CHCH(Ph)$CH(CO_2Me)_2$	99 (99)	51 – 53, 56
	PhCH = CHCH(OAc)Ph	$[Pd(All)Cl]_2$	**40**	PhCH = CHCH(Ph)$CH(CO_2Me)_2$	94 (98)	82
	PhCH = CHCH(OAc)Ph	$[Pd(All)Cl]_2$	**41**	PhCH = CHCH(Ph)$CH(CO_2Me)_2$	99 (95)	83
	PhCH = CHCH(OAc)Ph	$[Pd(All)Cl]_2$	**43n**	PhCH = CHCH(Ph)$CH(CO_2Me)_2$	78 (98)	86
	PhCH = CHCH(OAc)Ph	$[Pd(All)Cl]_2$	**75h**	PhCH = CHCH(Ph)$CH(CO_2Me)_2$	70 (76)	112
	PhCH = CHCH(OAc)Ph	$[Pd(All)Cl]_2$	**76b**	PhCH = CHCH(Ph)$CH(CO_2Me)_2$	96 (96)	113
	PhCH = CHCH(OAc)Ph	$[Pd(All)Cl]_2$	**98**	PhCH = CHCH(Ph)$CH(CO_2Me)_2$	82 (86)	113
	PhCH = CHCH(OAc)Ph	$[Pd(All)Cl]_2$	QUINAP (**103**)	PhCH = CHCH(Ph)$CH(CO_2Me)_2$	94 (98)	140
	PhCH = CHCH(OAc)Ph	$[Pd(All)Cl]_2$	**121**	PhCH = CHCH(Ph)$CH(CO_2Me)_2$	85 (92)	151
	PhCH = CHCH(OAc)Ph	$[Pd(All)Cl]_2$	**138b**	PhCH = CHCH(Ph)$CH(CO_2Me)_2$	100 (87)	176
	PhCH = CHCH(OAc)Ph	$[Pd(All)Cl]_2$	**148b**	PhCH = CHCH(Ph)$CH(CO_2Me)_2$	99 (91)	182

[a] Followed by treatment with H_2O_2 and NaOH.



The use of phosphinodihydrooxazoles as ligands in cross-coupling, hydroboration and hydrosilylation of alkenes appears quite promising. It is necessary to study already known amino phosphites, amino phosphorous amides and phosphitodihydrooxazoles not only in allylic substitution reactions but also in all other catalytic processes in which ligands with electron-withdrawing P-donor centres can participate. These studies would substantially extend the scope of application of chiral P,N-bidentate ligands in enantioselective catalysis. Further perfection of well-developed processes is needed, first of all, in order to achieve quantitative enantioselectivity (for example,[185] it is known that certification of pharmaceutical preparations requires *ee* $\geqslant$99%). The enantioselectivity can be increased by introducing non-chiral additives.[185]

(iii) Investigation into the mechanisms of catalytic reactions can provide the basis for recommendations on the reaction conditions and for targeted synthesis of optimal ligands. Despite the impressive progress in modern asymmetric catalysis, it largely relies on the rules obtained empirically. This is partly due to the necessity of taking into account too many factors influencing the outcome of a catalytic reaction such as the nature of the ligand and the metal, the ligand : metal and catalyst : substrate ratios, the temperature, the concentration, the nature of the solvent, the additives present, *etc*. and, to some extent, this is due to the absence of a detailed investigation of the mechanisms of catalytic reactions.

(iv) In the field of coordination chemistry, it appears topical to continue the studies on the regularities of complexation of the main groups of ligands. Unfortunately, isolation and reliable characterisation of complexes with transition metals is far from being performed for all the P,N-bidentate ligands effective in catalysis .

Thus, despite the considerable contribution of iminophosphine derivatives, such as the ligands **118a**–**g** or **123a**–**f**, to asymmetric catalysis, the coordination behaviour of these ligands has scarcely been studied. This also concerns several other effective stereoselective ligands, **138**, **139** and **141**–**145**. The complex formation of related compounds **124**, **125**, **129** and **130**–**135** has been extensively studied; however, no data on the use of these compounds in catalytic processes can be found. Evidently, catalytic experiment and the study of the structures of pre-catalysts and related metal complexes for each group of ligands should be combined with investigation of the coordination and catalysis mechanism.

It appears useful to synthesise a series of related complexes with different ligands (as has been done, for example, for chloro carbonyl rhodium derivatives of phosphinoferrocenylpyrazoles **6a**–**t** [31]). Comparison of the characteristic features of coordination of these compounds to metals and their spectroscopic properties and estimation of the electronic effects of the electron-donating centres would permit more efficient prediction of catalytic experiments and elucidation of the corresponding correlations. This integrated approach has been realised to some extent for ferrocenylaminophosphines (including PPFA **1** and PTFA **3**), phosphinoferrocenylpyrazoles and phosphinodihydrooxazoles. However, even for these compounds, further studies are needed because P,N-bidentate coordination and chelation cannot be postulated *a priori* even for well-known ligands (for example, in the ligand **80b**, P,C_σ- rather than P,N-binding predominates).

It is clear that the current state of asymmetric catalysis and the prospects for its development are determined by not only P,N-bidentate ligands. Considerable contribution is made by P,P-, P,O- and N,N-bidentate systems (see, for example, several studies [4–10, 186]).

It can be stated with confidence that the use of P,N-bidentate compounds opens a new stage in the development of coordination chemistry and asymmetric catalysis.

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